Cyprus University of Technology

Faculty of Geotechnical Sciences and Environmental Management

Doctoral Dissertation

Sustainable Phosphate Recovery from Wastewater using Biowaste-based Materials

Panagiota Photiou

Limassol, October 2023 of dissertation submission

CYPRUS UNIVERSITY OF TECHNOLOGY

FACULTY OF GEOTECHNICAL SCIENCES AND ENVIRONMENTAL MANAGEMENT

DEPARTMENT OF CHEMICAL ENGINEERING

Doctoral Dissertation

Sustainable Phosphate Recovery from Wastewater using Biowaste-based Materials

Panagiota Photiou

Limassol, October 2023 of dissertation submission

Approval Form

Doctoral Dissertation

Sustainable Phosphate Recovery from Wastewater using Biowaste-based Materials

Presented by

Panagiota Photiou

Supervisor: Faculty of Geotechnical Sciences and Environmental Management, Department of Chemical Engineering, Dr Ioannis Vyrides, Assistant Professor

Signature ____

Member of the committee: Faculty of Biotechnology and Food Science, Department of Agricultural Sciences, Dr Nikos Tzortzakis, Assistant Professor

Signature ____

Member of the committee: Faculty of the Environment, Department of Environment, Dr Athanasios Stasinakis, Professor

Signature ____

Cyprus University of Technology

Limassol, October 2023 of dissertation submission

Approval Form of Advisory Committee

Doctoral Dissertation

Sustainable Phosphate Recovery from Wastewater using Biowaste-based Materials

Presented by

Panagiota Photiou

Supervisor: Faculty of Geotechnical Sciences and Environmental Management, Department of Chemical Engineering, Dr Ioannis Vyrides, Assistant Professor

Signature ____

Member of the committee: Faculty of Biotechnology and Food Science, Department of Agricultural Sciences, Dr Nikos Tzortzakis, Assistant Professor

Signature ____

Member of the committee: Faculty of the Environment, Department of Environment, Dr Athanasios Stasinakis, Professor

Signature ____

Cyprus University of Technology

Limassol, October 2023 of dissertation submission

Copyrights

Acknowledgments

I am profoundly grateful to all those who have contributed to the completion of this PhD thesis. Their unwavering support, guidance, and encouragement have been instrumental in shaping both my academic journey and personal growth.

My heartfelt gratitude goes to my advisor, Dr Ioannis Vyrides, whose mentorship, insightful feedback, and dedication to my research have been invaluable. Your guidance has not only enhanced the quality of this work but has also inspired me to strive for excellence in all endeavours. I am also deeply thankful to Dr Michalis Koutinas, who provided valuable insights, engaged in thought-provoking discussions, and contributed to the academic discourse that enriched my academic journey.

I am indebted to my colleagues who provided valuable comments that helped me expand my perspectives and refine my ideas.

I extend my sincere thanks to my family for their unwavering support and belief in my abilities. Their encouragement during the challenging times has been my driving force.

“It always seems impossible until it’s done.”, N.M.

Thank you.

ABSTRACT

Phosphorus plays a crucial role in plant growth and biological processes. Recovering phosphorus from waste streams is important for sustainable food production and environmental stewardship. Bio-based materials can be used for effective phosphate recovery through adsorption. This sustainable and cost-effective methodology reduces environmental pollution and eutrophication and contributes to the circular economy. The recovered phosphate solid can be used as a soil conditioner or fertilizer, promoting efficient nutrient management and sustainable agriculture. Thus, following this approach, this work aimed to explore low-cost biowaste materials for effective phosphate recovery from real wastewater. Various biowastes, including orange peels, spent coffee residues, fish scales, seagrass residues of *P. oceanica*, biochar produced from olive kernels, and biochar generated from vineyard prunings, were tested for their phosphate adsorption capacity. Thermally treated seagrass (SG-TT) and eggshell (EGSL-TT) residues exhibited the highest capacity from the biowastes examined. The optimum pre-treatment temperature and exposure time were determined as 500ºC for 1 h and 900ºC for 30 min, respectively. Moreover, chemical leaching experiments of phosphate from dewatered anaerobic sludge (DWAS) were conducted, evaluating sonication and inorganic acids (sulfuric acid (SA), thermal-sulfuric acid (TSA), and nitric acid (NA)) as extraction methods to determine the most suitable acid medium to leach out phosphate. SA and TSA processes with 84.9 and 93.2% extraction efficiency, respectively. Adsorption batch experiments with real wastes (anaerobic effluent wastewater and leached solution from DWAS), demonstrated that SG-TT and EGSL-TT have high adsorption efficiency and selectivity towards phosphate (>78.4% for both materials). After phosphate adsorption, the solid residues were mixed with compost in different ratios and then tested as fertilizer substitutes on plant growth. The SG solid residue after adsorption produced from anaerobic effluent or synthetic solutions imposed a positive effect on plant growth with germination index (GI) values 96.7 – 111.1%, for all types of seeds tested (*Solanum lycopersicum*, *Lepidium sativum*, and *Sinapis alba*), while the solid residue after adsorption produced from DWAS leached solution negatively affected the germination of seeds, probably due to potentially refractory compounds contained in DWAS. Similar behaviour was observed in EGSL solid residue remaining after adsorption from DWAS leachate, while

a positively effect was distinguished on plant growth for *Sinapis alba* and *Lepidium sativum* seeds. EGSL-TT were additionally tested in AD systems as a new approach to counteract excessive acidification and alleviate low pH in anaerobic digestion and showed substantially higher methane generation than the control. This new proof of concept contributes to the circular economy; the EGSL-TT is integrated with anaerobic digestion both in-situ for buffering acidification and ex-situ for phosphorous removal and potential use as a soil conditioner.

Finally, a process for the valorisation of different type of wastewaters was developed, which was including SAnMBR system in combination with adsorption method. The first system involved the combination of a submerged anaerobic membrane bioreactor (SAnMBR) and two biowaste adsorption columns (SG-TT and EGSL-TT) to assess the recovery of phosphates from low-strength wastewater relatively high in phosphate ion (reject wastewater from anaerobic sludge dewatering process). The results showed a chemical oxygen demand (COD) removal of 50%. However, the phosphate removal efficiency in the reactor was low and as such, the effluent from SAnMBR was then passed through two columns containing SG-TT and EGSL-TT residues for further removal (resulting in over 95% recovery). In addition, the fractionation analysis of phosphorus showed that inorganic phosphorus was the substantial phosphorus fraction in eggshell and seagrass end product, accounting for 92.6 and 95.7% of TP, respectively. Eggshell end product had the highest proportion of apatite phosphorus fraction (87.4%), which require further time for the dissolution process, leading to low concentrations of bioavailable phosphorus fractions and consequently poor germination of seeds. Overall, this study shows that the seagrass and eggshell could be effectively reclaimed as selective adsorbents towards phosphates in advanced wastewater treatment processes when combined with a SAnMBR. The second system used a SAnMBR to treat synthetic and domestic wastewater. The COD was effectively treated, with average removal percentages of 82.3 and 87.8% for synthetic and domestic wastewater, respectively. Then, the SAnMBR effluent was independently exposed to EGSL-TT and SG-TT, and the phosphate ions were recovered with percentages up to 71.8 - 99.9% and 60.5 - 78.0%, respectively, for all the flow rates tested. The effluent from EGSL and SG was exposed to powder-activated carbon (PAC), and the COD was further reduced

to a concentration of 20.2 ± 5.2 and 57.0 ± 13.3 mg L^{-1}. The respective final effluent was evaluated in phytotoxicity trials demonstrating that the SAnMBR effluent after the PAC treatment was significantly better for *Lepidium sativum* and *Sinapis alba* seeds tested than the untreated domestic wastewater. Finally, the determination of volatile organic compounds (VOCs) depicted a significant decrease from the very first steps of the process, with a reduction of common wastewater contaminants such as dimethyl disulfide, dimethyl trisulfide, phenol, p-cresol, nonanal and decanal. The tested technology might be considered a promising treatment system since can effectively treat domestic wastewater, reduce the VOC, generates biogas for energy, produces solid products high in inorganically bound phosphate and the effluent can be used for irrigation.

Keywords: Adsorption, Biowaste, Wastewater treatment, Phosphate recovery, SAnMBR

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AD	Anaerobic Digestion
ADF	Acid Detergent Fiber
ADL	Acid Detergent Lignin
AnMBR	Anaerobic Membrane Bioreactor
ANOVA	One-way Analysis of Variance
AOPs	Advanced Oxidation Processes
AP	Apatite Phosphorus
BOD	Biological Oxygen Demand
CEL	Cellulose
COD	Chemical Oxygen Demand
CVD	Compost
D	Digestate
DAP	Diammonium Phosphate
DEP	Diethyl Phthalate
DI	Distilled Water
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DTN	Data Transmission Network
DWAS	Dewatered sludge
EBPR	Enhanced Biological Phosphorus Removal
EDS	Energy-dispersive X-Ray Spectroscopy
EEA	European Environment Agency

EGSL-TT	Thermally Treated Chicken Eggshells
FW	Food waste
G	Glucose
GC	Gas Chromatography
GI	Germination Index
GR	Gardening Residues
GS	Granular Sludge
HAIX	Hybrid Anion Exchanger
HRT	Hydraulic Retention Time
HS	Hazelnut Shells
IC	Internal Circulation
IP	Inorganically Bound Phosphorus
MAP	Monoammonium Phosphate
MBR	Membrane bioreactor
MF	Microfiltration
MOFs	Metal–Organic Frameworks
MSB	Blue Mussel Shell
MSWI	Municipal Solid Waste Incinerator
NA	Nitric Acid
NAIP	Non-Apatite Inorganic Phosphorus
NDF	Neutral Detergent Fiber
NH_4^+	Ammonium
NO_2^-	Nitrites

NO_3^-	Nitrates
OLR	Organic Loading Rate
OP	Organically Bound Phosphorus
OPD	Onion Peel Dust
OSB	Oyster Shell
PAC	Powder Activated Carbon
PAN	Polyacrylonitrile
PAO	Phosphorus-Accumulating Organisms
PES	Polyethersulfone
PO_4^{3-}	Phosphates
PVDF	Polyvinylidene Fluoride
PZVI	Powder Zero-Valent Iron
RO	Reverse Osmosis
SA	Sulfuric Acid
SAnMBR	Submerged Anaerobic Membrane Bioreactor
SBC	Fir Wood Waste - Seawater
SBLA	Sewerage Board of Limassol-Amathus
SCOD	Soluble Chemical Oxygen Demand
SEM	Scanning Electron Microscope
SG-TT	Thermally Treated Seagrass
SMT	Standards Measurements and Testing
SS	Suspended Solids
SZVI	Scrap Metal Zero-Valent Iron

TCOD	Total COD Chemical Oxygen Demand
TD	Thermal Desorption
TIC	Total Ion Chromatogram
TN	Total Nitrogen
TP	Total Phosphorus
TS	Total Solids
TSA	Thermal-Sulfuric Acid
UF	Ultrafiltration
NF	Nanofiltration
USEPA	United States Environmental Protection Agency
UWTPs:	Urban Wastewater Treatment Plants
VFAs	Volatile Fatty Acids
VOCs	Volatile Organic Compounds
VS	Volatile Solids
VSCs	Volatile Sulfide Compounds
WAS	Waste Activated Sludge
XRD	X-Ray Powder Diffraction
ZVI	Zero-Valent Iron

1 Introduction

The circular economy is a resource management technique that prioritizes material reuse, recycling, and repurposing in a closed loop system, reducing waste and environmental impact. Phosphate recovery from wastewater using readily available biowaste-based adsorbents is beneficial for both eutrophication control and waste management. Urban wastewater treatment plants (UWTPs) are a major source of phosphorus pollution and a possible source of recovery. This study uses biowaste-based materials for sustainable phosphorus recovery from waste streams, which fits within the circular economy framework. More specifically, the utilization of materials derived from biowaste (eggshells and seagrass) as adsorbents, coupled with the utilization of wastewater streams (anaerobic effluent, rejected wastewater, domestic wastewater) as sources of phosphate, represents an innovative approach that offers a dual benefit of recovering a finite resource and transforming waste into a valuable input for both agricultural and industrial purposes. Following circular economy concepts, the utilization of biowaste-based materials can also support sustainable development and contribute to a more efficient and resilient system of resource management.

1.1 Role and importance of phosphorus

Phosphorus is an essential nutrient that is often growth-limiting for organisms in water ecosystems (Correll, 1999). It is present in aqueous environments in various forms (Fig. 1-1), including organically bound phosphate (OP), inorganic phosphate (IP), and polyphosphate (Biswas et al., 2008). Inorganic phosphate can be classified into two categories, namely apatite (AP) and non-apatite phosphate (NAIP). AP minerals (mainly $Ca_3(PO_4)_2$) are the main raw materials used in fertilizer manufacture (Tan and Lagerkvist, 2011). Struvite (mainly $Mg(NH_4)PO_4$) is a slow release fertilizer due to its low solubility in neutral pH solutions (Shu et al., 2006). $AlPO_4$ and $FePO_4$, classified as NAIP, exhibit low bioavailability and cannot be used directly by plants or as an industrial raw material. Phosphate reserves of substantial magnitude are present in several countries, most notably in Morocco with an estimated quantity of 50 billion metric tons, followed by China (3.2 billion), Egypt (2.8 billion), Algeria (2.2 billion), Syria (1.8 billion), Brazil (1.6 billion), Saudi Arabia

(1.4 billion), South Africa (1.4 billion), and Australia (1.1 billion) (Fig. 1-2). Phosphorus in numerous products is primarily sourced from phosphate rock mining, and these rocks are gradually decreasing in availability, resulting in a growing import dependency and insecurity for countries with limited phosphate rock resources (Cordell et al., 2009; Quist-Jensen et al., 2018; Monea et al., 2020; Geissler et al., 2019; Smol et al., 2020).

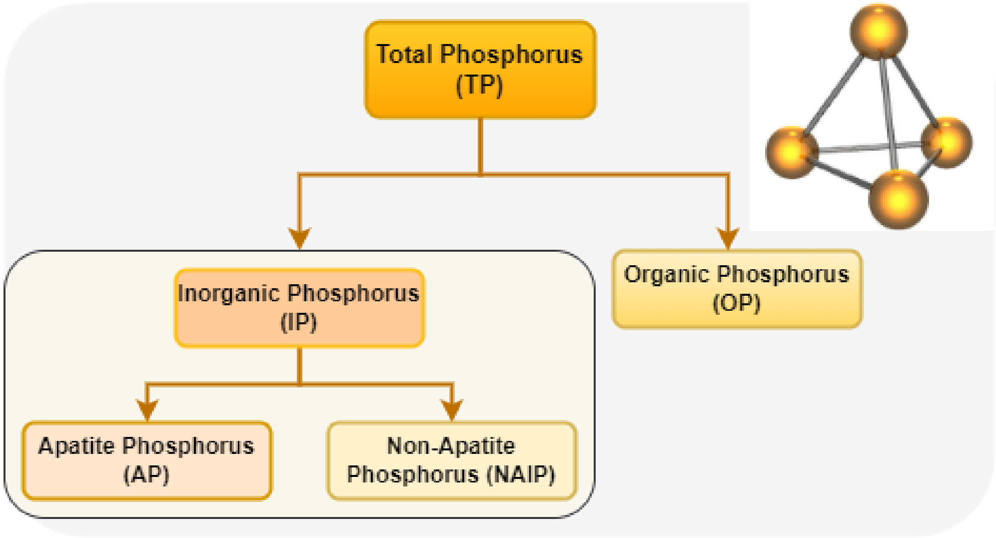


Figure 1-1. Fractionation of phosphorus.

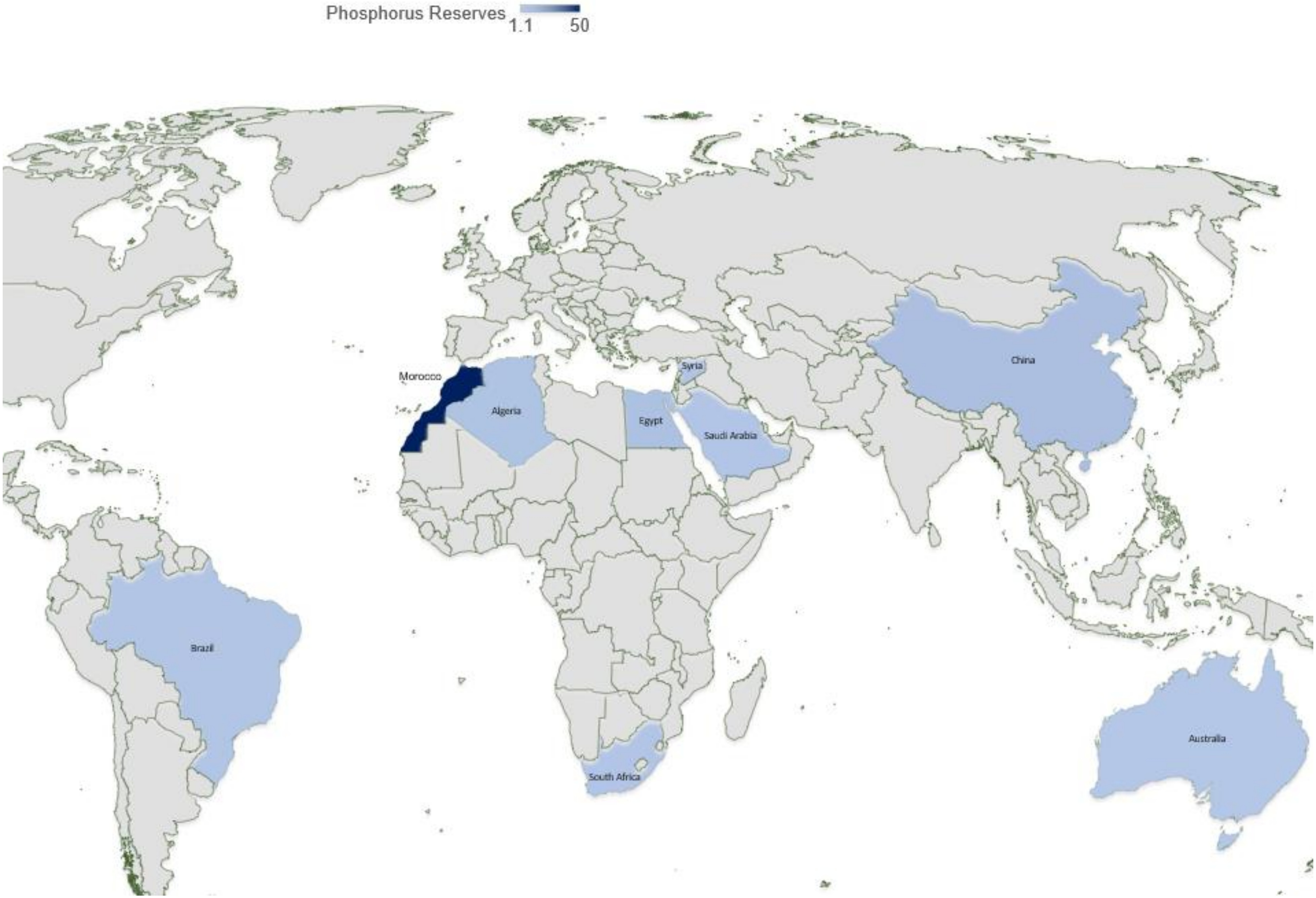


Figure 1-2. Phosphorus rock reserves worldwide (Statista, 2022).

Furthermore, phosphate rocks are the primary source of phosphorus for producing fertilizers. Recent studies highlighted the amount of phosphorus extracted in 2021 to 22 million tons, with 95% being utilized for agricultural purposes, such as fertilizers or animal feed (Macdonald et al., 2011; Salkunic et al., 2022). According to the findings of the Data Transmission Network (DTN), an upward trend in the pricing of various fertilisers was also noted during 2023, as demonstrated by the comprehensive array of fertiliser prices in Table 1-1. As the global population continues to grow, there will be a higher demand for phosphorus to sustain the increasing food production. However, phosphorus overuse in agriculture can cause environmental issues. The United States Environmental Protection Agency (USEPA) reports that the application of phosphorus-based fertilizers to soils over the threshold of 0.025 mg L^{-1} will lead to high concentrations of phosphate released in water ecosystems, resulting in toxic algal blooms and eutrophication.

Table 1-1. Fertiliser's prices in 2023 from the DTN

Fertiliser - Chemical Formula	**Description**	**Content**	**Price (€/ton)**
Anhydrous - NH_3	Highly effective type of nitrogen fertilizer.	82% nitrogen	913.76
Diammonium Phosphate (DAP) - $(NH_4)_2HPO_4$	Widely used phosphate fertilizer.	18% nitrogen 46% phosphorus	728.51
Monoammonium Phosphate (MAP) - $NH_4H_2PO_4$	Granular fertilizer with a high analysis source of phosphorus.	11% nitrogen 52% phosphorus	721.39
Potash - KCl	Source of soluble potassium and a universal fertilizer.	51% potassium 47% chloride	573.55
Urea - $CO(NH_2)_2$	White crystalline solid nitrogen fertiliser.	46 % nitrogen	557.52
10-34-0	Liquid ammoniated phosphate fertilizer.	10% nitrogen 34% phosphate	659.93
UAN28	Liquid fertilizer with three forms of nitrogen (urea, ammonium-N, and nitrate-N).	28% nitrogen	381.18
UAN32	Liquid fertilizer with three forms of nitrogen (urea, ammonium-N, and nitrate-N).	32% nitrogen	456.88

However, the depletion of phosphorus, whether it happens in decades or centuries from now, will have catastrophic consequences for humanity. Thus, phosphorus-containing waste streams can provide a valuable source of this nutrient for agricultural and industrial applications while also reducing the produced wastes and the environmental impact of their disposal. In addition, phosphate constitutes an important nutrient for various industries that produce streams of wastes with high phosphorus content (Biswas et al., 2007) and can be found in numerous other waste sources, including industrial effluent, animal manure, and municipal wastewater. According to European Commission, the percentages of phosphorus in industrial effluent, animal manure and municipal wastewater reach 100 mg L^{-1} and 10 g kg^{-1}, while the typical level in urban wastewater is around 4.5 mg L^{-1}, respectively. However, despite the existence of phosphate resources, there is a shortage of feasible and cost-effective methods for their extraction. Therefore, researchers began to consider modifying current practices for attaining better management of the phosphorus resources. Following this, alternative sources of phosphorus and research directed towards developing efficient and sustainable processes for phosphorus recovery from these sources consist of a novel approach developed by scientists and engineers (Luyckx et al., 2020).

1.2 Urban wastewater treatment plants (UWTPs)

UWTPs are crucial infrastructure that treat and dispose of wastewater generated in urban areas by households, commercial buildings, and industry. The design of such plants focuses on delivering high-quality wastewater by targeting the removal of pollutants, including pathogens, organic materials, and nutrients to prevent the spread of waterborne diseases, reduce the pollution in surface water bodies and protect the public health and the environment (Sikosana et al., 2019). In this regard, the treatment process involves the primary, secondary, and tertiary treatment of municipal wastewater (Fig. 1-3), which include the removal of: (a) large solids using physical processes such as sedimentation and screening; (b) organic matter and nutrients with the use of biological processes such as activated sludge treatment and (c) disinfection and filtration of treated wastewater to improve its quality using additional physical and chemical processes (Demirbas et al., 2017). At each stage of the process, the quality of the effluent wastewater is improved. The preliminary treatment protects the equipment from damage and reduces the organic loading. During the primary treatment, the settleable solids and suspended particles are being removed and the effluent typically contains low levels of organic matter, however the content of nutrients and other contaminants are significantly high (Sikosana et al., 2019). Following this, the secondary treatment is responsible for the removal of pathogens, nutrients, dissolved and suspended organic matter from the wastewater. The biodegradable organic matter is reduced through microorganisms' metabolic processes and the nutrients (P, N) are converted into biomass or gas. The effluent from secondary treatment is considered suitable for discharge into the environment due to the low content in suspended and dissolved solids (Sikosana et al., 2019). Tertiary treatment is the stage of which the quality of effluent is of high-quality and can be used for various applications such as environmental restoration, irrigation, and for industrial purposes. As such, this process further reduces the concentration of specific pollutants to reach the strict discharged limits prior to the release in sensitive water ecosystems.

UWTPs positively influence public health and the environment through the treatment of municipal wastewater, but even so, it produces considerable amounts of sludge that require measures and further treatment for its proper disposal. According to data published from the European Environment Agency (EEA) the production of sludge by UWTPs reached 12.8 million tons in 2019. The disposal of sludge demands its prior treatment since heavy metals, bacteria, and organic materials are among the toxins present in this sludge, which, if not adequately managed, can pose severe dangers to the environment and human health. Furthermore, the high concentrations of nutrients present in the sludge can lead to environmental problems such as eutrophication, increasing the need for sludge treatment and disposal. However, the same data regarding the sludge treatment and disposal in terms of expenses state that treatment and disposal costs account for up to 50% of a UWTP's overall operational costs. Thickening, dewatering, and stabilization are frequently used in sludge treatment to lower volume and enhance sludge stability. Depending on regional regulations and the needs of the market, the treated sludge has the potential to be used for land applications, incineration, or composting. Low-cost solutions consist of the land application and composting, while landfilling and incineration consider as expensive options primarily due to the high capital and operational costs.

The research community focuses on addressing these challenges, and thus, the direction of scientists moved towards the recovery of fertilizer-used nutrients (P, N etc.) from the UWTP sludge and wastewater as a sustainable approach for waste management aiming to assist in the reduction of UWTP costs. In addition, UWTPs can mitigate the impact on the environment, while providing an important resource for agricultural and industrial applications by capturing and reusing these nutrients under the concept of circular economy in the wastewater industry.

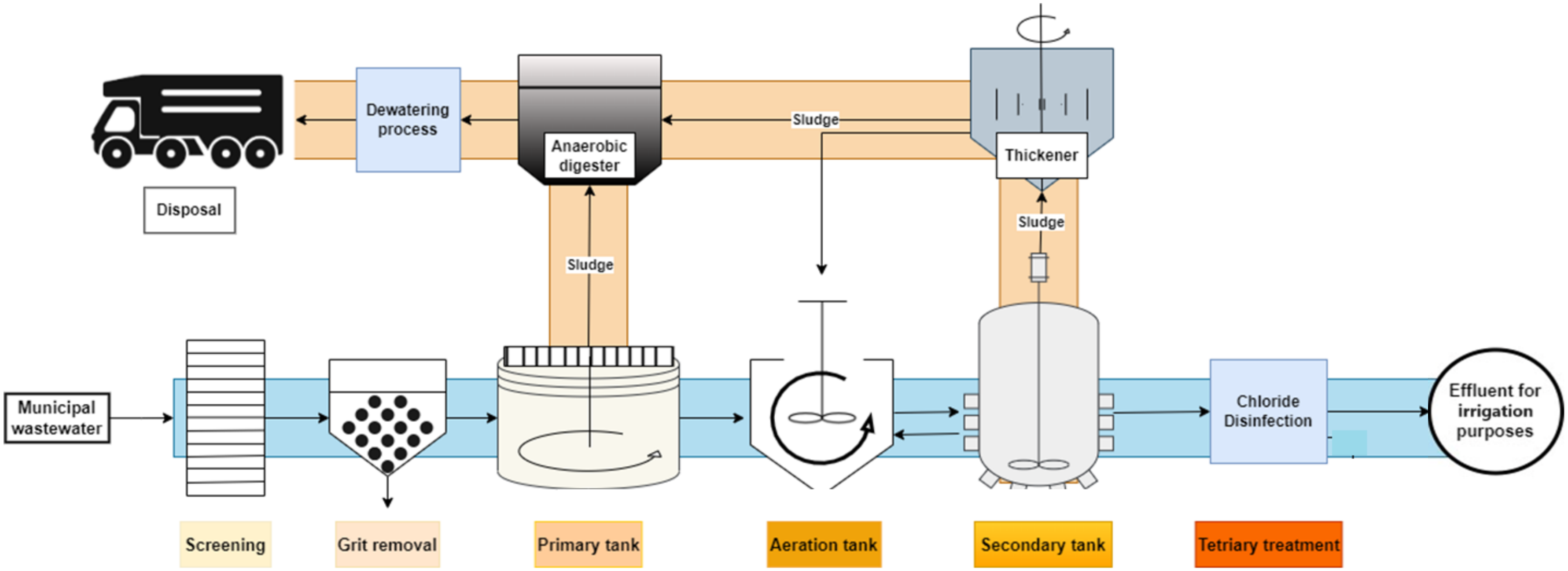


Figure 1-3. Traditional treatment of municipal wastewater in UWTPs.

1.2.1 MBR process for the treatment of wastewater

The development and testing of novel and emerging approaches are currently essential for designing low-cost solutions that treat municipal wastewater. Membrane bioreactor (MBR) is an innovative wastewater treatment method that replaces secondary clarifiers in conventional systems with a membrane filtration unit. Utilizing ultra or microfiltration membranes, MBRs retain sludge and increase microbial concentration within the reactor. This promising approach can meet stricter water reclamation and usage requirements, making it suitable for treating various types of wastewater. The MBR system has emerged as an alternative to the traditional activated sludge process, which has been plagued by problems such as high cost, low efficiency, and large space requirements (Van der Roest et al., 2002). The conventional activated sludge (CAS) process and tertiary filtration can be replaced by immersed and side-stream MBR. The MBR process efficiency is highly influenced by various design parameters such as membrane surface properties, permeate flux, retention time, pH, alkalinity, temperature, cleaning frequency, and structural features (Rahman et al., 2023). However, the quality of sludge, equipment requirements, and fouling remain significant challenges for the MBR process. Nevertheless, conventional wastewater treatment systems face significant obstacles due to energy limitations, climatic changes, and resource depletion (Deng et al., 2022). MBR outperforms CAS in terms of permeate quality, operational management, and footprint requirements, making it an efficient tool for sustainable water treatment (Rahman et al., 2023). In general, MBRs may be utilized in either a side-stream or submerged mode, as illustrated in Fig. 1-4, depending on the placement and manner of operation of the membrane. In side-stream MBRs, the membrane is situated externally to the biological reactor, through which the mixed liquor is passed into the membrane module. Within the membrane module, a permeate stream is produced, while the concentrated sludge is reintroduced into the bioreactor. In the side-stream configuration, membrane filtration is carried out using a conventional crossflow process. On the other hand, in submerged MBRs, the membrane module is directly immersed in the mixed liquor, within the aerated bioreactor. This operating strategy was applied for reducing the energy consumption associated with the recirculation pump in the side-stream configuration.

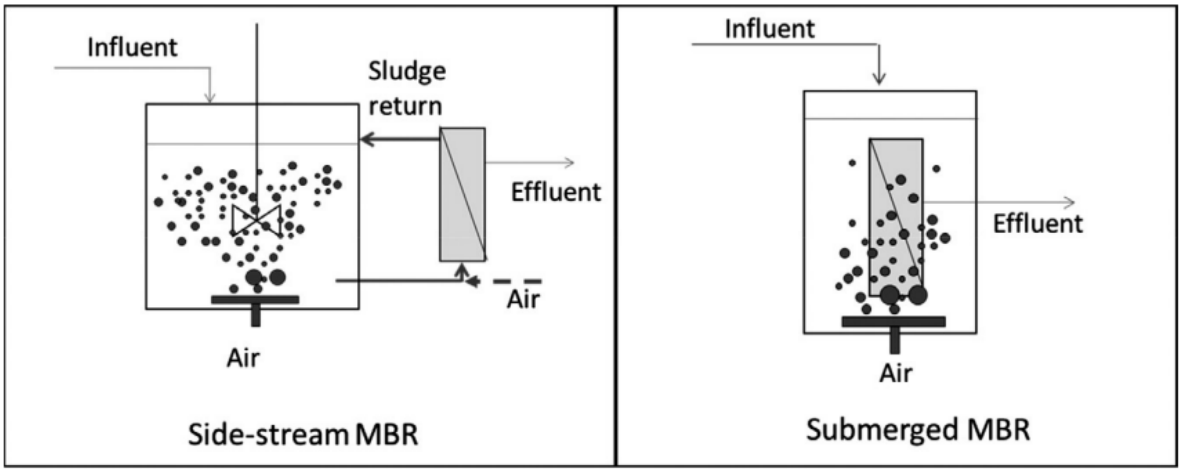


Figure 1-4. Types of MBR reactors (adapted from Galinha et al.,2018).

Thus, a combination of an anaerobic bioreactor with a submerged membrane, classified as Submerged Anaerobic Membrane Bioreactor (SAnMBR), can have multiple benefits such as: (1) high effluent quality free of particles, (2) small footprint, making them appealing in limited available space, and when water treatment for internal recycling is desired, (3) modularity, (4) consistent and effective operation, (5) decreased downstream disinfection requirements, and (6) biogas production utilised for electricity generation (Liu et al., 2020; Vu et al., 2020). More specifically, anaerobic treatment methods can effectively reduce the organic load in raw wastewater, with recent studies presenting chemical oxygen demand (COD) removals up to 90% (Gautam et al., 2022; Putra et al., 2020; Bui et al., 2021; Wang et al., 2021; Xiang et al., 2023). In the study of Yang et al., (2020) for the treatment of textile wastewater, three processes were tested; (1) an MBR, (2), a conventional activated sludge technology and (3) a moving bed biofilm reactor and the results revealed that among all technologies, MBR consisted of the most efficient process. However, to remove nutrients and other contaminants from the treated anaerobic effluent and meet strict discharge standards, it is necessary to apply additional treatment technology. A 2020-updated review by Vinardell et al., (2020) pointed out through numerous surveys that the application of anaerobic MBR as the main process for the municipal wastewater treatment could make UWTP energy neutral or even positive due to the methane-rich biogas produced and its high energy potential production.

1.2.1.1 SAnMBR

MBR significantly improves wastewater treatment. Fig. 1-5 presents the advanced MBR method for treating the municipal wastewater in UWTPs. The main advantages offered by such systems over conventional treatment technologies comprise the reduction of footprint by sustaining a high biomass content in the reactor, the handling of wide fluctuations in inlet quality, and the solid residue that can be applied directly in the field for non-potable applications. For the last two decades, aerobic MBRs are extensively being used for the treatment of industrial and domestic wastewater (Shahid et al., 2020). To lower the energy demand, the use of a submerged anaerobic membrane bioreactor (SAnMBR) can also be even more sustainable compared to aerobic MBR due to biogas production, which can be exploited for electricity. In addition, the production of relatively low sludge residual, the complete liquid-solid separation, the ability to treat numerous types of wastewater and the high effluent quality without any bacteria make the SAnMBR a promising technology for wastewater treatment (Du et al., 2022; Lee et al., 2002; Stuckey, 2012).

According to a review study (Mai et al., 2018) on this topic, although SAnMBRs can attain high performance, their effluents hardly comply with the regulation's discharge limits. Hence, the incorporation of advanced treatment methods plays a vital role to reach an acceptable amount of nutrients in the effluents (Zhang et al., 2021). Vyrides et al., (2010) investigated the post-treatment of anaerobic effluent from a SAnMBR, which was fed with saline sewage and found that with the use of powder activated carbon (PAC) the reduction of dissolved organic carbon (DOC) was higher than 80%. Gebretsadkan et al., (2022) examined the recovery of ammonium from an effluent produced from a membrane bioreactor under anaerobic conditions (AnMBR) with the use of sludge-derived activated hydrochar and showed that activated hydrochar can sufficiently remove the ammonium. Mai et al., (2018) studied the treatment of AnMBR effluents (initial feed was synthetic wastewater containing ciprofloxacin) utilizing six activated carbons. At a dosage of 1 g_{PAC} L^{-1}, 22–82% COD was eliminated. The 13.4 and 1 kDa fractions were the hardest to adsorb, according to size characterisation, while ciprofloxacin was removed with high removal efficiencies. In another study (Ittisupornrat et al., 2019), magnetic powdered activated carbon (Mag-PAC) was used as an adsorbent for the reduction of dissolved organic matter (DOM) from a MBR effluent. In batch experiments, a dosage of 4 g L^{-1} Mag-PAC achieved, in relatively short contact time (5 min), high efficiency concerning the DOM adsorption. However, the topic of phosphorus recovery from SAnMBR effluent appears to be relatively underexplored.

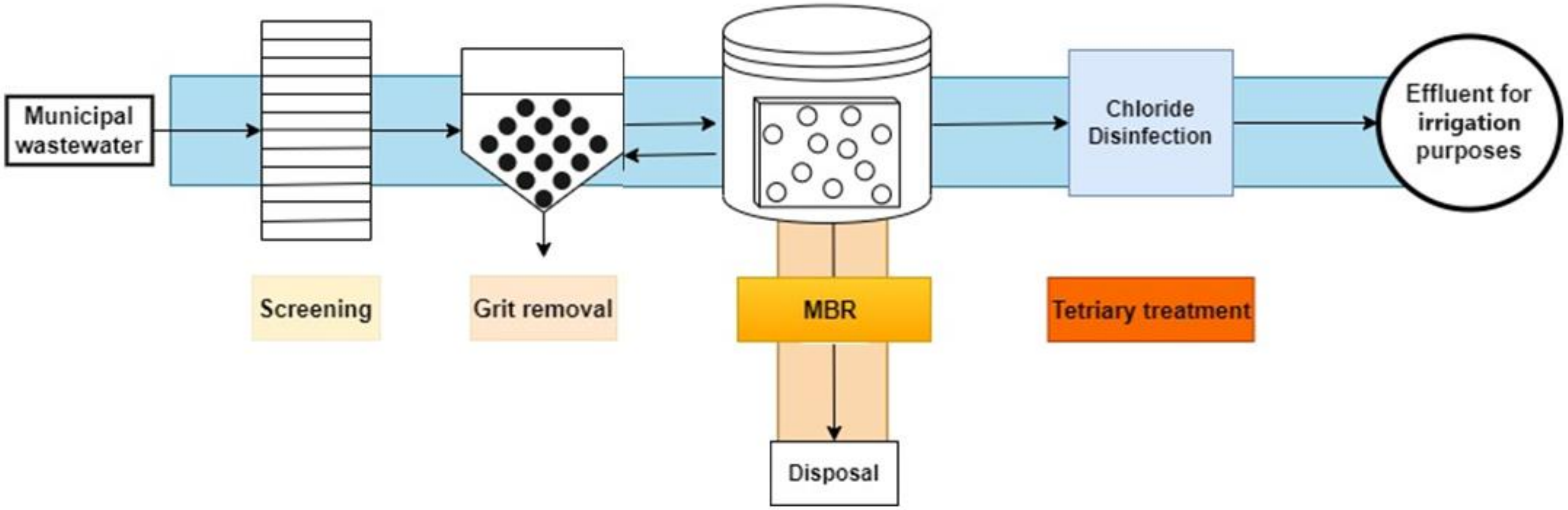


Figure 1-5. Advanced MBR treatment of municipal wastewater.

1.3 Phosphorus in waste streams

Waste streams that exhibit high levels of phosphate content are numerous, and include agricultural runoff, food and food-processing wastes, animal manures, municipal wastewater, and sewage sludge (Mayer et al., 2016). These waste streams contain several forms of phosphorus, such as polyphosphate, organic phosphorus compounds, and orthophosphate. Fertilizers also implemented to farms end up in nearby aquatic environments such as lakes, rivers, and streams (Salkunic et al., 2022), causing elevated levels of such compounds endangering potable water sources. Thus, the high waste streams' phosphorus content has a significant impact on the environment, especially in aquatic ecosystems and leads to high demand on costly treatment operations to mitigate (Koul et al., 2022). Human waste and phosphorus-containing detergents are other main sources of phosphate in domestic wastewater, which comprises home and sanitary waste and can further increase the phosphorus content in the municipal wastewater (Fig. 1-6). Typically, the influent wastewater ranges from a few milligrams per liter (mg L^{-1}) to many tens of milligrams per liter phosphate concentrations entering the UWTPs through the primary inlet stream (Salkunic et al., 2022). However, specific restrict regulations regarding the treatment of such wastewaters impose limits on the allowable phosphate concentrations in the effluent wastewater, which may influence the design and operation of UWTPs (Witek-Krowiak et al., 2022). Enterprises that produce fertilizer or prepare food, for example, have wastewater effluents with higher phosphate contents; hence, the amount of phosphates in discharged industrial wastewater varies depending on the industrial operations implemented (Nobaharan et al., 2021). Inadequate management of waste streams with high phosphate content can result in eutrophication and other types of environmental problems. As such, research has been conducted on phosphorus recovery from these waste streams, with the aid of solid sorbents, biochar, and natural adsorbents. The recovery and reuse of phosphorus from waste streams is a crucial research area due to the depletion of non-renewable resources and the environmental impact of phosphorus pollution.

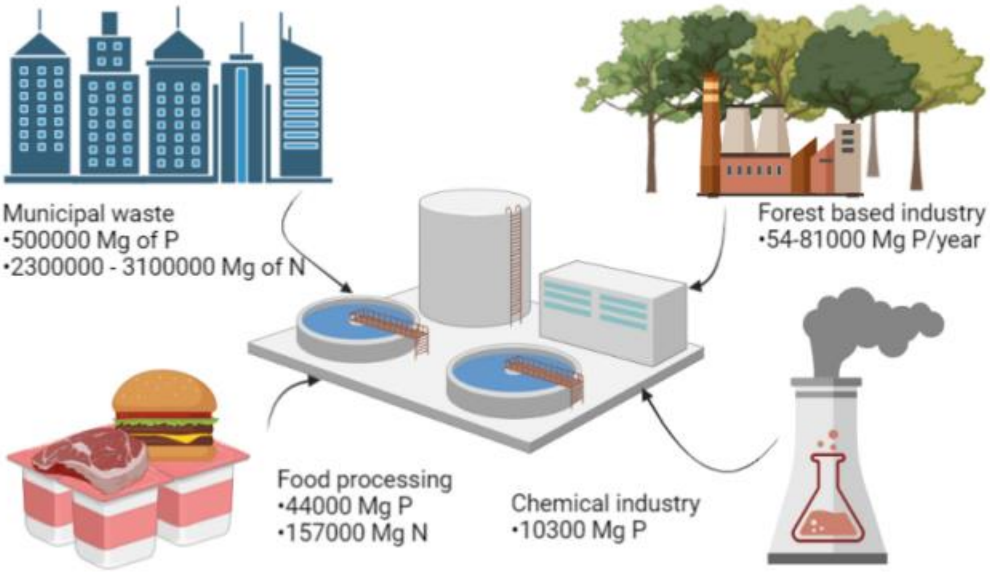


Figure 1-6. Potential for the recovery of phosphorus from wastewater, industries along with the phosphorus and nitrogen content (adapted from Witek-Krowiak, 2022).

According to the study of Vardanyan et al., (2018), phosphorus removal is most significant during the secondary biological treatment phase. This is due to the accumulation of phosphorus by microorganisms and precipitation in highly aerated conditions. Only a small amount of phosphorus is removed during the primary treatment stage. As also stated in Vardanyan et al., (2018) study, during the process of UWTP, it is evident that the rejected wastewater has the highest phosphate content, with a concentration range that usually falls between 50 to 70 mg L^{-1}. Furthermore, DWAS contains the highest concentration of accumulated phosphorus in solid waste streams (Fig. 1-7), making it a valuable source for recovery. The mass balance analysis of the same study emphasizes that DWAS accounts for 94% of incoming phosphorus, underscoring the importance of considering it for phosphorus recovery. Thus, the assessment of DWAS and rejected wastewater as potential sources for the recovery of phosphate may result in the development of more efficient and effective approaches to nutrient recovery and resource management within wastewater treatment facilities.

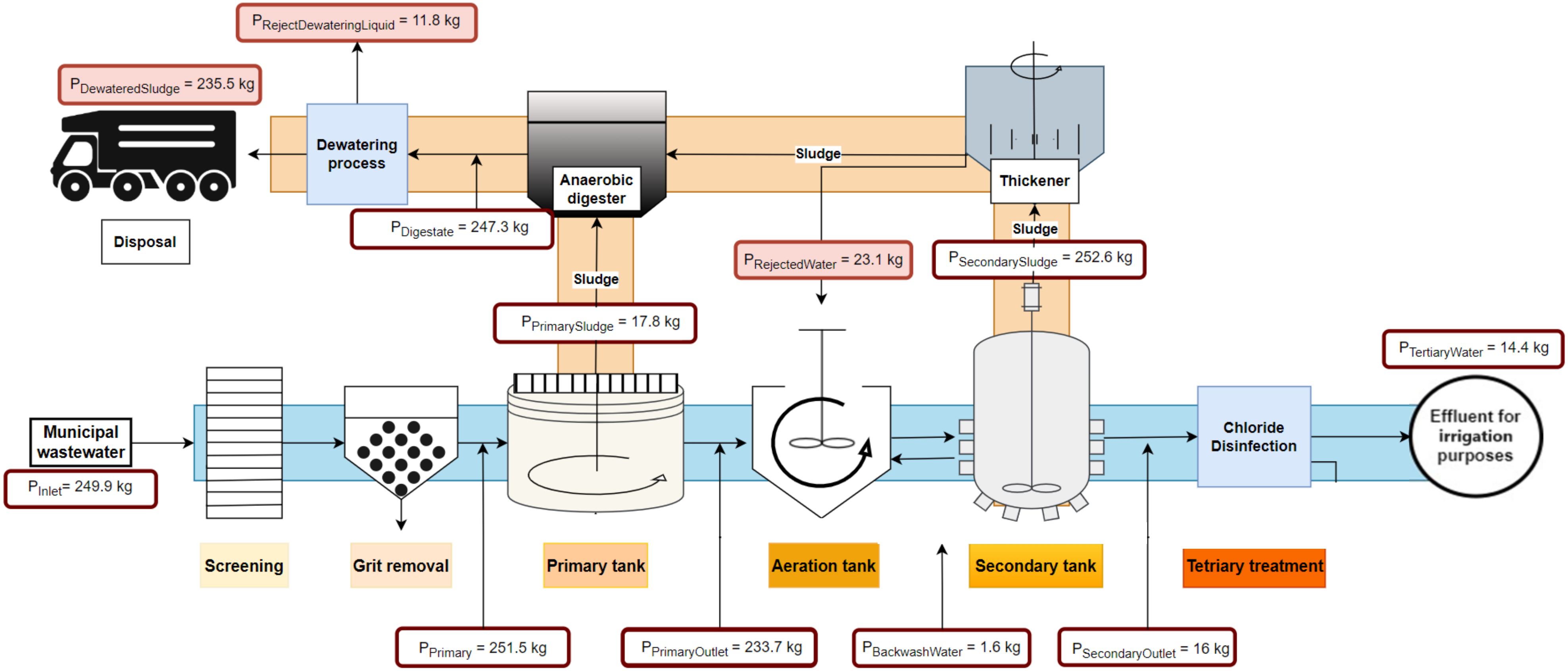


Figure 1-7. Phosphate mass balance during the UWTP operation (data adapted from Vardanyan et al., 2018)

1.3.1 Domestic wastewater

Domestic or primary wastewater refers to the wastewater generated from residential sources, including households and contains significant volumes of organic materials and nutrients (Koul et al., 2022). In recent years, there has been a growing interest in the recovery of resources from wastewater. The utilization of domestic wastewater consists of one of the most promising methodologies, which has the potential to reduce the pressure on water resources. Numerous studies in the last decade have focused on the recovery of resources from wastewater along with domestic wastewater treatment, which is believed to become a central goal in newly designed UWTPs (Kehrein et al., 2020; Renfrew et al., 2022). These studies have highlighted the high level of biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, and nutrient content found in wastewater. In particular, domestic wastewater contains a significant amount of nutrients, such as phosphorus, nitrogen, and potassium. These nutrients mainly come from human waste, as well as from phosphorus-based detergents and cleaning products. As a result, domestic wastewater contributes significantly to the overall phosphate levels in wastewater. Proper management and treatment of domestic wastewater is crucial due to its potential environmental impact.

Effective treatment processes utilized by UWTPs aim to decrease the nutrient content, the suspended solids, BOD, and COD found in domestic wastewater (Rout et al., 2021). This is essential to ensure compliance with water quality standards and ultimately safeguard public health and the environment. Therefore, the recovery of resources from wastewater and the treatment of domestic wastewater have become crucial areas of focus for researchers and policymakers alike. Treated domestic wastewater can be reclaimed and repurposed for a multitude of purposes, contributing to the sustainability of water resources and the environment.

1.3.2 Reject wastewater

The presence of nitrogen, phosphorus and carbon compounds in effluent streams causes serious pollution problems and affects human health (Jung et al., 2006). As a result, the wastewater discharge law has become stricter, requiring technologies with high standards in wastewater effluent discharge and capable of removing the high content of COD, ammonium, phosphate and suspended solids. Phosphorus content in the inlet of the UWTPs is much lower compared to the concentration in the liquid removed from the sludge during the dewatering process (termed reject water) (Kim et al., 2020; Vardanyan et al., 2018). As more phosphorus is released during digester treatment, higher phosphate concentrations are obtained in the rejected wastewater that could be subsequently recovered (50-70 mg L^{-1}). For this reason, this study also tested the rejected wastewater from the anaerobic sludge dewatering process as a source rich in phosphate ions.

Rejected wastewater is a concentrated form of wastewater produced after the primary and secondary treatment processes treatment process at UWTPs or other treatment facilities. Although various techniques are implemented for the removal or decrease of pollutants present in the wastewater, certain pollutants are still present in the treated effluent. This residual wastewater is the fraction that contains a higher concentration of these remaining contaminants (Gokyay and Alshami, 2017). The composition of reject wastewater can vary depending on several factors, including the initial quality of the influent wastewater, the treatment methods employed, and the efficiency of the treatment processes (Mucha and Mikosz, 2021). Typically, it contains high levels of suspended solids, organic matter, nutrients (such as nitrogen and phosphorus), heavy metals, pathogens, and other pollutants that were not entirely removed during the treatment (Mucha and Mikosz, 2021). As such, the treatment strategy aims to further reduce the concentrations of remaining contaminants before disposal or reuse in order to ensure compliance with environmental regulations and minimize the potential environmental impacts (Meyer and Wildere, 2004). To achieve this, additional treatment processes that include the use of advanced filtration, chemical precipitation, adsorption, disinfection, or biological treatment methods should be considered (Baldisserotto et al., 2023).

1.3.3 DWAS

Dewatered sludge (DWAS) is one of the outlet streams of the physical, chemical and biological operations employed in UWTP systems (Biswas et al., 2009). The use of DWAS as fertilizer is minimal due to the increasing concerns about contamination with pathogens, heavy metals and toxic organic compounds (Vardanyan et al., 2018). Mass balance from UWTP pointed out that the DWAS contained 94% of the incoming phosphorus from the UWTP (Vardanyan et al., 2018). Recovery of phosphorus from the dewatered anaerobic digestate can be a good option as it contains the highest concentration of phosphorus per kg of sludge (Fig. 1-7) (Vardanyan et al., 2018). Phosphate can be leached from DWAS using inorganic acids (H_2SO_4, HCl, and HNO_3) or organic acids at low pH; however inorganic leaching is one of the most effective methods for phosphorus extraction (Acelas et al., 2014; Vardanyan et al., 2018; Quist-Jensen et al., 2020, 2018). After phosphorus dissolution from DWAS, its selective recovery is critical for the sustainability of the process.

1.4 Technological options for phosphate removal from waste streams

Excessive phosphorus concentration in water bodies is known to stimulate algal growth by reducing the dissolved oxygen in aqueous environment, which in turn, imposes a harmful effect on the aquatic life (Biswas et al., 2007). In addition, intensive phosphorus mineral exploitation results in significant reduction of phosphorus reserves in both quality and quantity. The literature on phosphorus exhibits a variety of approaches applicable for the removal of phosphorus from wastewater (Reddy and Nair, 2022; Saleh et al., 2020; Tambat et al., 2023). Nutrient recovery technologies have the potential to reduce the environmental impact of wastewater treatment and create new revenue streams. The developed technologies for phosphate removal from aqueous solutions consist of a wide range of processes such as precipitation, anion exchange, crystallization, adsorption, reverse osmosis, microfiltration, magnetic separation, and electrodialysis (Karunanithi et al., 2015; Chowdhury et al., 2017; Cieślik and Konieczka, 2017). Those technologies have positive impact on the environmental contamination but also facilitate the extraction and recovery of phosphorus, enabling the production of high value-added products (Panagiotou et al., 2018).

1.4.1 Chemical precipitation and crystallization

Chemical precipitation has been extensively studied and consists of a common and easy-to-use technique for removing phosphorus from water and wastewater. The procedure entails adding chemicals to water, such as salts of Calcium (Ca), Aluminum (Al), Iron (Fe) and Magnesium (Mg) to cause the phosphates to precipitate out as insoluble solids, which can subsequently be removed using sedimentation or filtration (Chen et al., 2021). Metal cations often remove phosphate from wastewater through a combination of electrostatic interaction, adsorption by an Al or Fe oxide floc, and direct precipitation of Al or Fe phosphate (Adelagun et al., 2016). The type and amount of the chemical used, and the presence of competing ions or complexing agents are some of the variables that affect the efficiency of chemical precipitation (Deng and Dhar, 2023). Huang et al., (2015) also observed the high effect of pH in chemical precipitation of orthophosphate compounds from anaerobic digestion supernatant.

Several studies have been highlighting the efficiency of chemical precipitation in phosphate recovery, particularly in the form of struvite (magnesium ammonium phosphate (MAP)) (Lorick et al., 2020; Siciliano et al., 2020), and especially in the context of resource recovery or the generation of fertilizer products. Struvite is a white crystalline mineral compound that forms in wastewater treatment plants and other systems with a characteristic shape and structure. Mavinic et al., (2007) successfully removed over 90% of phosphate ions from wastewater solution using struvite crystallization at pilot-scale. However, although laboratory and pilot-scale studies have demonstrated the potential of struvite precipitation, significant obstacles remain in the upscaling of this technology for large-scale implementation, including the need for process optimization, cost-effectiveness, and successful integration with existing wastewater treatment systems (Siciliano et al., 2020). This is due to the struvite crystals that tend to adhere to surfaces and accumulate on equipment such as pipes, pumps, and valves causing clogging issues which reduce the efficiency of the treatment. In addition, a current limitation in this respect is the separation of phosphate and the insufficient effectiveness observed in relation to low phosphate concentration wastewater. Thus, a variety of process modifications to further improve the effectiveness of chemical precipitation have been evaluated, including the use of coagulants or adsorbents in conjunction with chemical precipitation, as well as the use of alternative chemicals or methods of chemical dosing (Fang et al., 2019; Lu et al., 2020).

1.4.2 Biological treatment

The biological elimination of phosphorus is a process that is based on the uptake of phosphorus that exceeds the metabolic needs of bacteria and is being recommended as a potential alternative for the chemical approach (Yeoman et al., 1988). The fundamental concept behind biological phosphorus removal entails subjecting bacteria to alternating anaerobic and aerobic conditions, which stimulates the process of “luxury uptake” of phosphorus (Witek-Krowiak et al., 2022). This technique incorporates the phosphorus into the sludge, making it easier to remove through WAS or filtration and lessening sludge production in comparison to chemical addition. During biological phosphorus removal, the phosphorus present in the influent wastewater is assimilated into cell biomass, which is subsequently extracted from the system through sludge wasting. The reactor configuration confers a competitive edge to the phosphorus-accumulating organisms (PAO) over other types of bacteria (Metcalf and Eddy, 2003). Recently, there has been a great deal of research focused on the Enhanced Biological Phosphorus Removal (EBPR) method that employs activated sludge systems, which has been identified as a viable and economical substitute for chemical treatment (Bunce et al., 2018). In Poland, UWTPs have successfully removed a minimum of 1470 mg of phosphorus by solely utilizing biological treatment methods (Preisner and Smol, 2022).

However, the Minnesota Pollution Control Agency has stated that the efficiency of phosphorus elimination by biological treatment might be lower than the chemical precipitation method. Thus, it appears that the most effective approach to treat wastewater sludge and recover phosphorus is through a combination of biological, chemical, physical methods along with thermal treatment to achieve optimal efficiency. The utilization of biological treatment in wastewater treatment, while a common method, requires a longer retention period and may pose challenges in limited space situations, as noted by Yeoman et al., (1988). Moreover, variations in environmental factors such as temperature and pH can hinder the effectiveness of the process (Bunce et al., 2018), while proper disposal of the resulting sludge is also critical to prevent environmental contamination (Liu et al., 2021).

1.4.3 Ion exchange

Ion exchange has emerged as a promising approach for the removal of phosphates from wastewater, which involves the use of a resin to exchange phosphate ions with other ions in the water, allowing the phosphate to be removed from the resin (Fig. 1-8). Anion exchange resins with a positive charge are widely employed for this purpose (Guida et al., 2021). The effectiveness of adsorbents in removing phosphate from wastewater is frequently compromised by the multitude of anions present in the solution, causing practical limitations (Martin et al., 2009; Guida et al., 2021; Nobaharan et al., 2021). To overcome this limitation, a novel type of ion exchange media that exhibits remarkable selectivity for phosphate and is easily regenerable has been developed. This media comprises hydrated ferric oxide nanoparticles that are dispersed within the pore structures of polymeric anion exchanger beads. It combines the mechanical robustness and durability of ion exchange resins with the high sorption capacity of ferric oxide for phosphate. The efficacy of this approach has been evaluated in fixed bed mini column experiments using real final effluent from two sewage treatment facilities in the UK, and the results demonstrate its high capacity for removing phosphate (Muhammad et al., 2019). The comparison of the water constituents on the individual components (hybrid resin, base resin, nanoparticles) revealed the importance of the nanoparticle that effectively transform the ion exchange media into a mono component absorber for phosphorus that enables sustained removal even in complex wastewaters (Muhammad et al., 2019). Hybrid ion exchange nanotechnology (HIX-Nano) is a technique that is utilized for the purpose of selective removing and retrieving phosphorus from wastewater (Ownby et al., 2021).

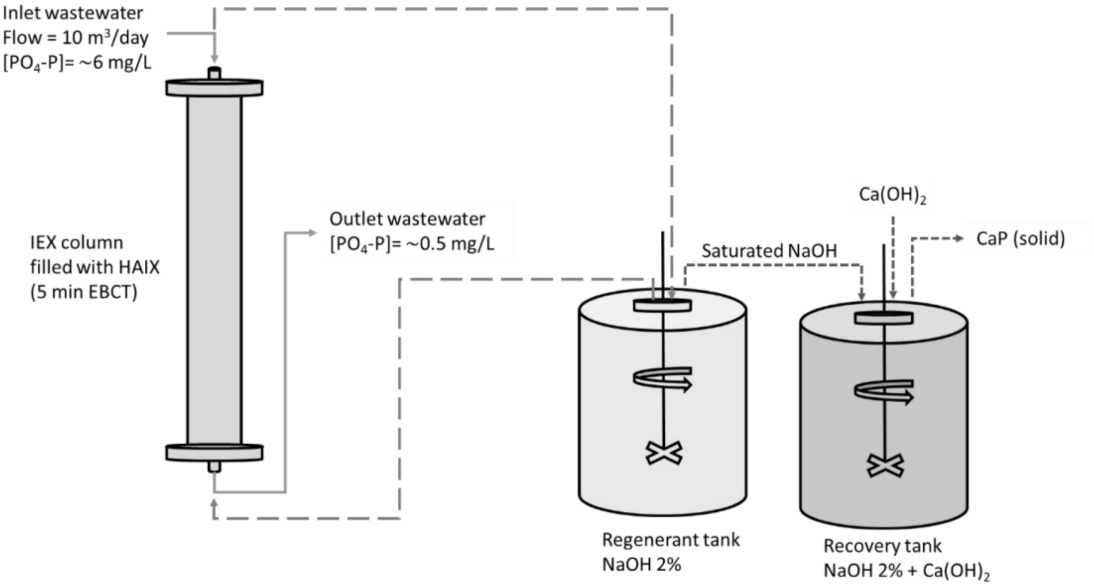


Figure 1-8. Schematic representation of a hybrid anion exchanger (HAIX) demonstration plant (adapted from Guida et al., 2021).

However, ion exchange technologies, although capable of selectively removing phosphate from solutions, pose operational challenges due to their high cost (Usman et al.,2022) and the production of significant amounts of difficult to dispose wastes (Martin et al., 2009). Moreover, the technology was implemented in conditions of reduced phosphate ion concentrations in wastewater, but unfortunately failed to produce the desired outcome (Bunce et al., 2018). This was due to the relatively diminished levels of phosphate ions present in wastewater and the fact that the efficacy of conventional ion exchange systems is contingent upon the charge and mass of the particular ion in question. Therefore, while ion exchange remains a promising method for phosphorus removal, it is crucial to consider its limitations and compare it with other methods to determine the most appropriate approach for a specific situation.

1.4.4 Membrane treatment

Membrane filtration is a highly effective technique for the selectively elimination of phosphates from wastewater (Ali, 2015). It encompasses different methods such as reverse osmosis and nanofiltration, which have been successfully employed to treat effluents containing both suspended and dissolved forms of phosphates (Obotey Ezugbe and Rathilal, 2020). The efficiency of phosphate removal from wastewater is significantly impacted by the selection of membrane material. Various factors, such as membrane pore size, material composition, surface charge, and filtering capacity, influence the membrane material used for phosphorus removal from wastewater (Xia et al., 2021). Main membrane types consist of the microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes, which are created using commonly employed membrane materials such as polyacrylonitrile (PAN), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyamide, and ceramic (Gao et al., 2019). Due to their high efficiency in phosphate removal, membrane nanofiltration processes have emerged as a promising alternative to traditional methods (Visvanathan and Roy, 1997). Additionally, membrane filtration can be applied for the treatment of both industrial and domestic wastewater due to the negative response observed in the presence of competitive compounds during phosphate removal. Therefore, it is evident that membrane filtration processes hold great potential as a method for the removal of phosphates from wastewater and can be supplemented with other methods to achieve superior results (Koh et al., 2020).

However, the task of removing phosphates from wastewater effluents through membrane filtration is considered challenging due to the low concentration of phosphate ions as compared to other competing species (Bunce et al., 2018). In addition, reports indicate that the reuse and regeneration of the membrane are often inadequate, leading to additional expenses but also consumes a large amount of energy (Koh et al., 2020). As such, these technologies are designed to treat wastewaters in larger wastewater treatment plants, making them less suitable for small-scale domestic wastewater treatment systems (Bunce et al., 2018).

1.4.5 Coagulation and flocculation

Coagulation-flocculation has been established as a commonly utilized approach for the treatment of wastewater containing phosphorus (Owoduni et al., 2023). The coagulation process consists of three sequential steps: (1) coagulant formation, (2) colloid/particle destabilisation, and (3) particle aggregation. Natural coagulants have emerged as a viable alternative for the treatment of phosphorus-containing wastewater, offering a comparable level of effectiveness in comparison to chemical coagulants (Owoduni et al., 2023). The most commonly used inorganic coagulants are calcium, magnesium, aluminium sulphate ($Al_2(SO_4)_3$), ferric sulphate ($Fe_2(SO_4)_3$) and ferric chloride ($FeCl_3$). When added to water, Al/Fe(III) ions hydrolyse to form soluble monomeric and polymeric species and solid precipitates. Although these chemical coagulants are frequently used for coagulation, organic polymers have been increasingly adopted in coagulation/flocculation processes for water purification (Ozacar and Sengil, 2003). The selection of coagulant and flocculant in such procedures is based on the type of wastewater being treated, the concentration of phosphates, and the desired efficiency level of removal (Owoduni et al., 2023). According to the study of Ozacar and Sengil (2003), the utilization of clay and polyelectrolytes as coagulant has been found to increase phosphate removal efficiency while reducing the necessary alum dosage. The combination of coagulation and flocculation has high efficiency towards removing phosphate ions from water, while it can attain the destabilization of particles in water solutions containing high suspended solids content.

Nevertheless, to achieve low phosphorus effluent levels, vast amounts of metal coagulants are required, surpassing stoichiometric quantities. Moreover, the combination of coagulants and flocculants with an additional coagulant aid may result in increased toxicity (Kurniawan et al., 2020). Chemical coagulation, besides being expensive, has the potential to produce excessive and harmful sludge (Alazaiza et al., 2022). As such, the use of metal-based coagulants raises environmental concerns due to their toxic nature (Owoduni et al., 2023; Bahrodin et al., 2021; Kurniawan et al., 2020). Thus, the integration of coagulation and flocculation with complementary methods, such as adsorption and membrane filtration, could enhance the efficiency of removal and reduce the negative environmental impact from the use of metal-based coagulants (Ali, 2015).

1.4.6 Adsorption

Adsorption, a widely studied phenomenon in various fields of science, refers to the process whereby a substance is transferred from one phase to another, ultimately leading to its accumulation or concentration at the surface of the latter (Nageeb, 2013). This intricate process has been extensively researched and has been documented in numerous scientific literature; specifically, as a promising approach for sustainable resource management, efficiently removing nutrients and compounds from domestic wastewater permeate (Asimakopoulos et al., 2021; Han et al., 2020; Singh et al., 2018).

According to literature (Fig. 1-9), the recovery of phosphates using adsorption method has been thoroughly researched in recent years. In addition, employing biowaste as an adsorbent, represents a groundbreaking innovation, which significantly reduces the reliance on conventional chemical precipitation methods, which are less eco-friendly and entail high operational costs. The importance of phosphate recovery from genuine wastewater solutions is also highlighted in Fig. 1-9, which will lead to a more sustainable future in which waste becomes a valuable resource and environmental protection integrates smoothly with resource recovery.

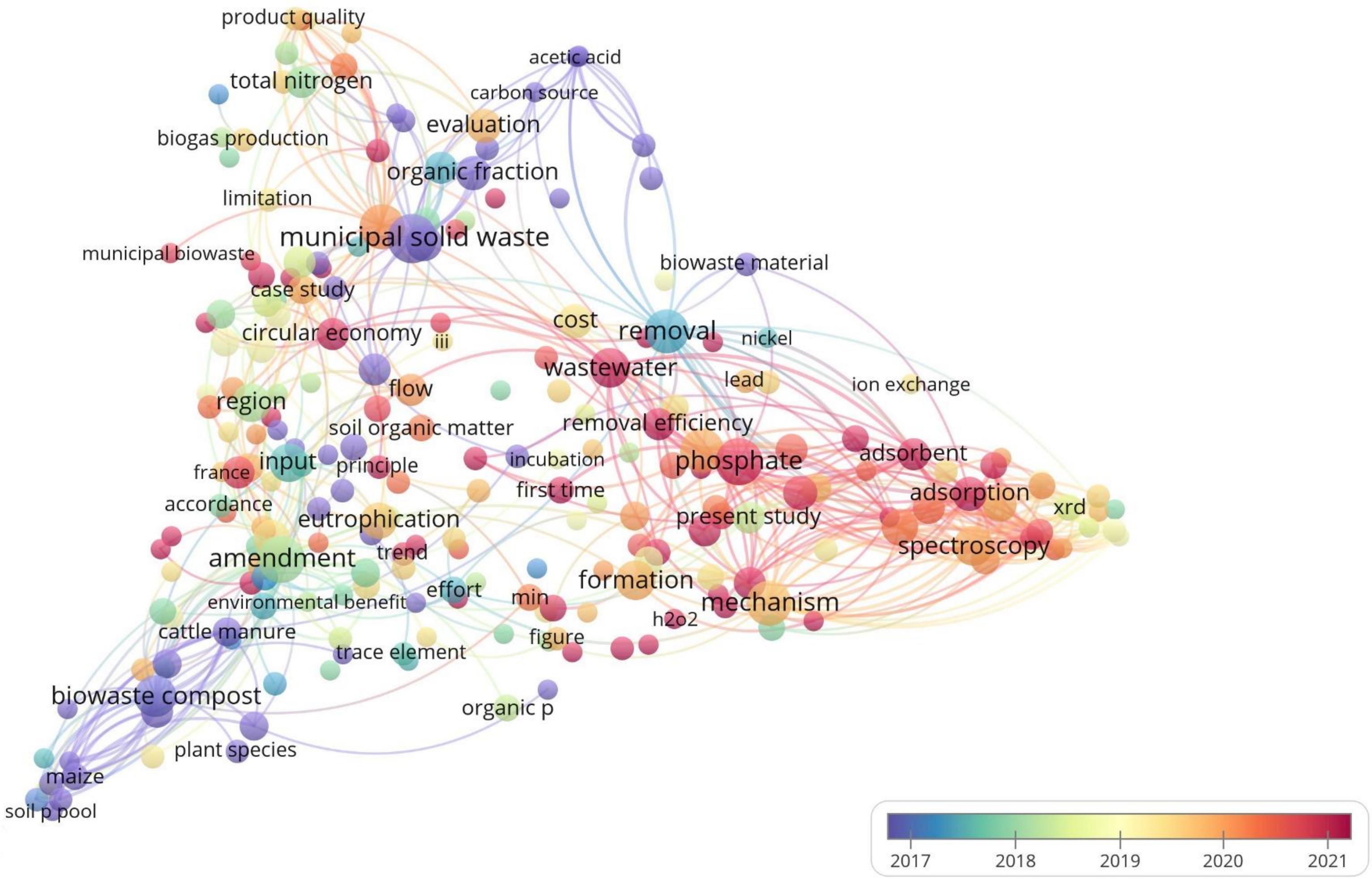


Figure 1-9. Visual figure of phosphorus removal by adsorbent in recent four years (information collected from Scopus, including keywords "adsorption" + "phosphate", larger spheres represent higher research frequency, and yellow spheres represent research frontier).

Adsorption is a technique that has been employed successfully in eliminating phosphates from the liquid phase (Humayro et al., 2021; Robalds et al., 2016; Wang et al., 2015). This technique involves the transfer of the impurities to a solid phase, which is commonly referred to as the adsorbent (Gizaw et al., 2021). The adsorbent used in this process may be of natural and synthetic origin and typically has a high surface area-to-volume ratio, which makes it highly effective in removing impurities from the wastewater. The activated alumina, silica gel, PAC, molecular sieve carbon or zeolites, and polymeric adsorbents are among the primary and extensively used adsorbents (Pourhakkak et al., 2021). These methods can help reduce the levels of phosphorus in water bodies, thus reducing the negative impacts of excess phosphorus in aquatic ecosystems.

Various parameters significantly impact the chemical transfer kinetics between the liquid and solid phases, such as the adsorbent's characteristics and surface area, the rate of adsorption (Nageeb, 2013), the substance's characteristics being absorbed, the temperature, the pressure (De Gisi et al., 2016), the pH and the substance concentration being absorbed (Usman et al., 2022). The greater the surface area, the more adsorbate volume can be adsorbed, making the surface area of the adsorbent critical (Sukmana et al., 2021). Phosphorus also exhibits tripartite valences, ranging from -1 to -3, in concordance with the pH of the solution, as depicted in Fig. 1-10. Moreover, polar molecules tend to readily adsorb to polar surfaces, whereas nonpolar molecules tend to readily adsorb to nonpolar surfaces. Thus, it is crucial to comprehend this process to optimize its potential in wastewater treatment.

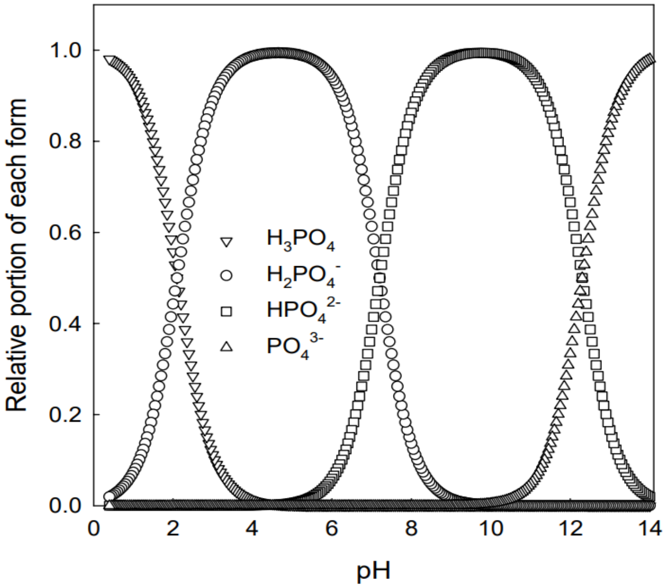


Figure 1-10. Different forms of phosphorus according to pH (adapted from Baek et al., 2004).

Adsorption is an advantageous process due to its lack of harmful byproducts and eco-friendly nature (Metcalf and Eddy, 2003). Moreover, adsorption is also a straightforward and cost-effective process that can be scaled easily to meet industrial demands (Usman et al., 2022; Rathod et al., 2014). Recent advancements in adsorption have focused on producing advanced, sustainable, and highly effective adsorbent materials (Nageeb, 2013). For instance, Fe-based MOFs of MIL-101 (Metal–Organic Frameworks) have demonstrated effectiveness in removing phosphates from aqueous solutions and eutrophic water (Xie et al., 2017; Kumar et al., 2019). Porous biochar loaded with La-Fe(hydr)oxides/montmorillonite has also been developed to efficiently remove phosphorus in wastewater (Sun et al., 2022). As depicted in Fig. 1-11, various interactions might be involved in phosphorus adsorption onto biochar-based adsorbents such as electrostatic attraction, complexation, ligand exchange, anion exchange, precipitation, and physical adsorption. Furthermore, the use of natural and modified clinoptilolite has been explored for the purpose of eliminating ammonium ions and phosphates from wastewater (Stepova et al., 2023). However, adsorption has certain limitations, the most significant of which is the requirement for a substantial surface area to achieve optimal results. A high surface area-to-volume ratio with porosity is essential for the adsorbent material. Additionally, the adsorbent needs to undergo periodic regeneration to maintain its efficacy, which can be both costly and time-consuming (Wu et al., 2020). The aforementioned challenges can be effectively addressed by employing biowaste-derived materials as adsorbents in the process of the recovery of high-value nutrients, such as phosphates, from wastewater streams (see section 1.5).

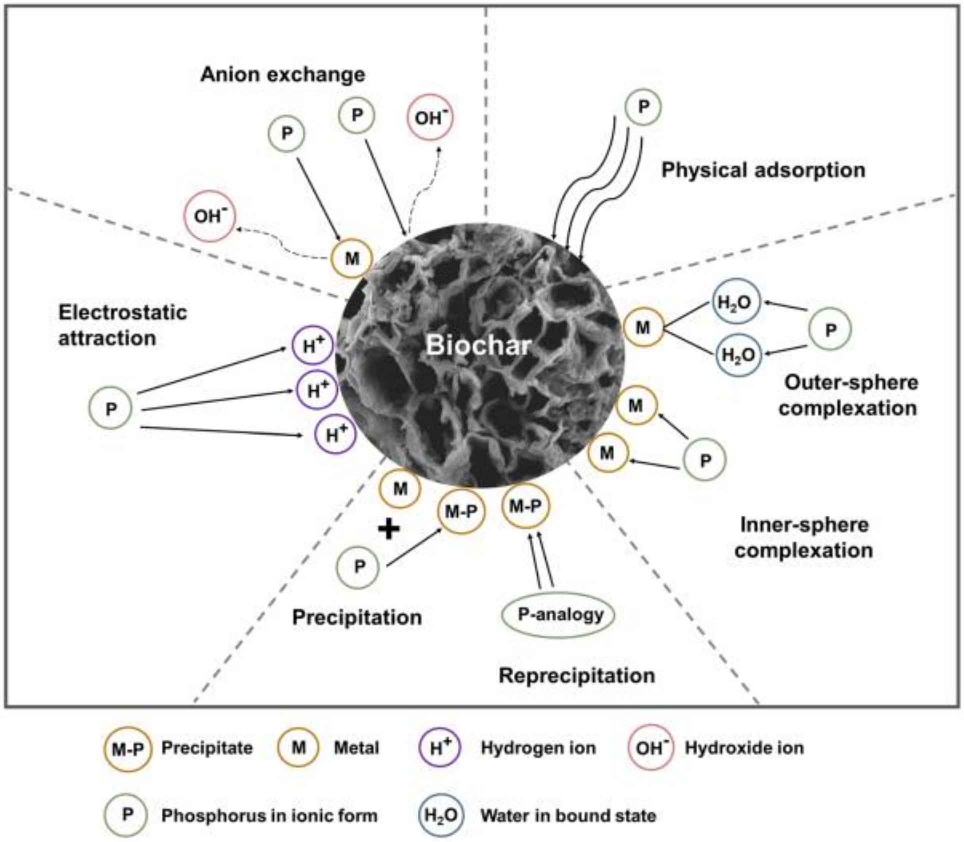


Figure 1-11. Adsorption mechanisms of biochar-based phosphorus adsorbent. The adsorption mechanisms involve electrostatic attraction, complexation, ligand exchange, anion exchange, precipitation, and physical adsorption (adapted from Luo et al., 2022).

1.5 Waste-based biosorbents

Aligned with the concept of circular economy, the conversion of waste biomaterial to an adsorbent for phosphorus from wastewater can be exploited as an approach to eliminate the disposal cost of biowaste and to significantly decrease the adsorbent cost. Several studies demonstrated that use of waste biomaterials constitute the method of phosphate adsorption more attractive and environmental friendly due to the fact that wastes become valuable resources (Krika et al., 2015). Various adsorbents such as thermally treated waste eggshells (Köse and Kıvanc, 2011; Panagiotou et al., 2018), mussel shells (Paradelo et al., 2016), gastropod shells (Oladoja et al., 2015), land snail shells (Oladoja et al., 2012), orange waste gel (Biswas et al., 2008), digested and sugar beet tailing biochar (Yao et al., 2011), dewatered alum sludge (Yang et al., 2006), metal loaded orange waste (La(III), Ce(III), Fe(III)) (Biswas et al., 2007), rice husk ash (Mor et al. 2016), waste-derived fungal biomass (Jack et al., 2019) as well as raw and calcinated dolomite (Karaca et al., 2006) have been widely investigated for phosphate exploitation. A key limitation of most of these studies is the sole use of synthetic solutions which exclude the application of real wastes containing valuable nutrients, such as wastewater or leached solution from anaerobic sludge, failing to fully exploit their content and produce high-value commodities. Table 3-6 shows studies that used biowaste as a phosphate adsorbent from both synthetic and real wastewater. Most of these studies have applied pre-treatment steps for the activation of each material and these biowaste pointed out relatively high phosphate adsorption capacity from wastewater (Table 3-6).

Apart from the aforementioned waste-based biosorbents, this study focused on exploiting a new biowaste that has been scarcely studied for the valorization of phosphate from synthetic and real wastewater solutions. Herein, several biowastes such as orange peels, spent coffee residues, fish scales, seagrass residues of *P. oceanica*, olive kernels biochar and vineyard prunings biochar were examined for their capacity to adsorb phosphate from synthetic wastewater. Based on experimental data (Section 3.1) it was concluded that thermally treated seagrass residues demonstrate the highest potential to adsorb phosphate. Therefore, the aim of this study was to evaluate the potential of seagrass residues of *P. oceanica* as a phosphate adsorbent from real wastewater applications. Additionally, the study aimed in characterizing the compounds formed following phosphate adsorption at seagrass residues of *P. oceanica*, to determine the structure of seagrass residues before and after phosphate adsorption and to identify the mechanisms of phosphate binding. Apart from this, very few studies were focused on the use of biowastes as phosphate adsorbents and their direct application to agriculture. More research studies were devoted to the adsorption as a two-step process; adsorption and desorption (Aslam et al., 2022; He et al., 2022).

Table 1-2. Biowaste used for the removal of phosphate from synthetic and real wastewater.

Source of phosphate and concentration	Biowaste	Method of Phosphate analysis	Pre-treatment method	Adsorbent dose (g L^{-1})	Adsorbent capacity (mg g^{-1})	Adsorption yield (%)	Reference
Synthetic solution (20 mg L^{-1})	Orange waste gel (OW)	ICP/AES spectrometer	OW and $Ca(OH)_2$ rinsed and dried in oven for 48 h at 70°C	1.7	57.0	99	Biswas et al., (2008)
Synthetic solution (100 mg L^{-1})	Calcined Waste Eggshells	Ascorbic acid method	Thermally treated at 800°C for 2 h	10.0	23.0	99	Kose et al., (2011)
Wastewater (300 mg L^{-1})	Land snail shell (SS), source of gastropod shell	Ascorbic acid method	Dried in the oven at 90°C for 4 h	2.0	222.2	92	Oladoja et al., (2012)
Swine wastewater (27.4 mg L^{-1})	Ground corn loaded with Mg	Vanado-molybdo-phosphoric acid method	Pyrolysed at 300°C in nitrogen gas for 3 h	10.0	2.7	90	Fang et al., (2014)
Aquaculture wastewater (2.5-30 mg L^{-1})	Gastropod shell	Ascorbic acid method	Thermally treated at 750°C for 2 h	10.0	3.0	60	Oladoja et al., (2015)
Wastewater (350 mg L^{-1})	Calcined mussel shells	Vanado-molybdo-phosphoric acid method	Thermally treated at 550°C for 15 min	13.3	-	80	Paradelo et al., (2016)
Swine anaerobic digestate effluent (227-283 mg L^{-1})	Wood (WDB) Corncobs (CCB)	Ascorbic acid method	Slow pyrolysis 600°C for 10 h	12.5	22.6	90	Kizito et al., (2017)
Swine wastewater (25 mg L^{-1})	Poplar tree, Wood sawdust, Natural dolomite	Colorimetric method not specified	Pyrolysed at 900°C in nitrogen gas for 1 h	1.9	13.2	99	Kizito et al., (2017)
Wastewater (30 mg L^{-1})	Calcined Waste Eggshells	Ascorbic acid method	Thermally treated at 900°C for 30 min	40.0	0.7	89	Panagiotou et al., (2018)
Leached Solution form DWAS (418.5 mg L^{-1})	Calcined Waste Eggshells	Ascorbic acid method	Thermally treated at 900°C for 30 min	40.0	10.5	98	Panagiotou et al., (2018)
Wastewater (1.56 mg L^{-1})	Mussel shells	Ascorbic acid method	Thermally treated at 800 ◦C for 4 h	3.3	2.5	98.5	Lee et al., (2022)
Synthetic solution (150 mg L^{-1})	Modified bamboo-eggshell	Ascorbic acid method	Thermally treated at 800 ◦C for 2 h	0.25	98	-	Sarker et al., (2023)

1.5.1 Seagrass *P. oceanica*

Posidonia oceanica is an endemic species in the Mediterranean Sea, and its dead leaves are accumulated in enormous quantities along sandy coasts, especially in autumn (Dural et al., 2011). The dead leaves of *P. oceanica* are very promising biomass waste that has no implementation applied and has high treatment cost (collection and transportation) (Photiou et al., 2021) while the excess amount is causing aesthetic problems on the beach (Cengiz and Cavas, 2010). The applicability of thermally treated *P. oceanica* residues in the adsorption process has been reported in several studies in the literature for the removal of orthophosphates (Wahab et al., 2011), textile dyes (Guezguez and Mhenni, 2008), methylene blue (Dural et al., 2011; Elmorsi et al., 2019; Han et al., 2020), anionic and non-ionic surfactants (Ncibi, 2008), phenol (Ncibi et al., 2014) and heavy metals (Asimakopoulos et al., 2021; Aydin et al., 2012). Seagrasses that have been dried at 100°C, and then thermally treated at 500°C for 1 hr are displayed in Fig. 1-13. It is obvious that as the temperature rises, the powder produced has finer-grained particles. Thus, the thermally treated seagrass consists of a great and low-cost adsorbent for the recovery of phosphates from both synthetic and real wastewater solutions.

Figure 1-12. Seagrass dried at 100°C (left) and thermally treated (right) at 500 °C for 1 hr.

1.5.2 Chicken eggshells

The production volume of eggs worldwide exceeded 82.17 million metric tonnes in 2019, and since 1990, the global egg production volume has increased by over 100 percent (Statista, 2021). The worldwide egg production rate results from its high global consumption rate (Waheed et al., 2020). More than 250,000 tonnes of eggshells are annually disposed of worldwide (Faridi and Arabhosseini, 2018; Lee et al., 2022) in landfills with minimal or no pre-treatment (Gao and Xu, 2012; Oliveira et al., 2013). Therefore, eggshell becomes a source of pollution, which leads to environmental issues such as the odour production and microbial growth. According to the European Union (EU) Regulation (EC) N° 1069/2009, the level of risk that arises from animal by-products ABP can fall into three categories from 1 (highest risk) to 3 (lowest risk). Eggshells are considered a low-risk material (Category 3), and options for its use and disposal are much broader than higher risk ABP. In addition, eggshells waste can be used under certain conditions without pre-treatment (Quina et al. 2017). Turning eggshell waste into added-value products can lead to an economic benefit besides the high environmental benefit (Oliveira et al., 2013). Research studies concerning the utilization of eggshells provide numerous applications, such as their use in medicinal supplements, bone graft substitute and denture base (Waheed et al., 2020). Eggshell wastes can also be employed in constructing floor tiles and in cement to enhance compressive strength or may be included in animal feed, plant fertilizer, batteries, and removal of heavy metals and other components from soil and water (Vandeginste, 2021; Waheed et al., 2020). Eggshells are composed of inner shell membranes and an outer calcium carbonate layer known as calcite (Oliveira et al., 2013). More specifically, eggshell constitutes 94% calcium carbonate, 4% organic substances, 1% calcium phosphate, and 1% magnesium carbonate (Aditya et al., 2021; Murakami et al., 2007). Thermogravimetric analysis by Murakami et al., (2007) and Santos et al., (2019) suggested that the conversion of eggshell (mainly calcium carbonate) to calcium oxide is attained by thermal treatment as follow:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad (1)$$

The calcination process reduces the mass of the material due to the release of CO_2, as presented in the reaction (1). Specifically, Santos et al., (2019) found that slight mass variance of eggshells until nearly 700 °C. However, at 784 °C the loss was more than 40% which indicates the thermal conversion of $CaCO_3$ into CO_2 and CaO. After 800 °C, the mass remains constant, and it is likely to conclude that the thermal decomposition of $CaCO_3$ was complete. Panagiotou et al., (2018) found that the increase in calcination temperature increased specific surface area. Fig. 1-13 shows a collection of eggshells that have been calcinated at various temperatures and durations after being rinsed with deionized water and dried at 100 °C. It is evident that with increasing calcination temperature the resulting powder exhibits a more refined particle size. The solubility of CaO in water is higher than the solubility of $CaCO_3$ (1.19 and 0.019 g L^{-1}, respectively) (Santos et al. 2019); therefore, the phosphorus removal takes place due to calcium precipitation and adsorption. In addition, calcinated eggshell adsorption demonstrated high capacity of phosphorus removal and fast kinetics in a wide pH range of 2-10 (Köse and Kıvanc, 2011), increasing its potential applications in agricultural field.

Figure 1-13. Eggshells rinsed with deionized water and dried at 100 °C, (b) calcinated at 600 °C for 3 h and (c) calcinated at 900 °C for 30 min (adapted from Panagiotou et al., 2018).

1.5.2.1 Thermally treated eggshells in AD

During anaerobic digestion (AD) of easily biodegradable substrates, a complex series of microbial processes takes place in the absence of oxygen. These processes break down organic matter in the substrate, releasing various compounds, including phosphorus in the form of orthophosphate. Orthophosphate is a dissolved form of phosphorus that is particularly favourable for recovery through adsorption methods (Hafuka and Kimura, 2022).

Furthermore, during AD process, the rapid generation of volatile fatty acids (VFAs) could significantly decrease pH. This inhibits methanogenesis and causes difficulties in maintaining a stable operation of an anaerobic digester (Charalambous et al., 2020). A common strategy to counteract the pH drops due to VFAs is adding a considerable amount of NaOH. Yang et al., (2015) found that the addition of NaOH in a thermophilic AD system using high organic substrates, such as food waste increased the feasibility of controlling the pH and avoided the acidification due to the background production of lactic acid and VFAs. Besides the increase of the AD operational cost due to the addition of chemicals, the presence of NaOH demands considerable safety precautions. Similar results attained by the addition of bicarbonates as a conventional pH control strategy (Ye et al., 2018). Even so, the high concentrations of the required neutralizer or buffer chemicals could inhibit the methanogenesis (Charalambous et al., 2020).

Different waste by-products were introduced as novel additives to AD systems, which could restore excessive acidification and alleviate low pH. Kong et al., (2016) investigated two types of zero-valent iron (ZVI) (powder (PZVI) and scrap metal (SZVI)) and both restrained excessive acidification. Banks and Lo, (2003), assessed the effect of municipal solid waste incinerator (MSWI) bottom ash on the AD process. According to the results, the addition of ash appeared to have beneficial effects on the degradation process, as there was an increase in gas production, alkalinity, and pH as compared to the corresponding control reactor without MSWI ash addition. Nevertheless, this is the first study (Chapter 5) using biowaste such as eggshells as a strategy to control pH reduction due to the high VFAs production that occurs during the anaerobic fermentation process, as well as to recover orthophosphates from real wastewater solutions.

1.6 Objectives and Scope

Phosphorus is an essential nutrient for plant growth and plays a critical role in various biological processes. Phosphorus deficiency can limit agricultural productivity, making efficient management and recycling of phosphorus crucial for sustainable food production and environmental stewardship. Phosphate-rich wastes, such as wastewater, anaerobic digester effluents and DWAS, contain phosphorus that can be recovered for reuse (see section

1.3.3). These wastes serve as suitable sources for phosphorus recovery due to their high phosphate concentrations and the potential environmental benefits of their treatment and resource recovery. Adsorption is an effective method for phosphate recovery from phosphate-rich wastes. Thus, among a wide range of biowastes tested in this study, thermally treated seagrass and eggshells residues were chosen as bio-based materials for adsorption due to their abundance, low-cost, and favourable adsorption properties. Seagrass residues have shown potential for phosphate adsorption due to their high surface area and inherent affinity for phosphate ions. Similarly, thermally treated eggshells have demonstrated adsorption capacity and can act as a sustainable and renewable resource for phosphate recovery. The combination of adsorption using bio-based materials from waste streams address several problems. They offer a sustainable and cost-effective approach for phosphorus recovery, reducing the dependence on scarce phosphate rock resources. By recovering phosphorus from phosphate-rich wastes, we have developed an efficient approach which helps mitigate environmental pollution and eutrophication caused by the discharge of nutrient-rich effluents into water bodies. Additionally, we contribute to the circular economy by transforming waste materials into valuable products. Finally, the recovered phosphate solid fraction obtained through adsorption with seagrass residues or eggshells can be utilized as a soil conditioner or fertilizer. The phosphate-rich solid can provide essential nutrients to plants, enhance soil fertility, and support sustainable agriculture. Many researchers have also extensively studied the high phosphate loaded end product after adsorption through its direct application as a soil supplement (Humayro et al., 2021; Santos et al., 2019; Sun et al., 2018; Yao et al., 2013). However, to the author's best knowledge, very few publications are available in the literature that addresses (Li et al., 2018; Robalds et al., 2016) the issue of using real wastewater as a phosphate source and then the examination of the end product after adsorption as a fertilizer or soil conditioner (Table 1). Most studies apply desorption methods or evaluate the end product composed using synthetic phosphate solutions; however, this far from actual conditions that can lead to false conclusions (Humayro et al., 2021; Santos et al., 2019). The implementation of the recovered phosphate as a soil amendment promotes efficient nutrient management, reduces the need for chemical fertilizers, and contributes to the long-term sustainability of agricultural practices.

Aligned with the concept of circular economy, this study proposes a novel approach (Fig. 1-14) aiming at a sustainable recovery of phosphates from real wastewater and DWAS using thermally treated biowaste-based materials and the evaluation of end products in the agricultural industry as soil conditioners. Thus, the present study established a set of objectives in order to attain the aforementioned goal:

- Exploitation of new biowastes that have been scarcely studied for the valorisation of phosphate from synthetic and real wastewater solutions was mandatory. Herein, several biowastes such as orange peels, spent coffee residues, fish scales, seagrass residues of *P. oceanica*, olive kernels biochar and vineyard prunings biochar were examined for their capacity to adsorb phosphate from synthetic wastewater.
- Determination of the performance of thermally treated eggshell and seagrass residues towards phosphate ions from synthetic and real wastewater solutions and estimate the effect of other ions in the adsorption process. Calculation of the Langmuir and the Freundlich constants based on the linear form of the isotherms to examine the relationship between sorbed and aqueous concentration.
- Characterisation of the raw materials to identify their content and structural changes before and after thermal pretreatment, as well as after the adsorption procedure to identify the mechanisms of phosphate binding.
- Evaluation of the most efficient extraction process to investigate the potential phosphate recovery from DWAS as well as determination of biowastes' selectivity towards phosphate ions from synthetic and real wastewater solutions (extracted solution from DWAS and effluent from anaerobic digester).
- Implementation of final products after adsorption process (from synthetic solutions, anaerobic wastewater effluent and DWAS) as soil conditioners and estimation of their impact on different types of seeds (*Solanum lycopersicum*, *Lepidium sativum*, and *Sinapis alba*) through seed germination and root elongation. The implementation of fractionation analysis also assisted in the practical determination of distinct phosphorus forms in each end product.

- Evaluation of thermally treated eggshell in AD systems as a strategy to counteract the pH drop due to the high concentrations of VFAs and increase methane production. This approach was considered as a second potential application of thermally treated eggshells after phosphate adsorption in the anaerobic digester and the anaerobic effluents (AD effluent and wastewater leached from DWAS).
- Evaluation of a SAnMBR treating rejected and domestic wastewater as well as determination of thermally treated biowastes' efficiency on the recovery of phosphate from the SAnMBR effluent (particle-free effluent with low COD concentrations) both in columns and in reactors, aiming to optimise the entire process.
- Assessment of PAC as a follow-up adsorbent for further COD removal from biowaste-treated wastewater. A vast array of crucial parameters was measured throughout SAnMBR and followed adsorption reactors operations to evaluate the overall system performance.

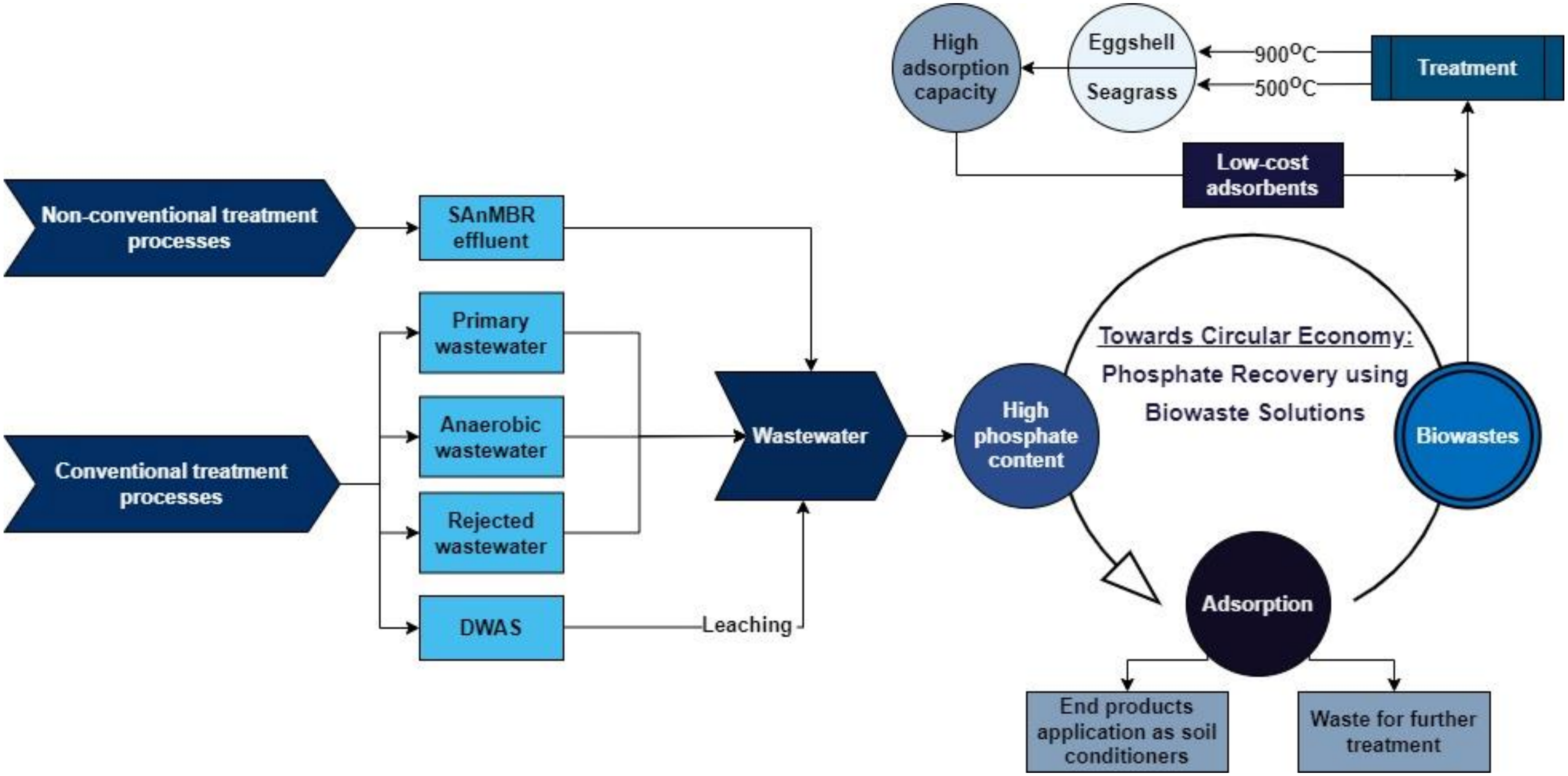


Figure 1-14. Sustainable recovery of phosphates from real wastewater and DWAS using thermally treated biowaste-based materials.

2 Research Methodology

2.1 Common Research Methodology for Chapters 3-7

From the preliminary experiments of this study (see Section 2.2), two biowastes (eggshell, seagrass) were selected due to their high adsorption efficiency of phosphates exhibited after being evaluated under different conditions. The pre-treatment of these biowaste and the common research methodology followed for the forthcoming experiments are presented below:

2.1.1 Pre-treatment of seagrass residues and eggshells

Chicken eggshells were collected from local food restaurants, washed with tap, and distilled water to remove impurities and pollutants. Once cleaned, the eggshells were naturally dried and crushed at room temperature for 24 h. Subsequently, the eggshells were calcinated (thermally treated) in the furnace at 900°C for 30 min to obtain the thermally treated eggshell specimens, prior to each application. The thermal treatment generates nanometer scale porous, which provide a significant amount of surface area for the interaction of phosphate ions. According to the literature, the surface area of the thermally treated eggshell ranged from 1.82 to 6.74 m^2 g^{-1} (Ahmad et al., 2021; Awogbemi et al., 2020; Santos et al., 2019). The obtained calcined samples were denoted as EGSL-TT.

Spent leaves of seagrass were collected from Limassol’s coasts in Cyprus and were dried at ambient temperature for 24 h. Subsequently, the seagrass residues were thermally processed at 500 ^{o}C for 1 h. The obtained thermally treated seagrass samples were denoted SG-TT. Both wastes were thermally treated to obtain higher surface area, prior to their application. Before experiments, both materials were stored in a desiccator to prevent adsorption of water vapor.

2.1.2 Adsorption isotherm kinetics

The controlling mechanisms of the adsorption process were evaluated by batch experiments, which were performed using 20 g L^{-1} seagrass with various concentrations of phosphate (10-500 mg L^{-1}) for 24 h at neutral pH. The conical flasks were placed in the incubator at 33ºC and 100 rpm. Phosphate concentration was measured for six different contact times (0, 15, 30, 60, 120, 1440 min). At the end of each contact time, the suspension was immediately filtered through a 0.45 µm filter paper and the filtrate was analyzed within 2 h. To simulate the adsorption isotherm, two commonly used models, the Langmuir (Eq. (1)) and Freundlich (Eq. (2)) isotherms, were selected to explicate in their linear form the adsorption isotherms of phosphate. These equations are expressed as follows:

Eq. (1):

$$q_e = \frac{QbC_e}{I + bC_e}$$

Where q_e is the amount of adsorbed phosphate (mg g^{-1}), C_e is the concentration of phosphate in solution at equilibrium (mg L^{-1}), b is a constant related to the energy of adsorption (L mg^{-1}), and Q is the maximum adsorption capacity of the sample (mg g^{-1}).

The Freundlich isotherm applicable to non-ideal adsorption on heterogeneous surfaces with multi-layer adsorption is expressed as:

Eq. (2):

$$q_e = KC_e^{1/n}$$

Where K is related to the adsorption capacity of the adsorbent ((mg g^{-1} (L $mg^{-1})^{1/n}$), n is the Freundlich constant related to adsorptive capacity (mg g^{-1}) and intensity of adsorption (L mg^{-1}) favourability (Köse and Kıvanc, 2011).

2.1.3 Kinetic studies

Pseudo-first and pseudo-second order models were applied to interpret the experimental data and the controlling mechanisms of phosphate adsorption from wastewater solutions. A simple pseudo-first order equation is given by Lagergreen equation:

Eq. (3):

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303}$$

Where q_e and q_t are the amounts of phosphate adsorbed (mg g^{-1}) at equilibrium time and any time t (min), respectively, and k_1 is the rate constant of adsorption (min^{-1}).

A pseudo-second order equation based on adsorption equilibrium capacity may be expressed in the form:

Eq. (4):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Qe}$$

Where k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}). The equilibrium adsorption capacity (Q_e), and the second order constants (k_2) can be determined experimentally from the slope and intercept of plot t/Q_t versus t.

2.1.4 Analytical techniques

A colorimetric measurement technique was carried out using a HACH UV/VIS scanning spectrophotometer (JENWAY 7315, Staffordshire, UK). The combined reagent used constituted: a) H_2SO_4, b) potassium antimonyl tartrate, c) ammonium molybdate and d) ascorbic acid. When added to a sample containing phosphates, a blue colour is rapidly formed due to the antimony-phospho-molybdate complex shaped which can be reduced by ascorbic acid, indicating the presence of phosphate ions into the samples. The phosphate concentration was determined by absorbance at 880 nm and the chemicals used were of analytical grade (obtained from Sigma-Aldrich Company Ltd). The selectivity of seagrass residues was also evaluated testing different parameters such as the chemical oxygen demand (COD), nitrites

(NO_2^-), nitrates (NO_3^-), and ammonium (NH_4^+) present in the waste solution. The COD analysis was measured according to APHA colorimetric method, where 2.0 mL of the sample was added into glass tubes, followed by the addition of 1.2 mL digestion solution and 2.8 Ml sulphuric acid reagent. The glass tubes were then closed tightly, mixed properly, and refluxed in a Hach COD reflux reactor at 150°C for 2 h. Following cooling to room temperature, the COD was determined by a Shimadzu UV/Vis scanning spectrophotometer at 600 nm. The NO_2^-, NO_3^- and NH_4^+ ions were determined using spectroquant cell test kits (Merck Millipore), which allows the accurate quantification of these ions into water samples. Total solids (TS) and volatile solids (VS) were measured according to Standard Methods from (APHA, 2012). The molybdenum blue method (APHA 4500-PE) was selected for the determination of phosphates concentration by a HACH UV/VIS scanning spectrophotometer (JENWAY 7315, Staffordshire, UK) during the adsorption process. The biogas volumes were regularly measured using a wetted 50 mL glass syringe and reported at atmospheric pressure and a temperature of 33 °C. The gas composition in the headspace was determined by withdrawing 1 mL from the headspace and analyzed using a gas chromatograph (Agilent Technologies, 7820OA, Santa Clara, CA, USA) equipped with a ShinCarbon ST 50/80 (2 m length, 2.2 mm ID) mesh column (Restek Corporation, Bellefonte, PA, USA) and thermal conductivity detector, as previously described by Vyrides et al., (2018). To equilibrate the headspace with the atmospheric pressure, the volume after each measurement was discharged. The coefficient of variation for 10 samples was ±2%. The cumulative methane yield was calculated, as previously reported (Charalambous et al., 2020). VFAs concentration during the anaerobic digestion were evaluated using High-Performance Liquid Chromatography-UV detector (LC20AD, Shimadzu, Japan) (Vyrides and Stuckey, 2009). Finally, the pH and conductivity values were monitored using a portable meter after each gas and liquid sampling (Photiou and Vyrides, 2021).

2.1.5 Statistical analysis

Significant differences in the mean content values of the root, shoot and total length of the germinated seeds involved in the phytotoxicity trials were determined. The data obtained from the experiments were compared with each control through one-way analysis of variance

(ANOVA) to assess significant differences. The level of significance used was $p < 0.05$. The error bars presented on figures correspond to standard deviation.

2.2 Research Methodology of Chapter 3

2.2.1 Biowaste selection

The following biowaste were tested for their capacity to adsorb phosphate: (a) orange peels (obtained from KEAN Ltd, Limassol, Cyprus), (b) spent coffee residues (obtained from coffee shop "Gloria Jean's Ltd", Nicosia, Cyprus), (c) fish scales (obtained from Blue Island Ltd, Limassol) (d) seagrass residues of *P. oceanica* leaves of seagrass *P. oceanica* were collected from different coasts in Limassol, Cyprus). In addition, several types of biochar were examined for their capacity to adsorb phosphate: (e) biochar produced from olive kernels (obtained from Pettemerides Olive Oil Mill Ltd, Limassol, Cyprus), (f) biochar generated from vineyard prunings (obtained from Dafermou Winery, Larnaca, Cyprus) and (g) eggshells. The aforementioned wastes prior to test their potential to adsorb phosphate were rinsed several times with deionized water, in order to get rid of impurities and pollutants, and subsequently dried in an oven. Specifically, orange peels, spent coffee residues and fish scales were dried at 105°C and subsequently thermally treated at 550ºC for 2 h. The same procedure was followed for eggshells, however the conditions selected for their pre-treatment were selected from the study of Panagiotou et al., (2018) where eggshells were thermally treated at 900ºC for 30 min. Slightly different process was followed for seagrass residues, which were first dried at room temperature for 48 h. Then, the seagrass residues were ground, and the resulting powder was screened through a sieve lower than 1 mm, due to the higher surface area of the adsorbent. Then, the seagrass samples collected were processed: a) using conventional pyrolysis method under nitrogen stream or b) by thermal treatment method (550 ºC for 15 min). The majority of the experiments were conducted using the thermal treatment method (550ºC for 15 min) since the produced seagrass had the same adsorption capacity as the seagrass generated by pyrolysis.

2.2.2 Phosphate sources

Both synthetic and real phosphate sources were employed in this study:

a) Stock solutions were prepared by dissolving anhydrous potassium dihydrogen phosphate (KH_2PO_4) with deionized water. Different phosphate concentration solutions were also prepared, for use in batch experiments. The concentrations of the synthetic aqueous solutions were selected based on the range of phosphate-contents found in the waste streams used in this study.

b) Wastewater from anaerobic digester effluent and dewatered sludge were also obtained from the UWTP at Moni, Limassol. Anaerobic effluent wastewater was used due to relatively high concentration of phosphate (Vardanyan et al., 2018). The wastewater was filtered using 90 mm Whatman cellulose filter paper. The value of total phosphorus (TP) concentrations from real UWTP at Moni, Limassol from rejected water is 50 ± 2.1 mg L^{-1} (communication with Chemical laboratory at Moni, UWTP). Based on the average total phosphorus in rejected water from Moni UWTP (50 ± 2.1 mg L^{-1}) (Vardanyan et al., 2018) and the experimental concentration of phosphate (100.18 mg L^{-1}) it was calculated that the phosphate consisted of 61% of the total phosphorus.

c) Dewatered anaerobic sludge containing the highest phosphate concentration from all the solid fractions of the UWTP at Moni, Limassol (Vardanyan et al., 2018). The samples containing 20 g of dewatered anaerobic sludge were first acidified using 150 mL of 2 M, H_2SO_4 for 2 days. The pH of the solution was around 3.0. The leach solution was filtered using 90 mm Whatman cellulose filter paper and subsequently the filtrate was neutralized using 2 M NaOH. The final concentration of the leached solution was 274 mg L^{-1} phosphate. Based on the average total phosphorus in dewater anaerobic sludge from Moni UWTP (6926 mg kg^{-1}) (Vardanyan et al., 2018) and the extracted concentration of phosphate using aqua regia (967 mg L^{-1}, for 5 g in 100 mL) it was calculated that the phosphate consisted of 89.3% of the total phosphorus. This is in line with the findings of the study of Vardanyan et al., (2018) which pointed out that the major fraction of P in dewatered anaerobic sludge is inorganically bound (93.5%) and little portion is organically bound.

2.2.3 Batch experiments

Batch laboratory-scale experiments were conducted in 250 mL conical flasks. The working volumes of synthetic solutions, wastewater and leachate from dewatered anaerobic sludge were 100 mL, 150 mL and 50 mL respectively. The conical flasks were subsequently capped, sealed and stirred inside a shaking incubator operating at 100 rpm at 33ºC, given that temperatures higher than 35°C affected the physical adsorption process (Afroze and Sen, 2018). Samples were taken at pre-determined time points (0, 15, 30, 60, 120 and 1440 min) to monitor the phosphate adsorption process. Afterwards, samples were filtered, and the liquid phase was analyzed for phosphate residues. All the experiments were conducted in triplicate (and the average and standard deviation were calculated for these), except of the experiment testing the phosphate concentration removal on seagrass *P. oceanica* from synthetic solutions in different heating time points (only the average was calculated). The dried samples were ground resulting in particles with diameters less than 1 mm.

At batch laboratory-scale experiments the effect of the following parameters were examined: (1) highest phosphate concentration adsorbed after 24 h over a wide range of materials, (2) treatment temperature on the selected sorbent (150-800ºC), (3) thermal treatment time (15, 60 and 120 min), (4) submerged of seagrass for 24 h to water prior adsorption; at batch tests (2-4) the initial synthetic phosphate concentration was 100 mg L^{-1}. In addition, (5) real wastewaters (anaerobic wastewater effluent and liquid extracted from dewatered anaerobic sludge) as sources of phosphate were also used. Moreover, (6) the effect of pH to the adsorption process in real wastewater was also tested.

2.2.4 Morphological, elemental, and crystallographic characterization

A Scanning Electron Microscope (SEM) from FEI (Quanta 200) has been used to acquire images of the surface topography of seagrass samples before and after thermal treatment, but also seagrass samples after the phosphate adsorption process. All samples were coated, prior to examination, with a thin (<10 nm) silver layer in order to increase surface conductivity and reduce electron charging from the microscope. Images were collected at 20 kV accelerating voltage in various magnifications. Energy-dispersive X-Ray spectroscopy

(EDS) was also conducted along with imaging, to acquire information about the elemental composition of the samples. Elemental maps were also obtained to reveal spatial information about the phosphate adsorption sites.

The existence of any crystalline phases within the specimens was detected by X-Ray powder diffraction (XRD) measurements. A Rigaku Ultima IV diffractometer was used to collect the diffraction patterns of samples, which were recorded in the 10-70^o 2theta angular range. The diffractometer was equipped with a Cu tube, operated at 40kV and 40mA and the X-ray beam was conditioned from convergent to parallel by a parabolic multilayer mirror, which also partially monochromatized it (Cu Ka, λ=0.154nm).

2.2.5 Calculation of specific heat capacity of dry seagrass residue

The amount of heat energy (*Q*) that seagrass residues gain in order to increase its temperature from 25°C to 550°C is equal to the mass of the seagrass (*m*) multiplied by its specific heat capacity (C_p) multiplied by the change in temperature (*T*):

$Q(kJ) = C_p\ (kJ\ kg.\ K^{-1}) \times m\ (kg) \times dT(K)$

The specific energy of seagrass C_p is unknown so was calculated using Kopp’s rule based on their elemental composition and the heat capacities of each element:

C_p, solids= $\sum x_i \times C_{p,i}$, where x_i is the mass fraction of each element *i*, and $C_{p,i}$ is the specific heat capacity of each element i at 25°C (Anastasakis and Ross 2015, Lide 2004)

The wt% of seagrass was calculated based on our findings in Table 2 using energy dispersive X-ray spectroscopy. The heat capacities of these elements at 25°C are: 0.709 J gK^{-1} for C, 0.918 J gK^{-1} for O_2, 0.228 J gK^{-1} for Na, 1.023 J gK^{-1} for Mg, 0.897 J gK^{-1} for Al, 0.705 J gK^{-1} for Si, 0.71 J gK^{-1} for S, 0.479 J gK^{-1} for Cl, 0.757 J gK^{-1} for K, 0.647 J gK^{-1} for Ca, and 0.769 J gK^{-1} for P.

2.3 Research Methodology of Chapter 4

2.3.1 Characterisation of raw seagrass leaves

Spent leaves of seagrass *P. oceanica* were collected from different coasts in Limassol, Cyprus. The seagrasses were subsequently left to dry at room temperature for 48 h prior analysis for determination of biochemical composition. A FibreBag System (Gerhardt, Konigswinter, Germany) was employed to measure the cellulose, hemicellulose and lignin content. The aforementioned constituents were determined in the form of acid detergent fiber (ADF), neutral detergent fiber (NDF) and acid detergent lignin (ADL) fractions using the analytical protocols provided by Gerhardt. The elemental analysis was performed in our previous study (Photiou et al., 2021). Photiou et al. (2021) found that tubular structure with 100s of nm in wall thicknesses and pore openings of 10–100 μm is the most pronounced microstructural feature of seagrass. This morphological arrangement provides a significant amount of surface area for the phosphate ions to interact, which becomes more enhanced following thermal processing of the material that also generates porous at the nanometer scale.

2.3.2 Adsorption capacity assessment

The adsorption capacity of seagrass residues was estimated in fed-batch experiments. The concentration of the adsorbent was stable at 20 g L^{-1}, and the synthetic phosphate solutions were prepared at 2347.2 and 1110.8 mg PO_4^{3-} L^{-1}. The SG-TT residues were in contact with each solution for several days until no further reduction on the phosphate concentration was observed. From the data obtained, the adsorption capacity was expressed as the amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent. More specifically, to calculate the sorption capacity of phosphate onto seagrass residues (mg g^{-1}), the following equation was used:

$$q_e = \frac{(C_i - C_f)\ V}{1000\ m}$$

where qe is the sorption capacity (mg g^{-1}), V is the volume of phosphate solution (L), m is the mass of adsorbent used (g), and C_i and C_f are the initial and final concentrations (mg L^{-1}).

2.3.3 Sources of phosphate

Sludge used in this study was collected from the sewage sludge treatment tank of UWTP at Moni, Limassol, after the dewatering process which aims to reduce the volume of waste before its final disposal. The main characteristics of the DWAS used were TS 20.9%, Zn 422 mg kg^{-1} sludge, Pb <2.7 mg kg^{-1} sludge, Cd 2.1 mg kg^{-1} sludge, Hg <0.2 mg kg^{-1} sludge, Cr 41 mg kg^{-1} sludge, Cu 194 mg kg^{-1} sludge, Ni 25 mg kg^{-1} sludge (SBLA Monthly report, 2022). Wastewater from anaerobic digester effluent were also obtained from UWTP at Moni, Limassol. Anaerobic effluent wastewater was used due to relatively high concentration of phosphate (Vardanyan et al., 2018), with an average concentration of 70.78 mg L^{-1}. The wastewater was filtered using 90 mm Whatman cellulose filter paper before use.

2.3.4 Leaching process

Among other solid fractions produced in the UWTP, DWAS was selected due to the high phosphate content as inorganically bound phosphate. Aqua regia was used in order to extract the maximum phosphate concentration contained in DWAS. Different extraction methods were applied and compared for their ability to extract phosphate from DWAS. The methods examined were as follows:

(a) Sonication method (5 g of DWAS were placed in 100 mL of deionized water and sonicated at 30 Hz for 1 hr).
(b) Nitric acid method (5 g of DWAS were acidified using 100 mL of 1 M HNO_3 for 1 d).
(c) Sulfuric acid method (5 g of DWAS were acidified using 100 mL of 1 M H_2SO_4 for 1 d).
(d) Thermal-Sulfuric acid method (5 g of DWAS were acidified using 100 mL of 1 M H_2SO_4 at 50 ^oC for 1 hr).

The leach solutions were filtered using 90 mm Whatman cellulose filter paper and subsequently the filtrate was neutralized using 1 M NaOH.

2.3.5 Adsorption of phosphate from different type of solutions

Lab-scale experiments were conducted using a) synthetic solution, b) anaerobic effluent wastewater and c) the leachate from DWAS as phosphate sources. Synthetic stock solutions were prepared by dissolving anhydrous potassium dihydrogen phosphate (KH_2PO_4) with deionized water (DI). The method performed for the adsorption experiments was as previously described (Photiou et al., 2021). Briefly, during the adsorption process, 20 g L^{-1} of SG-TT (500 ºC, 1 h) was in contact with both wastewaters and synthetic solutions for 24 h. The conical flasks were capped, sealed and stirred inside a shaking incubator operating at 100 rpm at 33 ºC. Samples were subsequently withdrawn at regular intervals to monitor the adsorption process and phosphate was determined by the ascorbic acid method on a UV/VIS spectrophotometer (JENWAY 7315, Staffordshire, UK) at 880 nm.

2.3.6 Phytotoxicity assay

2.3.6.1 Compost characterization

The solid fraction (SG-TT *P. oceanica*) remaining after adsorption were amended with compost, which was obtained from a mix of digestate (D), gardening and park trimming residues (GR) and then tested as a soil conditioner in seeds. For each test, an amount of DI water, compost and seagrass was mixed to obtained seagrass concentrations of 0, 1, 2.5, 5, 10%. For the characterization of compost used in the phytotoxicity trials, an analytical protocol was developed, which comprises the determination of carbon (C) and nitrogen (N) content, pH, temperature, TS, VSS, conductivity and moisture content (%).The estimation of $\%C_{org}$ was made based on the difference between the weight of sample at 105 °C and the weight of sample at 550°C. Total N was determined on 0.5 g of each compost sample withdrawn at the end of the composting process, to which, 2.5 g of potassium sulphate catalyst and 10 mL sulfuric acid in a glass tube were added. The mixture was heated at 420°C for 1 h. The tube was then left to cool, and 50 mL of water were added slowly under shaking. Subsequently, 30 mL of boric acid were added to the suspension and distillation was performed using a Kjeldahl apparatus (UDK 129, VELP Scientifica, Italy). The distillation process was completed upon collection of 100 mL condensate. Titration was performed using

0.01 M sulfuric acid and bromocresol green-methyl mixed indicator, which was added dropwise to the distillate until the solution was turned into a violet at endpoint. The pH was measured with a pH meter in a 1:5 (w/v) aqueous extract of fresh collected sample, after 15 minutes of mechanical stirring and 30 min of sedimentation. The moisture content, expressed as percentage of samples as received, was calculated from the difference between the weight of the wet sample and that of the dry sample (24 h at 105°C). The characterisation parameters of compost are shown in Table 2-1.

Table 2-1. Compost characterisation

Parameter	Value	Std
pH	7.50	0.00
T (^{o}C)	17.00	0.00
Humidity (%)	50.00	0.00
Conductivity (μS cm^{-1})	860.50	0.00
TS (% w/w)	44.67	1.64
VS (% w/w)	39.98	7.05
C (%)	17.80	2.49
TN (%)	2.68	0.27
C:N ratio	6.65	0.66
P (% w/w)	2.39	0.31

2.3.6.2 Testing with adsorbed phosphate from synthetic solution

Phytotoxicity is a toxic effect imposed by a compound on plant growth. The solid fraction composite/end product remained after the phosphate adsorption process from synthetic solution was kept for evaluating its potential as a soil supplement. This experiment aimed to find the optimum concentration of end product, which, when applied as a fertilizer, could enhance plant growth. Thus, different concentrations of this end product were amended with compost (0, 1, 2.5, 5, 10% w/w (g of SG-TT residues per g of compost)), which 0% was the control experiment, and tested in tomato seeds. The samples were shaken with DI water and the whole portion was transferred to petri dishes. Two layers of absorbent paper and 10 tomato seeds were placed in each petri dish. The petri dishes were sealed with parafilm and placed in a dark spot for 8 d at room temperature. Finally, the number of germinated seeds as well as the length of their roots were counted. The phytotoxicity was expressed by using the followed formulas:

$$\text{Germination Index (GI)}=\frac{\text{(\% Seed germination)* (\% Root growth)}}{100}$$

Where,

$$\text{Seed germination (\%)}=\frac{\text{No. of germinated seeds in compost}}{\text{No. of germinated seeds in control}}*100$$

$$\text{Root growth (\%)}=\frac{\text{Mean root length in compost}}{\text{Mean root length in control}}*100$$

Following this, the phytotoxicity was expressed by using the germination index (GI) formula and the length (cm) of shoot and root of each seed.

2.3.6.3 Testing with adsorbed phosphate from wastewater solutions

Based on the results of the pre-trials using synthetic solution as a source of phosphate, the most favourable conditions were selected for the evaluation of solid fraction composite as a soil conditioner. After the adsorption process using anaerobic effluent (58.5 mg L^{-1}) and leachate phosphate (862.0 mg L^{-1}), the end product of adsorption was evaluated by using the 5% concentration on *Sinapis alba* and *Lepidium sativum* seeds. The GI was calculated to characterize the phytotoxicity of each sample.

2.4 Research Methodology of Chapter 5

2.4.1 Coupling EGSL-TT with AD systems

2.4.1.1 Substrate and Inoculum Preparation

Glucose (G), food waste (FW) and cellulose (CEL) were used as substrates for the AD. G and CEL powder of analytical grade were purchased from Sigma-Aldrich Company Ltd (Darmstadt, Germany) and FW was provided by different hotels in the area of Limassol (Cyprus). Upon collection, FWs were immediately transferred to the laboratory for further treatment (blending and mixing) to produce a homogeneous mixture, which was subsequently stored at −20°C before use. The average characteristics of FW were Total Sugars (%) 41.07±2.45, Proteins (%) 7.96±0.04, Total Lipids (%) 10.42±2.22, Lignin (%) 4.50±0.68, Hemicellulose (%) 45.83±3.08, Cellulose (%) 10.58±2.28. Fermentation inoculum comprised the anaerobic granular sludge (GS), which was withdrawn from a full-scale dairy wastewater treatment bioreactor (Internal Circulation (IC)) at pH 7.0–7.5 (Charalambides Christis Ltd, Cyprus). The TS and VSS of GS was 11.2 and 65.1% (w/w), respectively. Anaerobic GS was sieved (1 mm) and rinsed with distilled (DI) water and then was subsequently capped, sealed and stirred inside a shaking incubator operating at 100 rpm at 33ºC, for 1 week for activation prior to application.

2.4.1.2 Anaerobic Fermentation Plan

G, FW and CEL were fermented in batch scale mode in 250 mL glass shake flasks with an effective working volume of 150 mL at mesophilic conditions (33°C). To each shake flask, 5 g of GS was placed as inoculum. In the fermentations (AD-G, AD-FW, AD-CEL), different concentrations of substrate were added (4, 6, 8 g L^{-1} G substrate, 3 g of FW and 1 g L^{-1} of CEL), respectively. Two different concentrations of EGSL-TT were used for AD-G fermentation (5 and 10 g L^{-1}), while the same concentration of 20 g L^{-1} EGSL-TT was used for AD-FW and AD-CEL fermentations. The medium selected for AD-G was the medium reported at Angelidaki et al., (2009), and tap water was used concerning the AD-FW and AD-CEL fermentations. The pH was measured at the beginning and ending of each experiment by withdrawing 1 mL from each flask. The serum bottles were sealed with rubber septa and a screw cup. All fermentation bottles were flushed with N_2 for 2 min. Control experiments were prepared in duplicates for the fermentations.

2.4.1.3 Influence of soluble carbonates (CO_2 flushing)

Laboratory-scale experiments were conducted using shake flasks as reactors with a working volume of 150 mL, which were operated under anaerobic conditions for the adsorption capability of the absorber regarding the CO_2 gas stream. FW were submerged in DI water for 24 h and the supernatant liquid was added in shake flasks. Five treatments were tested: (1) the supernatant liquid as the control experiment, (2) the shake flasks containing the supernatant liquid flushed with CO_2, (3) the shake flasks containing the supernatant liquid flushed with N_2, (4) the shake flasks containing the supernatant liquid with 20 g L^{-1} EGSL-TT flushed with CO_2, (5) the shake flasks containing the supernatant liquid with 20 g L^{-1} EGSL-TT flushed with N_2. The initial average phosphate and COD concentration in the supernatant liquid were 29.0 and 7489.0 mg L^{-1}, respectively. Each experiment was conducted in duplicate at 33°C.

2.4.2 Adsorption of phosphate ions and evaluation of end products as soil supplements

Adsorption experiments using a) anaerobic effluent wastewater b) the leachate from DWAS as phosphate sources, were initially performed using lab-scale reactors. The sludge and wastewater used in this study were provided from the wastewater treatment plant of Sewerage Board of Limassol-Amathus (SBLA) in Moni (Cyprus). The sludge was obtained after the dewatering process and the effluent wastewater from the anaerobic digester. Both wastes were chosen due to their relatively high P content as inorganically bound P (Vardanyan et al., 2018). The average concentration of phosphates in dewatered sludge and effluent wastewater were 114.35 and 70.78 mg L^{-1}, respectively. For 5 g of sludge, 100 mL of 1 M nitric and sulfuric acid were applied as extraction media to compare their ability to extract P from DWAS. The leachates of pH 2–2.5 were used after pH adjustment to neutral using NaOH.

The method applied for the adsorption experiments was as previously described (Photiou and Vyrides, 2021). The solid fraction composite remained after the phosphate adsorption process from a) anaerobic effluent wastewater and, b) the leachate from DWAS were kept for evaluating their potential as soil supplements. The end products were evaluated by using the 5% w/w (g of EGSL-TT/P per g of compost) on *Sinapis alba* and *Lepidium sativum* seeds, after being amended with compost (CVD) obtained from a mix of D, GR as specified in our previous experimental work (Photiou et al., 2021b). In brief, the end products were shaken with DI water and the whole portion was transferred to petri dishes. Two layers of absorbent paper and 10 seeds of each plant were placed in petri dishes. The petri dishes were sealed with parafilm and placed in a dark spot for 3 d at room temperature.

2.5 Research Methodology of Chapter 6

2.5.1 Feed Wastewater

The wastewater utilized in this study was obtained from SBLA wastewater treatment plant in Cyprus. The wastewater stream used was termed reject water, which was a mixture of the aqueous phase from the process of dewatering before and after the anaerobic digester (Vardanyan et al., 2018). Reject water was chosen as feeding water in the SAnMBR due to its relatively high phosphate concentration (29.68 mg L^{-1}). The characteristics of the reject wastewater are given in APPENDIX II (Table S6-1).

2.5.2 Experimental setup and operation conditions of SAnMBR

The SAnMBR process was consisted of a biological reactor (20 L cylindrical) combined with a submerged membrane unit. In this study, a Kubota membrane module (polyethylene) with total surface area of 0.1 m^2 and 0.4 μm pore size was used. The whole system was flushed with nitrogen gas to establish an anaerobic environment. The fermentation inoculum was a GS, which was withdrawn from a full-scale bioreactor treating dairy wastewater at neutral pH (Charalambides Christis Ltd, Cyprus). Anaerobic GS was activated prior to application as mentioned in the work of Photiou and Vyrides (2022). The 20 L SAnMBR system was fed with the reject water using a feeding pump at a flow rate of

10 L d^{-1}. The effective volume of the reject water was 15 L and the hydraulic retention time (HRT) of the reactor was maintained at 36 h until the end of the fermentation. The SAnMBR system was operating for 50 d at 33ºC. Simultaneously, while the membrane was severely fouled as a consequence of the continuously SAnMBR operation, a physical cleaning procedure including backwashing in high flow velocities was conducted to recover the membrane permeation flux and ensure the membrane module's condition and performance.

2.5.3 Column mode adsorption operation

Two adsorption columns were connected to the SAnMBR effluent tank. The columns had dimensions of 20 cm in height and 2.5 cm in diameter with an effective packing height of 13.5 cm. The biowaste materials were EGSL-TT and SG-TT residues. To evaluate the performance of each column, phosphate concentration was monitored through the process. The eggshell and seagrass effluents were designated as EGSL and SG after passing through the column system. The concentrations of COD, ammonium and other parameters were measured for both effluents. The operation of the columns ended when the initial concentration of phosphates was equal to the concentration of phosphates in the column effluents. The experimental set-up of the SAnMBR followed by the two adsorption columns, is presented in Fig. 2-1.

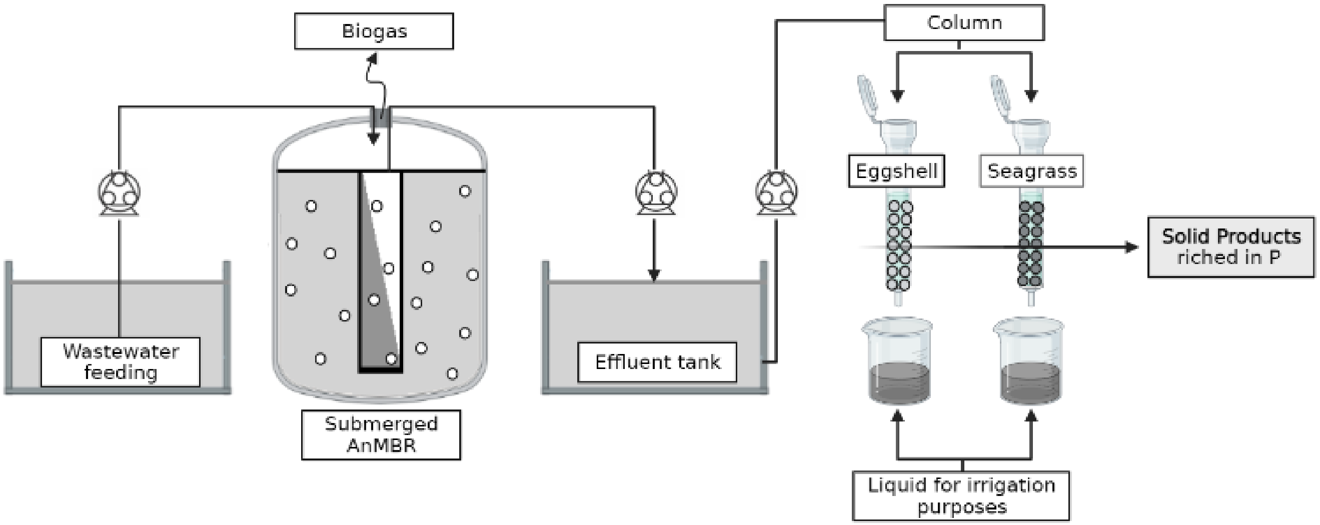


Figure 2-1. Schematic diagram of the submerged membrane anaerobic bioreactor (SAnMBR) followed by the EGSL-TT and SG-TT adsorption columns.

2.5.4 Phytotoxicity assessment

The EGSL and SG solid fractions that remained at the end of phosphate adsorption from the SAnMBR effluent were stored to evaluate the potential of each material to be used as soil supplements. Both P-riched adsorbents after the process were dried at 105°C at the oven for 24 h. The method and formulas applied for the assessment of the end products on *S. alba* and *L. sativum* seeds was as mentioned on the study of Photiou and Vyrides (2022). The GI comprise a measure for evaluating the number and speed of seed germination. Higher values of GI indicate a greater rate of germination.

2.5.5 Fractionation of phosphorus in the products

The Standards Measurements and Testing (SMT) protocol is a well-known method for the determination of sediment phosphorus fractions. The SMT protocol determines five different phosphorus fractions according to their extractability: (1) the TP, (2) the OP, (3) the IP, (4) the NAIP mostly bound to Fe, Al, Mn oxyhydrates and finally, (5) the AP, which is compound based to Ca. UV-Vis spectrophotometry technique in combination with the molybdenum blue method was used to measure phosphate content. Thus, the extraction protocols are a useful approach for studying phosphorus formation in different sediments (Pardo et al., 2004). In this work, the SMT protocol was followed for greater understanding the phosphorus fractions in the EGSL and SG end products after the adsorption of phosphates from SAnMBR effluent, as well as the GS from the anaerobic reactor.

2.6 Research Methodology of Chapter 7

2.6.1 Wastewater characteristics

The SAnMBR was initially fed with synthetic wastewater to maintain a uniform composition until day 44. Then, domestic wastewater was fed into the system for the last 17 days of the experiment. Domestic wastewater was obtained from the SBLA wastewater treatment plant in Cyprus after removing floatable objects and other materials by gravity (Vardanyan et al., 2018). Table 2-2 provides the characteristics of both synthetic and domestic wastewater.

Table 2-2. Synthetic and domestic wastewater characterisation

Parameter	**Unit**	**Synthetic**	**Domestic**
Temperature	°C	25.0	26.0
pH		8.0	7.9
Conductivity	µS cm^{-1}	3,736.0	1,832.1
Total COD (TCOD)	mg L^{-1}	n.m.*	624.8
Soluble COD (SCOD)	mg L^{-1}	945.8	238.3
Suspended solids (SS)	mg L^{-1}	n.m.	282.0
NO_3-N	mg L^{-1}	0.8	1.0
NO_2-N	mg L^{-1}	1.2	1.7
NH_4-N	mg L^{-1}	41.4	45.5
PO_4-P	mg L^{-1}	23.9	26.1

n.m.= not measured*

2.6.2 Experimental setup

A 20 L cylindrical biological reactor and a polyethylene Kubota membrane module with a total surface area of 0.1 m^2 and a pore size of 0.4 μm constitute the SAnMBR. The SAnMBR was initially fed with synthetic wastewater for 44 d and then was pumped continuously with actual domestic wastewater from a full-scale facility for 17 d at 33°C. Anaerobic granular sludge was used as the fermentation inoculum and was activated as previously reported in the work of Photiou and Vyrides, (2022), prior to the application. The HRT was stable at 36 h for the first two phases (Phase I and II), while at the final phase (Phase III) the HRT was 24 and 36 h to evaluate the effect of HRT on the organic compound removal. Samples were taken on regular time intervals to monitor the process. The SAnMBR effluent was also connected through a pump with two reactors of 600 mL working volume, which were consisted of thermally treated EGSL and SG. Different flow rates were also examined to find the optimum operational conditions of the adsorption system (0.1 – 0.8 mL min^{-1}) for both wastewaters tested. EGSL and SG of 25 g each was added in the reactors for the Phase I and II every 15 d, while an addition of 25 g was performed for the SAnMBR effluent treating domestic wastewater in phase III. The effluents were denoted as EGSL and SG after passing through the adsorption reactors. Following these reactors, the effluent of each biowaste was connected to two identical reactors with PAC, which was previously dried overnight at 105°C in an oven. PAC (Honeywell, Fluka, CAS-No: 7440-44-0) of 8 g was added in the reactors for the Phase I and II, while an increased to 16 g was performed for Phase III. The PAC characteristics are presented in the APPENDIX III (Table S7-2). The PAC addition after EGSL and SG were denoted as PAC_A and PAC_B, respectively. The experimental set-up of the SAnMBR followed by the four-adsorption reactors is depicted in Fig. 2-2. Five locations were sampled (Fig. 2-2): (1) synthetic/domestic influent feed, (2) synthetic/domestic effluent (3) eggshell effluent, (4) seagrass effluent and (5) effluent after PAC_A, and (6) effluent after PAC_B. The permeates were collected, filtered (0.2 μm filter) and placed in a 2 mL centrifuge tube. To examine the performance of each reactor, the permeates were analyzed for the determination of COD, phosphates (PO_4^{3-}), NH_4^+, conductivity, pH value, and VFAs.

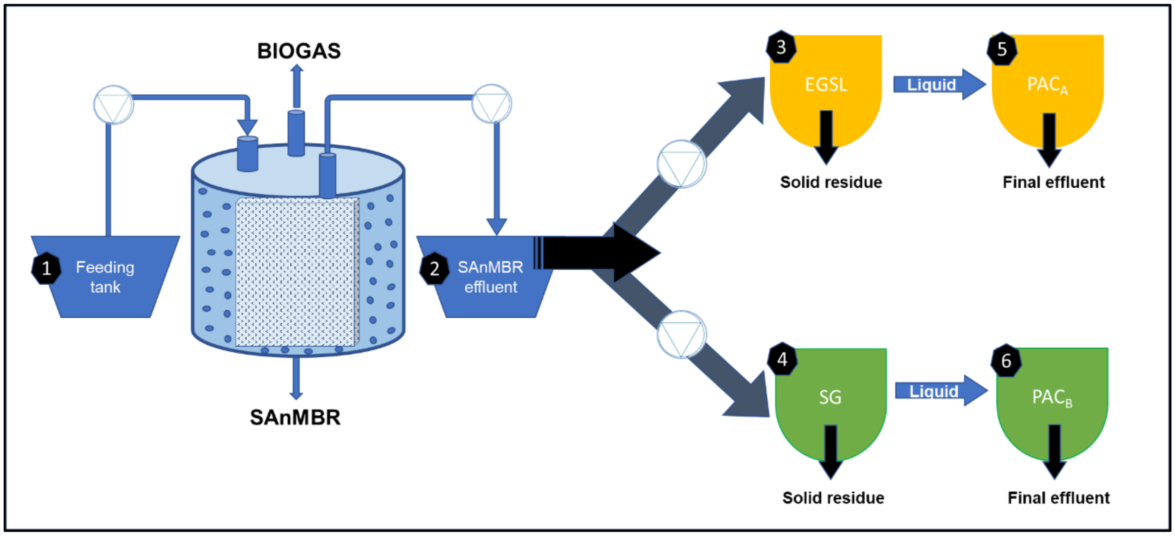


Figure 2-2. Schematic diagram of the SAnMBR followed by the EGSL-TT, SG-TT, and PAC adsorption reactors.

2.6.3 Phytotoxicity assessment

The utilization of the liquid fraction remained after the phosphate adsorption process from the SAnMBR effluent was assessed through phytotoxicity trials on *Sinapis alba* and *Lepidium sativum* seeds. The SAnMBR inlet and outlet, and the effluent after PAC treatment for both biowastes were mixed and then diluted (20% v/v) prior to the application. The final effluents of the process were filter through a 0.22 μm filter and kept for evaluating their effect on plant growth. The methodology applied for the assessment of the final effluents on seeds were previously used by Photiou and Vyrides (2021).

2.6.4 Fractionation of phosphorus in the products

The SMT protocol was applied for the determination of the phosphorus fractions in the EGSL and SG solid residues after the phosphate's adsorption from both SAnMBR effluents (synthetic and domestic wastewater), as well as the GS from the anaerobic reactor. The method used is reported in the work of Pardo et al., (2004), which determined five phosphorus fractions (TP, OP, IP, NAIP and AP).

2.6.5 Wastewater VOCs analysis

To extract volatile organic compounds (VOCs) from wastewater samples, 5 mL of the sample was placed in a 20 mL headspace glass vial and allowed to reach equilibrium at 25°C for 24 hr. The vials were then closed with a HiSorb septum, and the analytes were adsorbed onto a polydimethylsiloxane/carbon wide range HiSorb probe. Beforehand, the sample was mixed with 2 g of sodium chloride and stirred continuously at 700 rpm. Chlorobenzene-d5 was spiked in the sample as an internal standard. The probes were pre-conditioned at 260°C for 25 min under a helium flow rate of 75 mL min^{-1}. The VOCs were desorbed using a Unity-xr thermal desorption (TD) system connected to an Agilent GC-7890B gas chromatography and MSD-5977B mass spectrometry (TD-GC-MS). The desorption was performed at 250°C for 10 min and the analytes were focused on a graphitized carbon cold trap at -10°C. The cold trap was then rapidly heated to 320°C for 3 min with a split flow of 1:10. A SPB™-624 capillary column was used as the stationary phase. The initial temperature was 35°C, which was maintained for 5 min before being raised to 180°C at a rate of 4°C min^{-1} and remaining at that temperature for 20 min. The analysis was performed in full scan mode and the recorded masses were set from 35 to 350 m/z. The total analysis time was 61.25 min. The integration of the total ion chromatogram (TIC) peaks was performed using the ChemStation software (Agilent, USA). Finally, NIST 20 library was used to identify the emitted compounds.

3 Phosphate removal from synthetic and real wastewater using thermally treated seagrass residues of *Posidonia oceanica*

The objective of this work is to provide an insight into new low-cost adsorbent materials, for optimum recovery of phosphate from real wastewater. Herein, several biowastes were tested for their capacity to adsorb phosphate: (a) orange peels, (b) spent coffee residues, (c) fish scales, (d) seagrass residues of *P. oceanica*, (e) biochar produced from olive kernels, (f) biochar generated from vineyard prunings. SG-TT residues exhibited the highest phosphate adsorption capacity among the aforementioned biowastes at 100 mg L^{-1} initial phosphate concentration. Based on experimental data (Section 3.1) it was concluded that thermally treated seagrass and eggshell residues demonstrate the highest potential to adsorb phosphate. Therefore, the aim of this study was to evaluate the potential of seagrass residues of *P. oceanica* as a phosphate adsorbent from real wastewater applications. Additionally, the study aimed in characterizing the compounds formed following phosphate adsorption at seagrass residues of *P. oceanica*, to determine the structure of seagrass residues before and after phosphate adsorption and to identify the mechanisms of phosphate binding.

3.1 Biowastes' performance

The adsorbent dosage for all the thermally treated biowastes used (orange peels, spent coffee residues, fish scales, eggshells, seagrass residues of *P. oceanica*, biochar produced from olive kernels and biochar produced from vineyard prunings) ranged between 20-30 g L^{-1} and the synthetic solution used was prepared containing 100 mg L^{-1} phosphate. The experiments carried out were running for 24 h and the results obtained are shown in Table 3-1. Shortly after starting out the maximum phosphate removal (99.0 %) was recorded using SG-TT residues of *P. oceanica* at 30 minutes incubation while the lowest removal was observed using non-treated spent coffee residues (Table 3-1). Up to date there are no information regarding the adsorption of phosphate on thermally treated residues of *P. oceanica* and few studies have examined phosphate adsorption from real wastewater in biowaste. Therefore, the research in this Thesis focused on the phosphate adsorption using seagrass residues of *P. oceanica* from synthetic solution and from real wastewater. In addition, the mechanisms and the optimum conditions were examined.

Table 3-1. Percentage removal of phosphate from synthetic aqueous solutions using different biowastes. Initial phosphate concentration in all samples was 100 mg L^{-1}

Biowaste	Pre-treatment method	Adsorbent dose [g L^{-1}]	Phosphate removal [%]
Fish scales	Thermally treated at 550°C for 2 h	30	5.1 ± 0.3
Spent Coffee residues	-	30	0.0 ± 0.0
Spent Coffee residues	Thermally treated at 550°C for 2 h	20	38.9 ± 3.7
Orange peels	Thermally treated at 550°C for 2 h	30	13.2± 2.0
Olive kernels	Pyrolysis at 550°C for 3 min	20	15.4 ± 1.1
Vineyard prunings	Pyrolysis at 550°C for 3 min	20	15.4 ± 3.9
Eggshells	Thermally treated at 900 for 30 min	20	99.0 ± 1.5
P. oceanica	Pyrolysis at 550°C for 3 min	20	97.7 ± 0.4
P. oceanica	Thermally treated at 500°C for 1 h	20	99.1 ± 0.8

P. oceanica constitutes a naturally available low-cost biomaterial that can be used for the removal of phosphate from aqueous solutions (Wahab et al., 2011). The valorisation of this unexploited renewable lignocellulosic seagrass residue can be considered as a cheap alternative for the removal of phosphate from aqueous media (Krika et al., 2015). So far, it has been confirmed that *P. oceanica* residue can adsorb uranium (VI) (Aydin et al., 2012), chromium (VI), lead (II) (Allouche et al., 2011), methylene blue dye (Guezguez and Mhenni, 2008) and anionic species from synthetic solutions (Khiari and Belgacem, 2017). So far, few studies examined *P. oceanica* residue for Phosphate removal and this is the first study that has examined the use of *P. oceanica* residue for Phosphate removal from real wastewater.

3.2 Effect of pre-treatment temperatures

It is known that the adsorption properties of a material can be improved by chemical or physical activation treatments and in particular, thermal treatment of materials, such as seagrass, present great adsorptive capacity as opposed to un-treated specimens (Cataldo et al., 2018). Based on these findings, batch experiments were conducted to assess the optimum conditions required to produce a low-cost adsorbent with high potential in the fields of agriculture and industry. Different experimental parameters were studied including a wide range of seagrass treatment temperatures ranging between 150-800°C for 15 min (Fig. 3-1). Seagrass exposed to temperatures between 500-700°C exhibited the highest phosphate removal (95-99%). Interestingly the activation of seagrass was achieved in lower temperature compared to other studies and without applying pyrolysis or nitrogen and can be more economically viable to implement this process at a larger scale. More specifically, when the temperature was lower than 500°C or higher than 700°C, the removal percentage of phosphate decreased from 99 to 46%, while the adsorption time increased from 30 to 120 min. This can be explained due to the changes in the material's structure after the treatment through activation of the functional surface groups and pore volume.

Apart from the thermal treatment, pyrolysis was used as a treatment step using seagrass. The sample was pyrolysed at 500°C for 3 min, and subsequently tested for its ability to adsorb phosphate in aqueous solutions. Both thermally treated and pyrolysed seagrass exhibited almost the same yield concerning the removal and adsorption of phosphate in water. The difference in the yield of these two samples was less than 2%, and so the next experiments were performed using SG-TT at 500°C, which constitutes the most cost-efficient option.

According to Afroze and Sen, (2018), high treatment temperatures usually enhance the adsorptive removal of water pollutants, due to increased surface activity of the adsorbent. Nevertheless, high temperatures could also damage the physical structure of the adsorbent by decreasing the oxygen surface functional groups of the material. Direct application of untreated agricultural biowastes as adsorbents can cause difficulties in the adsorption process resulting in lower adsorption capacities, as well as release soluble organic compounds contained in the raw materials creating another problem related to secondary pollution (Zhao et al., 2014). Hence, physical and chemical activation of these materials are necessary to get the desired characteristics, which in turn enhance the adsorption process.

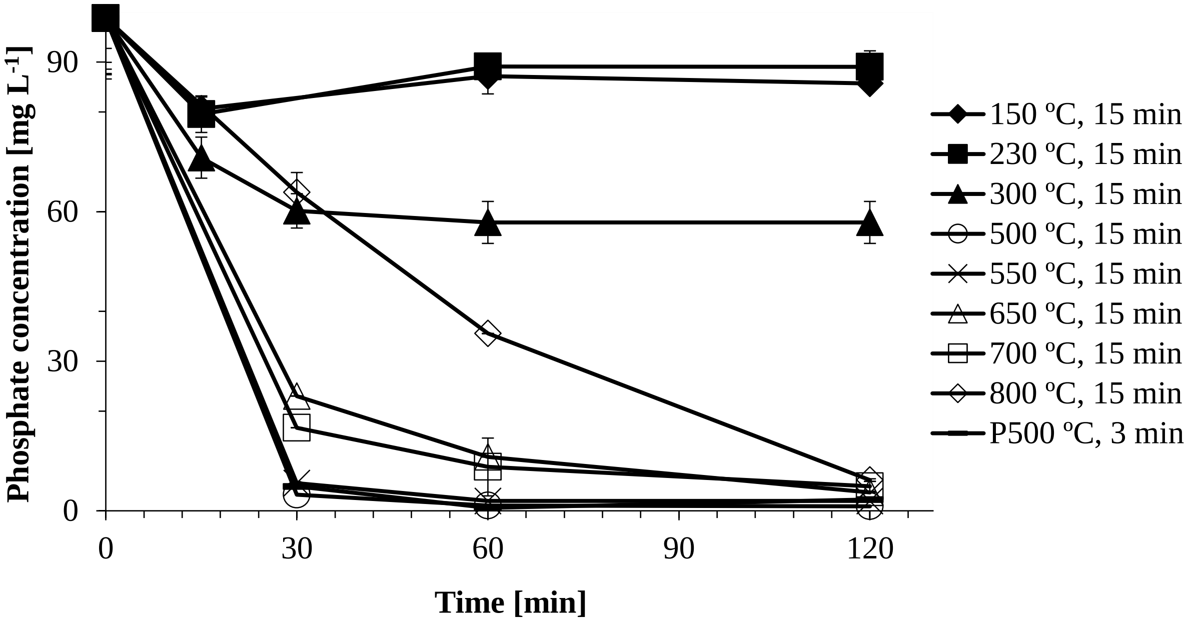


Figure 3-1. Adsorption of phosphate on seagrass *P. oceanica* from synthetic solution (100 mg L^{-1}) in different pre-treatment temperatures.

3.3 Effect of thermal treatment time at 500°C

As mentioned earlier, this experiment was performed using SG-TT residue at 500°C, due to the higher phosphate adsorption (findings from Section 3.2). Seagrass was exposed to 500°C for different heating durations (15, 60 and 120 min) to assess the optimum time in which seagrass yields maximum phosphate removal. The results demonstrate that the lowest phosphate removal was achieved at 500°C for the period of 15 min, while in the period of 120 min seagrass residues exhibited the highest adsorptive capacity (Fig. 3-2). The difference in the yield of these two samples was less than 2%, and so additional experiments were performed using SG-TT at 500°C for 60 min.

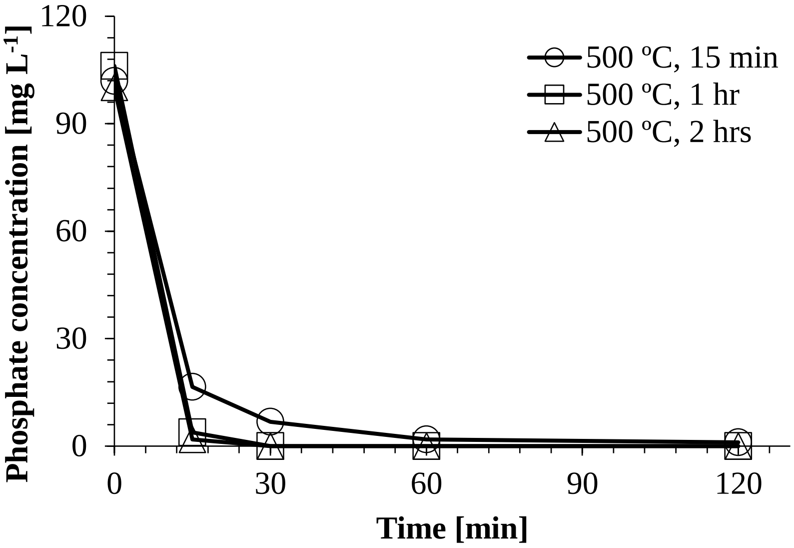


Figure 3-2. Phosphate concentration removal on seagrass *P. oceanica* from synthetic solutions in different heating time points (15, 60 and 120 min).

3.4 Effect of seagrass washing with water in the adsorption process

Seagrass surface incorporates a significant concentration of salts due to the high salt content existing in sea water. Sen et al., (2011) stressed that in general, adsorption decreases in the presence of salts due to the co-adsorption effect, but also the increase of salts further reduces the adsorption efficiency. In addition, it was suggested that apart from phosphate removal, phosphate precipitation with salt ions could also occur. Thus, the effect of seagrass washing with water in the adsorption procedure was evaluated through batch experiments repeated in two different phosphate concentrations, 100 and 200 mg L^{-1}. These two concentrations 100 and 200 mg L^{-1} were selected to simulate the content of phosphate in the reject water and leach solution from dewater sludge respectively and to test the performance of the adsorption in two different concentrations. The conditions for these trials for seagrass residues were selected based on previous experiments (Section 3.2. and 3.3). The results obtained (Fig. 3-3) do not demonstrate significant difference in the performance of washed with water seagrass and not washed seagrass. Thus, washing with water prior to the adsorption method has no effect on the procedure's performance.

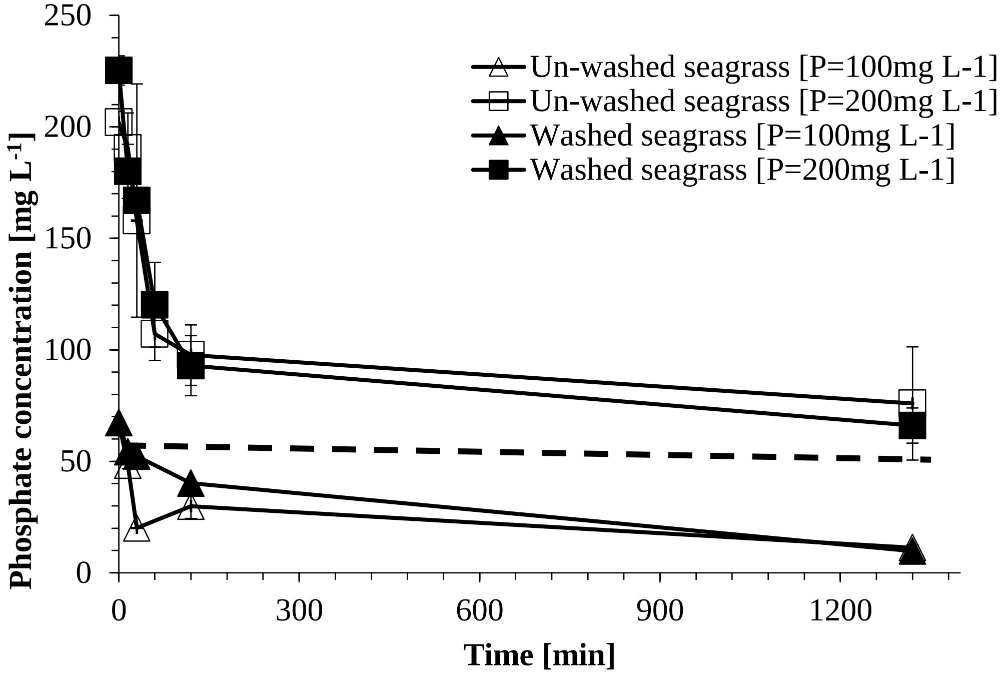


Figure 3-3. Phosphate concentration removal using seagrass P. oceanica previously washed with water and un-washed in synthetic solutions.

Black dashed line: - - -, separates the two concentrations tested.

3.5 Seagrass microstructure and chemistry

Seagrass samples were investigated using SEM, EDS and XRD in an attempt to get a better understanding of the mechanisms involved in the phosphate removal process. Figure 3-4 presents SEM images of seagrass ((a)-(c)) and seagrass after it has been heat treated at 500°C for 1 h ((d)-(f)). The most pronounced microstructural feature of seagrass relates to its tubular structure with 100s of nm in wall thicknesses and pore openings of 10-100 μm in size. This morphological arrangement provides a significant amount of surface area for the phosphate ions to interact, which becomes more enhanced following thermal processing of the material. In fact, after heat treatment of seagrass residues, part of their lining is decomposed exposing higher surface area and the internal structure of biomass, which has also generated porous at the nanometer scale (Figure 4(d)-(f)). This is in line with the findings of Section 3.2 where an increase in treatment temperature resulted in higher phosphate adsorption. Some cubic structures pertaining to salt crystals are also visible both on untreated and heat-treated seagrass. The salt appears to reside primarily within the tubular structures and gets exposed following heat treatment.

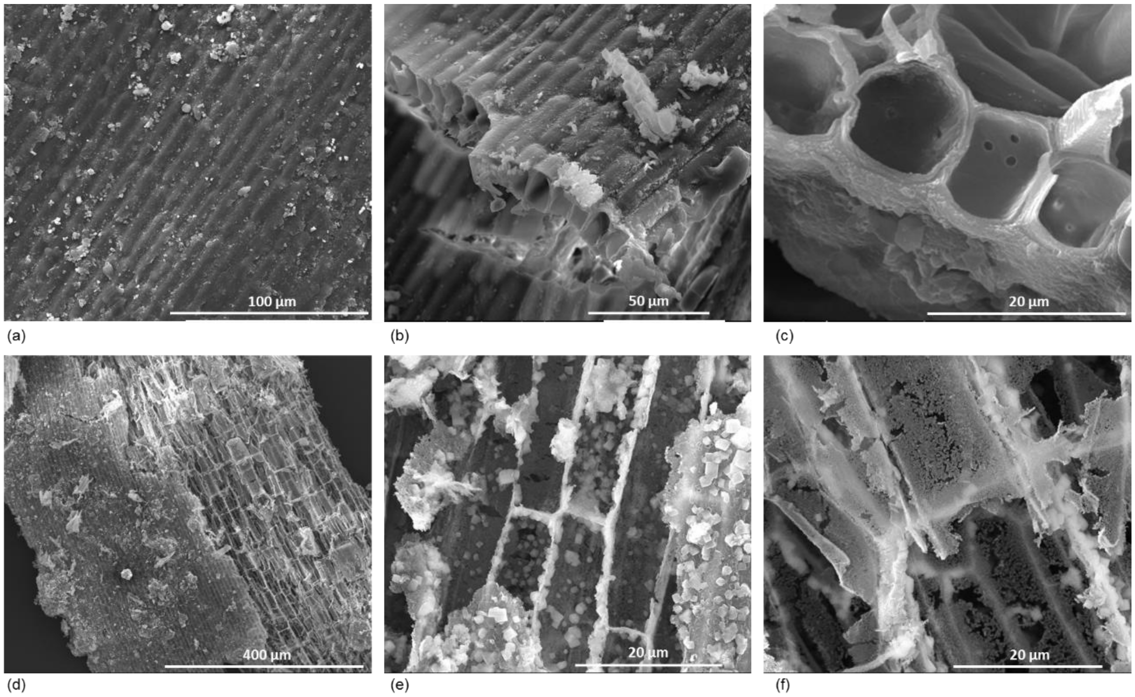


Figure 3-4. Scanning electron microscopy images of untreated (a-c) and SG-TT (d-f).

Table 3-2 presents the stoichiometric composition (in atomic percent) of all elements present in seagrass specimens before and after thermal treatment as well as after interaction with the synthetic phosphate solution. In untreated seagrass specimens carbon and oxygen comprised the dominant elements which relate to the organic matrix composed of cellulose ($(C_6H_{10}O_5)_n$) and lignin ($C_9H_{10}O_2$,$C_{10}H_{12}O_3$,$C_{11}H_{14}O_4$), as reported in the literature by Fouzi et al., (2019). Khiari et al., (2010) demonstrated that approximately 30% of *P. oceanica* dry weight is composed by lignin. The presence of sodium and chloride relate to salt whereas silicon composes the skeleton of diatom algae. Following thermal-treatment, carbon is reduced which probably relates to the partial decomposition of the organic matter; subsequently all unaffected quantities are increased in relative proportions. While EDS is not the most accurate technique for quantifying elemental composition of specimens, nevertheless it provides sufficiently accurate results for samples with similar consistency and concentration range and for comparative studies, as we did within this study; the conclusions drawn above are therefore considered reliable.

Table 3-2. Percentage elemental composition of seagrass specimens obtained through energy dispersive X-ray spectroscopy. SG: Seagrass; SG-TT: Thermally treated seagrass; SG-TT/P: Thermally treated seagrass after phosphate adsorption.

	C	O	Na	Mg	Al	Si	S	Cl	K	Ca	P	Fe
SG	55.64	28.68	2.79	2.87	0.46	0.82	0.52	6.72	0.35	1.15	0.00	0.00
SG-TT	22.45	34.41	8.23	11.86	0.31	0.46	1.06	14.95	1.16	5.01	0.17	0.00
SG-TT/P	20.48	43.06	5.22	5.99	0.38	2.69	0.26	2.01	3.36	5.64	10.92	0.32

Figure 3-5 shows the XRD patterns of untreated (SG) and heat-treated seagrass (SG-TT). The crystalline phases of sodium chloride (NaCl) and gypsum ($CaSO_4.2H_2O$) can be identified in the untreated seagrass sample. A broad peak in the region of 20-25° is usually attributed to the organic matter of seagrass, cellulose and lignin. In the thermally treated sample, the signal from the organic matter becomes weaker due its partial decomposition, while several other crystalline phases get dehydrated or transformed. For example, gypsum is converted to anhydrite ($CaSO_4$) and the appearance of periclase (MgO) is detected. While the dehydration/rehydration of calcium sulphate (gypsum) is still the subject of research investigations, there is a general consensus on the temperature that the main dehydration event occurs which is in the 95-170°C range (Tang et al., 2019, Strydom et al., 1995). This is consistent with our XRD results, given that the treatment temperature used herein (500°C), well exceeds this critical range. The salt crystals (NaCl) remain unaffected and peaks relevant to potassium chloride (KCl) appear (non-detectable prior to heat treatment).

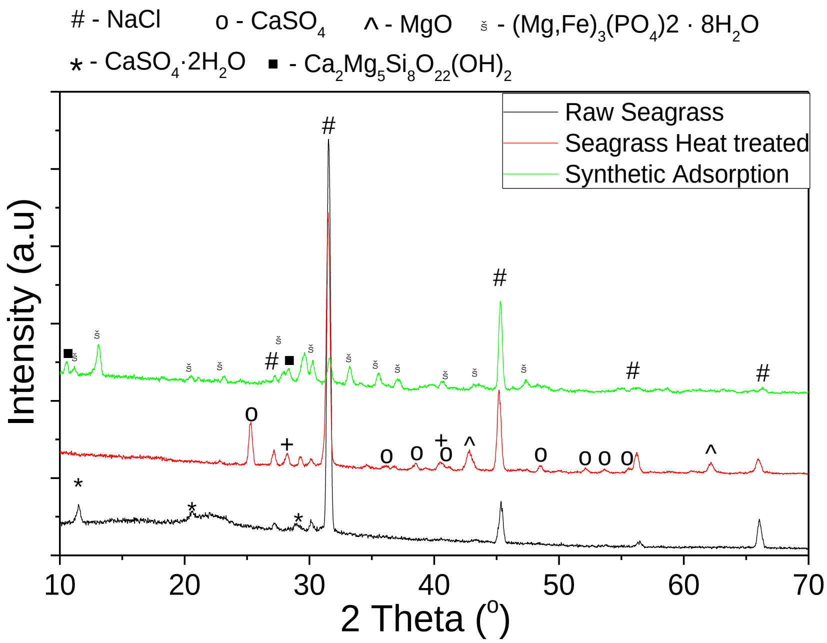


Figure 3-5. X-ray diffraction data of untreated seagrass, SG-TT and heat-treated seagrass after phosphate adsorption from synthetic media

The significant increase of the atomic percentage of phosphorus, as evidenced in Table 3-2 (SG-TT/P sample), confirms the ability of SG-TT to remove phosphate from phosphate-rich solutions. Towards understanding the mechanism of phosphate removal, XRD, SEM, and EDS measurements of the SG-TT specimens after they have been in contact with the synthetic phosphate solution have been undertaken. The elemental maps presented in Figure 3-6 show a spatial distribution of elements and suggest that phosphates are more or less homogeneously distributed within the majority of the specimen's surface. This can be in the form of physical or chemical adsorption on the surface or within the seagrass residue. The spatial distribution of P is in very good correlation with Mg and O suggesting a chemical structure that combines all three elements. In fact, XRD data (Fig. 3-5) suggest the existence of the baricite crystal (Mg, Fe^{++})$_3$(PO4)$_2$.8(H$_2$O) with peaks in the corresponding regions experimentally obtained in this study. Beyond baricite other crystalline phases appear to exist within the resulting solids, these being magnesite (MgCO$_3$), pargasite (NaCa$_2$(Mg$_4$Al)(Si$_6$Al$_2$)O$_{22}$(OH)$_2$), periclase (MgO) and potassium chlorite (KCl). The elemental spatial distribution of Na and Cl also correlates which suggest the existence of remaining sea salt crystals. Results at Section 3.4 pointed out that seagrass previously exposed to water prior to phosphate adsorption maintained their high adsorption capacity. It is possible several cations such as Mg^{2+} to be strongly attached to the surface (and not to be removed by previous exposure to water) or to be in the inner surface of seagrass and therefore to contribute also to phosphate removal through phosphate precipitation (e.g., baricite).

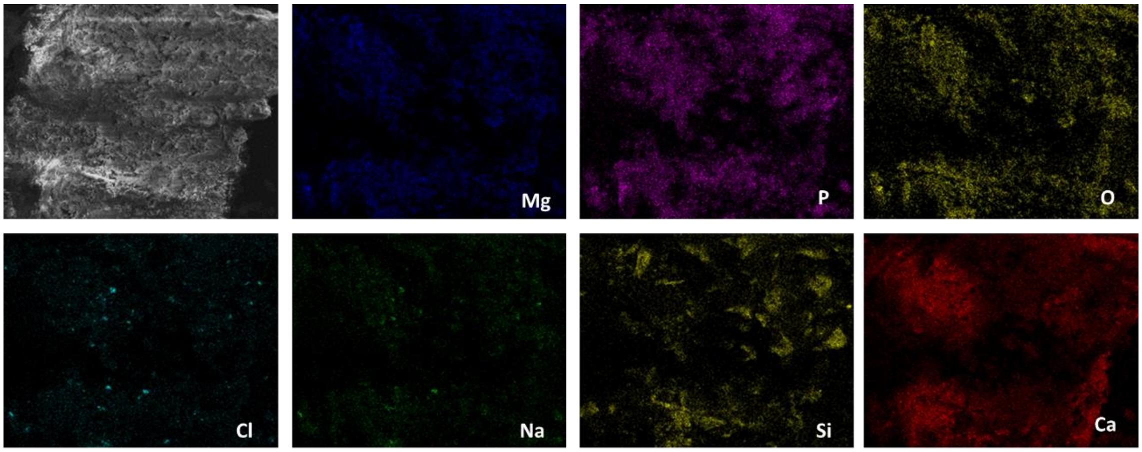


Figure 3-6. Elemental mapping for a SG-TT material after it has interacted with a synthetic phosphate solution.

3.6 Adsorption isotherms

The equilibrium isotherm analysis of the adsorption process was evaluated by contacting 20 g L^{-1} of seagrass residue thermally treated (at 500°C for 1 h) with concentrations of phosphate (10-500 mg L^{-1}) for 24 h at pH 7.

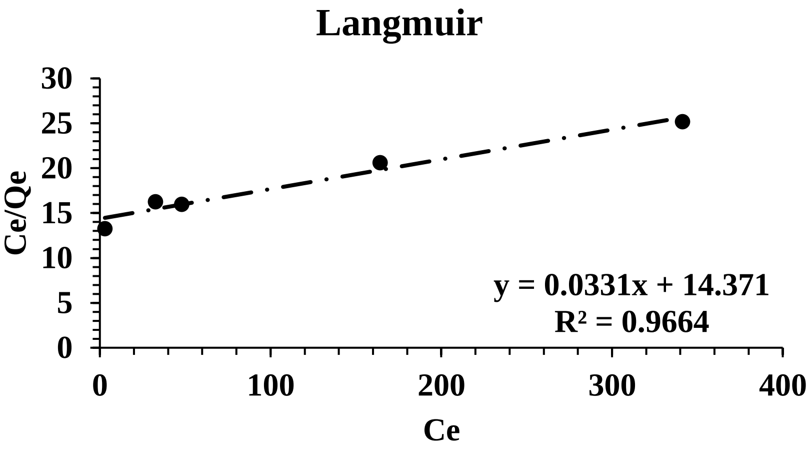


Figure 3-7. Langmuir isotherm plots for phosphate removal by seagrass residues *P. oceanica.*

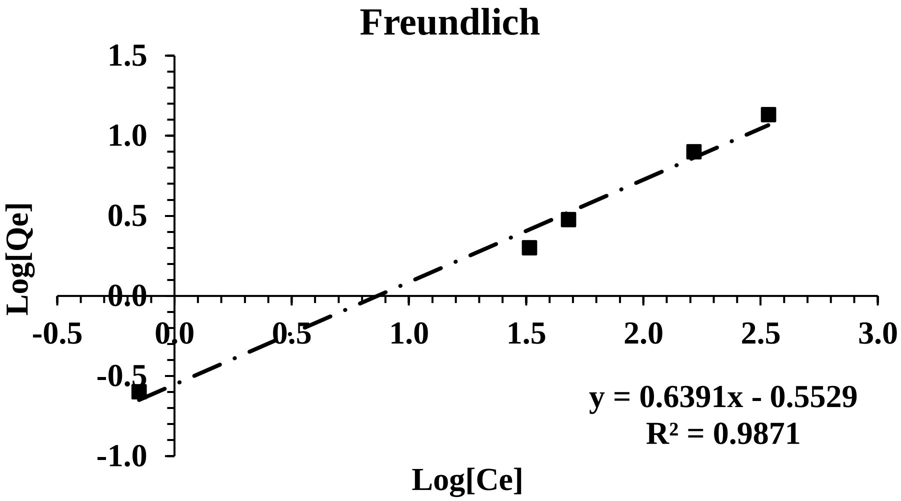


Figure 3-8. Freundlich isotherm plots for phosphate removal by seagrass *P. oceanica* residues.

The experimental data obtained for the use of seagrass residue were applied to the linear Langmuir and Freundlich isotherm equations and the findings are shown at Figs. 3-7 and 3-8. The Langmuir isotherm model assumes a completely homogeneous surface and the adsorption onto the surface has the same activation energy, whereas the Freundlich isotherm model is suitable for highly heterogeneous surfaces. Adsorption results derived using different phosphate concentrations demonstrated that the Freundlich isotherm provided the best fit predicting closely the process (Fig. 3-8). The constant parameters of the two isotherm equations and the linear regression coefficients R^2 ($0<R^2<1$) of measured and modelled adsorption results are summarized in Table 3-3. The Langmuir and the Freundlich constants were determined based on the linear form of the isotherms that were characterized by the best fit to the experimental data. The experimental data fitted very well the Freundlich equation since the R^2 values calculated were very close to 1, indicating a linear regression coefficient (R^2) of 0.9871. In addition, as shown in Fig. 3-4 the surface of seagrass residue seems heterogeneous and this is in line with the findings regarding Freundlich isotherm.

Table 3-3. Langmuir and Freundlich isotherm constants.

Isotherm	Constant		
Langmuir	Qo (mg g^{-1})	b (L mg^{-1})	R^2
	30.2115	0.0023	0.9664
Freundlich	K (mg g^{-1})	n	R^2
	7.9457	1.5647	0.9871

All the constants and the linear regression coefficient values of the models are given in Table 3-3. Based on the initial phosphate concentration the adsorption of phosphate by SG-TT increased with time until an equilibrium was reached. This suggests that increase in adsorption during the initial stage could be due to presence of abundant active sites available on the surface of SG-TT. The non-significant change in phosphate adsorption after reaching equilibrium suggests that all the active adsorption sites on SG-TT were saturated. As shown in Table 3-4 the pseudo first-order model provided a better fit to the data compared to the pseudo second-order model and this is an indication physical adsorption between phosphate and SG-TT whereas the pseudo-second-order model defines a chemisorption processes. (Shabnam et al., 2019 ; Jung et al., 2015).

Table 3-4. Kinetic parameters for the adsorption of phosphate onto seagrass *P. oceanica*

Phosphate concentration (mg L^{-1})		50	200	300
First Order	k_1 (min^{-1})	0.0263	0.0150	0.0078
	Qe (mg g^{-1})	0.4836	1.8174	4.5960
	R^2	0.9723	1.0000	0.9282
Second Order	k_2 (g mg^{-1} min^{-1})	0.0028	0.0032	0.0012
	Qe (mg g^{-1})	2.4115	3.3010	7.9697
	R^2	0.8251	0.8271	0.8465

3.7 Other components in real wastewater

The capacity of seagrass residues to adsorb other components (apart from phosphate) from real wastewater such as NH_4^+, NO_3^-, NO_2^- and COD was assessed in batch experiments using wastewater effluent from anaerobic digesters from an UWTP. Table 3-5 shows the results for the aforementioned compounds following 24 h in contact with SG-TT residues. Following 24 h phosphate was almost completely adsorbed whereas NH_4^+ concentration was slightly reduced. COD was reduced from 280 mg L^{-1} to 200 mg L^{-1} and NO_3^- decreased substantially from 0.86 to 0.36 mg L^{-1}. In addition, the UV/VIS spectra (Fig. 3-9) of anaerobic effluent wastewater demonstrated that the compounds detected around 330 nm as well as in the range of 600-800 nm can be substantially removed following 24 h in contact with seagrass residues. According to the study of Komatsu et al., (2020), the peaks detected around 320-390 nm could be humic-like or fulvic-like compounds. The spectroscopic characterization of these compounds has demonstrated to be an advisable methodology for the study of domestic and industrial solid wastes (Vieyra et al., 2009).

These results exhibit that SG-TT residues incorporate high adsorption capacity first towards phosphate, then to nitrate and then to COD demonstrating lower adsorption efficiency towards ammonium anions. These results indicate that the high selectivity of seagrass residues towards phosphate and the relatively high selectivity towards nitrate could potentially result in an end product that contains all the necessary nutrients for use as low-cost fertilizer. However, further research should be conducted for either the removal of adsorbed organics or the exclusive selectivity towards phosphate and nitrate.

Table 3-5. Adsorption of different components (mg L^{-1}) from wastewater solution following 24 h using seagrass residues

Time (h)	NH_4^+	NO_3^-	COD	PO^{3-}_4
0	3.94 ± 0.19	0.86 ± 0.00	281.3 ± 0.00	46.4 ± 1.34
24	3.44 ± 0.22	0.36 ± 0.12	200.7 ± 22.84	0.67 ± 0.10

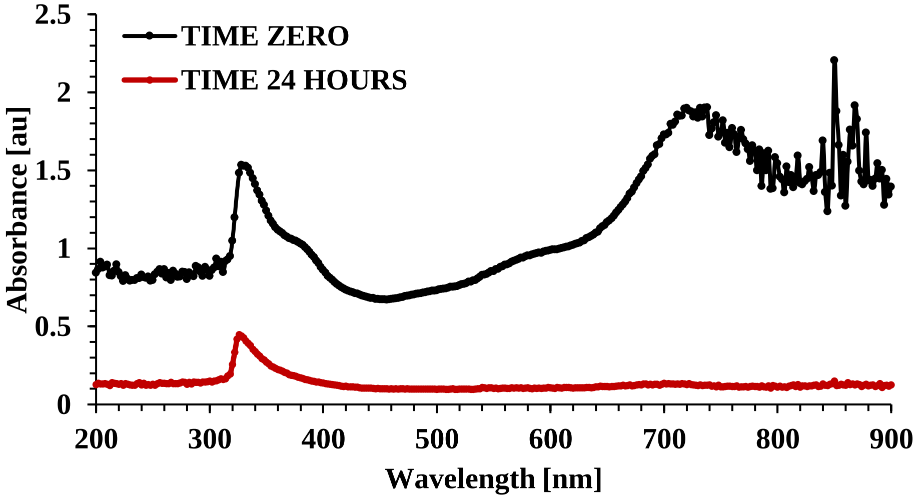


Figure 3-9. UV/Vis spectrum using real wastewater as phosphate source before and after the adsorption process.

3.8 Use of real wastes in the adsorption process

Studies show that in UWTPs, wastewater effluent from anaerobic digesters and dewatered sludge, contain 94% of incoming phosphate (Vardanyan et al., 2018). Moreover, considering the influence of the water matrix on the capacity of any material, laboratory experiments were subsequently implemented by using the effluent from an anaerobic digestion bioreactor and leached wastewater from anaerobic bioreactors, aiming to acquire certain information for the use of real waste in the adsorption process of seagrass *P. oceanica*. As shown in Fig. 3-10, five anaerobic wastewater streams from anaerobic digester in UWTP taken at different time points were examined, containing the same phosphate concentration (~100 mg L^{-1}), which is the 85.6% of phosphates contained in the sample. The results demonstrate that the highest phosphate removal was obtained within the first 15 min, while the removal reached 81% after 2 h.

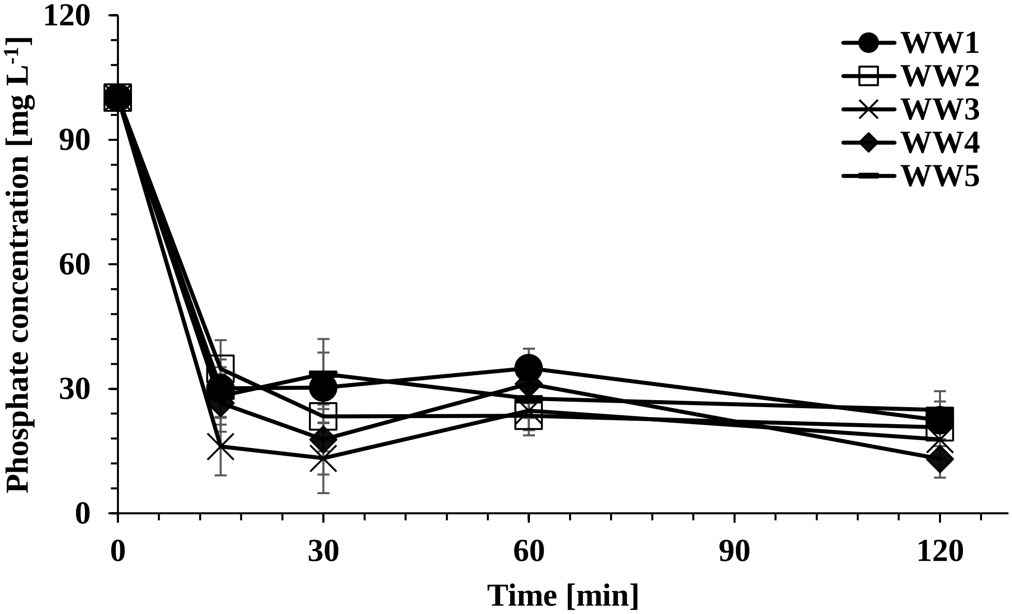


Figure 3-10. Phosphate concentration removal on seagrass *P. oceanica* residues from wastewater solutions (WW1-5).

In addition, dewatered anaerobic sludge was exposed in 2 M H_2SO_4 and after 2 days the leached solution contained 274 mg L^{-1} of phosphate, incorporating 89.3% of total phosphorus. The leaches were separated into samples with low pH (approximately ~3) and samples where the pH was maintained to 7-8, using 1 M NaOH prior exposure to 30 g L^{-1} of seagrass residues. The results show that at low pH phosphate adsorption on seagrass residues following 2 h was only 15.7%. However, at the same phosphate concentration at neutral pH, the overall removal of phosphate reached 86% and the majority of phosphate present in the solution was removed in the first 15 min of the experiment (Fig. 3-11). At low pH phosphate is mostly formed as phosphoric acid (H_3PO_4) and there are no anions that can be potentially adsorbed on seagrass residues. However, as the pH increased phosphate formed dihydrogen phosphate ion, $[H_2PO_4]^-$ and monohydrogen phosphate ion, $[HPO_4]^{2-}$ and at more alkaline conditions phosphate constituted PO_4^{3-}. Hence, it is likely the anions to be adsorbed at a higher capacity from seagrass residues compared to cations and this is in line with the experiments from Section 3.7 where NH_4^+ were slightly removed from seagrass residues as compared to anions (nitrate and phosphate). From the results, it can be stated that seagrass residues after adsorption have the potential to be used as a low-cost fertilizer due to its relatively high selectivity towards phosphate and nitrate.

To our knowledge, this is the first study that points out that seagrass residues of *P. oceanica* have the capacity to adsorb phosphate from real wastewater and even at a high concentration of phosphate (almost 300 mg L^{-1}). Previous studies by Aydin et al., (2012), Guezguez and Mhenni, (2008) and Allouche et al., (2011) demonstrated that seagrass can be used as adsorbent for uranium, methylene blue dye, and lead from synthetic solutions containing low pollutant concentration, respectively. In addition, Cataldo et al., (2018) used pyrolysed dead *P. oceanica* leafs as adsorbent material for Cd^{2+}, Pb^{2+} and Cu^{2+} ions and the results showed that the sorption ability of seagrass residues is as good as activated algal biomass.

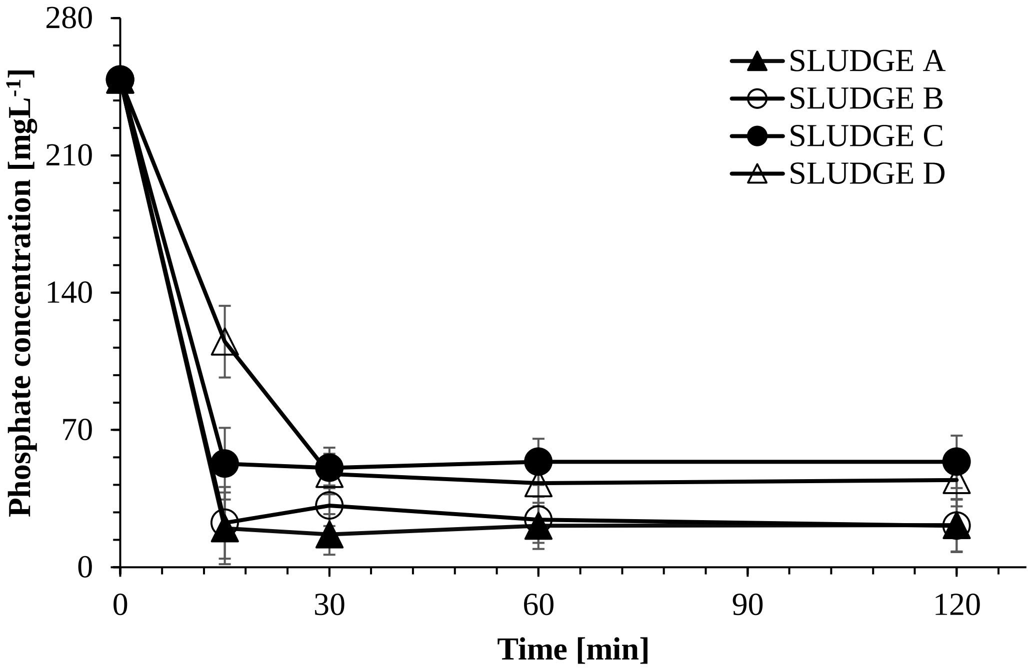


Figure 3-11. Phosphate adsorption concentration on seagrass *P. oceanica* from leached water from dewatered anaerobic sludge at neutral pH (SLUDGE A-D).

3.9 Economic analysis for collecting and processing seagrass residues.

According to Balata and Tola (2018), the presence of large quantities of *P. oceanica* residues on beaches cause odour (due to natural decomposition), reduced usability and untidy appearance. Herein, we proposed a sustainable approach for reuse of *P. oceanica residues*. Therefore, the problematic seagrass waste can be transformed through thermal treatment to an efficient adsorber for phosphate from wastewater offering a potential application as low-cost land fertilizer; this process can serve as a successful paradigm of the circular economy concept.

Adsorbent cost is consider one of the major cost parameters of the adsorption process (Banerjee et al., 2018). Thus, a brief cost estimation was conducted based on the current situation in Cyprus regarding seagrass residues (Table 3-6) not considering the capital cost. The cost for municipalities for collection and disposal of seagrass residues is approximately 70-80 € per tonne. So, a company that may invest in transformation of seagrass residues to adsorber could have a profit for the collection of seagrass from municipalities. However, it should consider the cost for collection and transportation and as well as the cost for converting seagrass residues to adsorbing material. The specific heat capacity C_p of dry seagrass residue was calculated (according to section 2.2.5) 0.82 KJ/kg/K and the required heat energy was 433182.8 KJ or 120.3 KWh. The net profit was calculated to be around 5-20 € per tonne of seagrass residue. Noteworthy, at this analysis the capital cost of sieving, drying and heating was not considered neither the potential profit for selling this product as an adsorber for phosphorus. A more detailed economic analysis can be made based on pilot scale study.

Table 3-6. Estimation for cost and profit for collection of 1 tonne of seagrass residue and conversion to adsorber.

Category	Energy per tonne of seagrass	Cost per ton (€)	Method used for cost estimation
Profit for Collection		+70 to 80 €	Communication with several municipalities in Cyprus
Cost of collection and transportation		-10 to 15 €	Municipality's data
Sieving	62.5 kWh[1]	-12.50 €	Mani et al. (2004)
Drying	69.3 kWh[1]	-13.8 €	Wright et al. (2010)
Heating[2]	120.3 kWh[1]	-24.06 €	
Overall cost per tonne of seagrass residue	-	-60 to 65 €	-
Overall profit per tonne of seagrass residue		5 to 20 €	

[1] According to Eurostat data for Cyprus 0.20 € per kWh.

[2] Based on calculation in research methodology section 1.

Chapter’s conclusions

In this study, different biomaterials (orange peels, coffee residues, fish scales, seagrass residues of *P. oceanica*, biochar produced from olive kernels, and biochar generated from vineyard prunings) have been examined for phosphate adsorption. The results demonstrated that among these materials, thermally treated *P. oceanica* residues could be used as potential low-cost biowaste for the adsorption of phosphate, not only from aqueous synthetic solutions (99%), but also from real wastewater (anaerobic effluent wastewater 81%, extracted liquid from dewatered anaerobic sludge, 86%). Therefore, this study points out that seagrass residues, which cause odors and an aesthetic problem, can be converted through thermal treatment to an excellent adsorber for phosphate from wastewater. Batch experiments showed that the best yield, regarding the utilization of phosphate, could be achieved at 500ºC for 1 h at neutral pH. The comparison of Langmuir and Freundlich isotherm models indicated that the Freundlich equation predicts the adsorption data efficiently. In addition, it was found that adsorption of phosphate followed pseudo-first kinetic and is an indication of physical adsorption as the main dominant mechanisms. The results from EDS maps also confirmed the presence of phosphate after adsorption and suggested that it is distributed homogeneously over the majority of the specimen’s surface. Chemical adsorption of phosphate could simultaneously take place with physical adsorption as indicated by the presence of phosphate-based crystal $(Mg, Fe^{++})_3(PO_4)_2.8(H_2O)$ in thermally treated *P. oceanica* residues after contact with phosphate synthetic solution. In addition, the adsorption of phosphate in the presence of other components in real wastewater, such as salt, COD, NH_4^+, NO_3^- and NO_2^- was found not to be influenced by other components except nitrates. In conclusion, it is evident that from these results (high nutrition content) and the considerably high adsorption capacity of seagrass residues, the end product can be potentially used as a low-cost fertilizer or soil conditioner, but also as a promising material for treating real wastewater contaminated with inorganic phosphate.

4 Recovery of phosphate from dewatered anaerobic sludge and wastewater by thermally treated *Posidonia oceanica* residues and its potential application as a fertilizer

The scope of this chapter was to examine the selective phosphate recovery from real wastewater (extracted solution from DWAS and effluent from anaerobic digester) using SG-TT residue and then to evaluate the recovered phosphate solid fraction as a soil conditioner or fertilizer. Firstly, laboratory data regarding the most efficient extraction process to investigate the potential for phosphate recovery from DWAS was obtained. At the same time, the maximum adsorption capacity of SG-TT was determined, while the raw biowaste was characterized. The adsorption using thermally treated *P. oceanica* residues loaded with phosphate from other wastes (synthetic solutions, anaerobic wastewater effluent and DWAS) were evaluated. Following this, the impact of recovered phosphate solid fraction was estimated through the seed germination and root elongation of different types of seeds (*S. lycopersicum*, *L. sativum*, and *S. alba*). Thus, the process for the valorization of seagrass residues was developed to investigate its potential as a phosphate adsorbent and the production of added-value products, which can be assessed in agricultural applications.

4.1 Characterization of adsorbent

4.1.1 Elemental analysis and biochemical content of *P. oceanica*

In the present work, the elemental and biochemical composition of *P. oceanica* residues were determined (Table 4-1). The analysis of raw seagrass residues resulted in high cellulose and lignin values that reached 34.5 and 22.6%, respectively. Moreover, the elemental analysis of raw seagrass specimens has been evaluated, demonstrating that carbon and oxygen comprised the dominant elements traced in *P. oceanica* residues. These data are in agreement with the literature reports, which showed that the major constituents of the seagrass cell wall are cellulose ($(C_6H_{10}O_5)_n$) and lignin forms ($C_9H_{10}O_2$,$C_{10}H_{12}O_3$,$C_{11}H_{14}O_4$) (Fouzi et al., 2019; Khiari and Belgacem, 2017; Torbatinejad et al., 2007). Following this and according to our previous study (Photiou et al., 2021), the carbon exist in raw *P. oceanica* seagrass is reduced after the thermal treatment, which probably relates to the partial decomposition of the organic matter; subsequently all unaffected quantities are increased in relative proportions.

Table 4-1. Elemental analysis and biochemical content of raw *P. oceanica* seagrass (wt.%, dry basis).

***P. oceanica* seagrass**	**Content (% dry basis)**
Biochemical composition	
Lignin	22.60
Hemicellulose	6.64
Cellulose	34.54
Elemental analysis	
C	55.64
O	28.68
Na	2.79
Mg	2.87
Cl	6.72
Ca	1.15
Al	0.46
Si	0.82
S	0.52
K	0.35

4.1.2 Saturation capacity assessment of thermally treated *P. oceanica*

Adsorption capacity is the amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent (Deng et al., 2011), and is largely influenced by other components present in wastewater. Synthetic phosphate solutions (2347.2 and 1110.8 mg L^{-1}) were prepared to determine the saturation capacity of SG-TT residues. Therefore, a fed-batch experiment was performed with the addition of synthetic phosphate solutions at regular time intervals. The phosphate concentration adsorbed was monitored through time, and the results are depicted in Fig. 4-1. At the beginning of the experiment, the first solution fed into the reactor was in contact with the SG-TT residues for 3 days, exhibiting low phosphate adsorption performance. Thus, the next fed batches were in contact with the adsorbent for a longer period of time. After day 13, the adsorption rate of phosphate ions was significantly reduced. From the results obtained, the saturation capacity of seagrass residues reached 179.13 mg g^{-1}, which confirms the suitability of the material for phosphate adsorption. In the literature, other compounds such as Cr (VI) and methylene blue were studied for their adsorption capacity into thermally treated *P. oceanica* from synthetic solutions exhibiting similar saturation capacities as compared to the current study (Asimakopoulos et al. 2021, Dural et al., 2011). More studies can be done towards using thermally treated *P. oceanica* as an adsorbent of other compounds not examined so far.

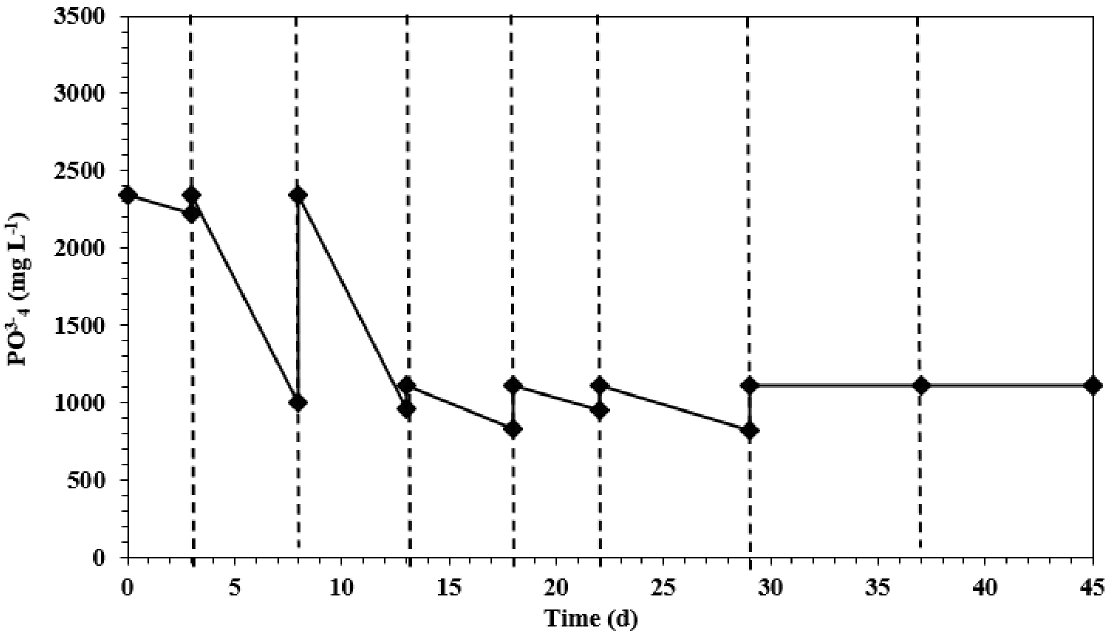


Figure 4-1. Adsorption of phosphate in mg L^{-1} from synthetic solution at regular time intervals.

4.2 Phosphate Leaching from DWAS

The scientific community has shown increased attention to the investigation of DWAS as a renewable and rich source of nutrients. In this experiment, phosphate recovery efficiency was assessed using different extraction procedures for leaching phosphate from DWAS. Fig. 4-2 depicts the four extraction processes tested compared to the maximum concentration eluted using the aqua regia solution. From the results obtained, the use of SA and the combination of TSA process exhibited the higher phosphate extraction from DWAS (821.9 and 902.2 mg L^{-1} respectively), while using the sonication as an extraction method much lower phosphate concentration was eluted (44.6 mg L^{-1}).

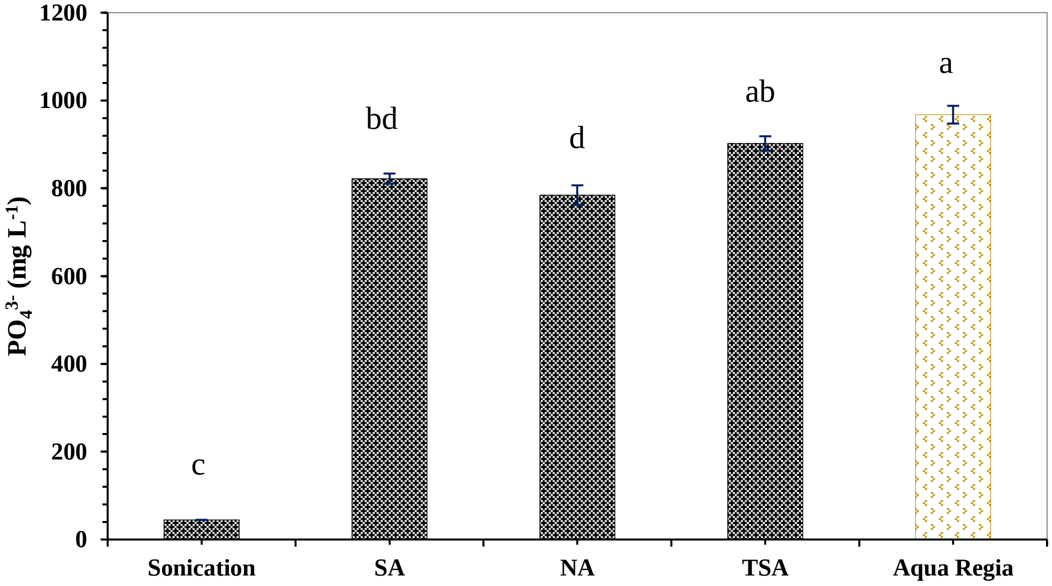


Figure 4-2. Phosphate concentration in mg L^{-1} using different extraction methods (Sonication, Sulfuric acid; SA, Nitric acid; NA, Thermal-Sulfuric acid; TSA, Aqua Regia). Values are given as mean and std (error bars) calculated over triplicates. Values with no letters in common differ significantly ($P < 0.05$).

Sulfuric acid can efficiently solubilize phosphate from sludge compared to nitric and hydrochloric acids (Shiba and Ntuli, 2017; Vardanyan et al., 2018), and thus, it constitutes a standard inorganic acid choice for many phosphate solubilization processes, such as artificial fertilizer production (Acelas et al., 2014). The extraction efficiency (%) of each method tested demonstrates that the most suitable acid medium to leach out phosphate from DWAS was the one used in SA and TSA process with 84.9 and 93.2% removal efficiency, respectively. Similar results were obtained in the work of Zimmermann and Dott, (2009), where sulfuric acid was used as an acid medium and exhibited 51 % removal efficiency of phosphate from incinerated sewage sludge ash. Thus, the two optimum leaching conditions obtained above (1M H_2SO_4, and 1M H_2SO_4 at 50^oC), were then used to adsorbed phosphate from the leachate produced after the application of SA and TSA extraction methods.

According to the literature, other inorganic or organic acids were examined for leaching phosphate from different sludge types such as hydrochloric (HCl), phosphoric (H_3PO_4), citric ($C_6H_8O_7$) or oxalic ($C_2H_2O_4$) acid. H_3PO_4 constitutes the most expensive extraction method compared to other acids (Cieślik and Konieczka, 2017). The least expensive process is considered to be the SA method. Moreover, leaching using HCl or organic acids results in high metal contamination contrasted with other acids since it can form soluble complexes with heavy metals (Acelas et al., 2014; Cieślik and Konieczka, 2017), while an extraction using sulfuric acid results in less complexation reactions and thus, leaching of minor amounts of heavy metals in the solution produced (Cieślik and Konieczka, 2017).

4.3 Adsorption experiments

4.3.1 Recovery of phosphate from different type of solutions

The findings of our previous research indicated that eggshell (Photiou and Vyrides, 2022) and seagrass (Photiou et al., 2021b), were promising materials for advanced phosphate recovery from real wastewater solutions, due to their excellent characteristics such as the high surface area, non-toxicity, and the worldwide abundance. More specifically, the results exhibited that thermally processed eggshell and seagrass residues have remarkable adsorption efficiency and selectivity towards phosphates, allowing the reformed of waste biomaterials into adsorbents for phosphate recovery and their further utilization in agricultural industries. In this study, thermally treated *P. oceanica* residues (20 g L^{-1}) were employed to adsorb phosphate a) from synthetic solution, b) anaerobic effluent wastewater and c) acid leachate (SA and TSA). The initial phosphate concentration of the solutions was

4694.3 mg L^{-1} for the synthetic solution, 70.7 mg L^{-1} for the anaerobic effluent and for acid leachates (SA and TSA) were 821.9 and 902.2 mg L^{-1}, respectively. The leachates of pH 1.2–2.5 were used after pH adjustment to neutral using NaOH. Each experiment conducted exhibited high phosphate adsorption efficiency with recovery percentages above 76% (synthetic solution). Fig. 4-3 depicts the reduction of phosphate concentration in the anaerobic effluent wastewater after 1 h in contact with *P. oceanica* residues. The results indicate that 93.9% of the initial phosphate concentration was adsorbed by the end of the adsorption process.

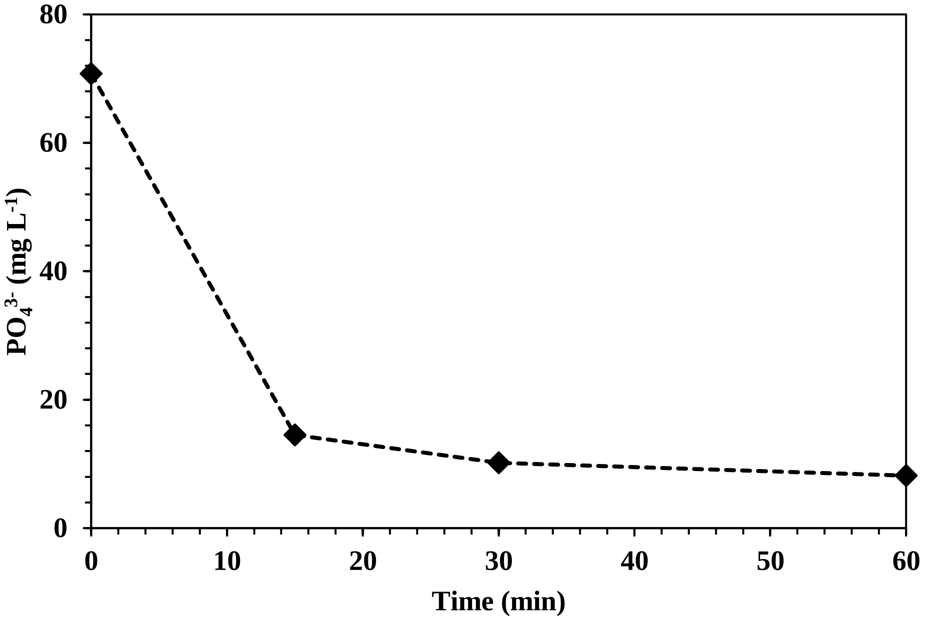


Figure 4-3. Adsorption of phosphate in mg L^{-1} from anaerobic effluent wastewater at different time points.

Similar results were obtained for phosphate removal using SA and TSA leachate as phosphate sources. Figure 4-4 shows the concentration of phosphate adsorbed for both leachate types. As can be seen from Figure 4-4, thermally treated *P. oceanica* adsorbed 98.0 and 98.3% of the phosphate contained in SA and TSA leachate and the majority of phosphate present in the solutions was removed in the first 15 min of the experiments. Moreover, these findings align with our previous work, where thermally treated *P. oceanica* residues demonstrated high adsorption efficiency towards phosphate, that exceeded 86 and 99% from leach and synthetic solutions in the first 15 min, respectively (Photiou et al., 2021).

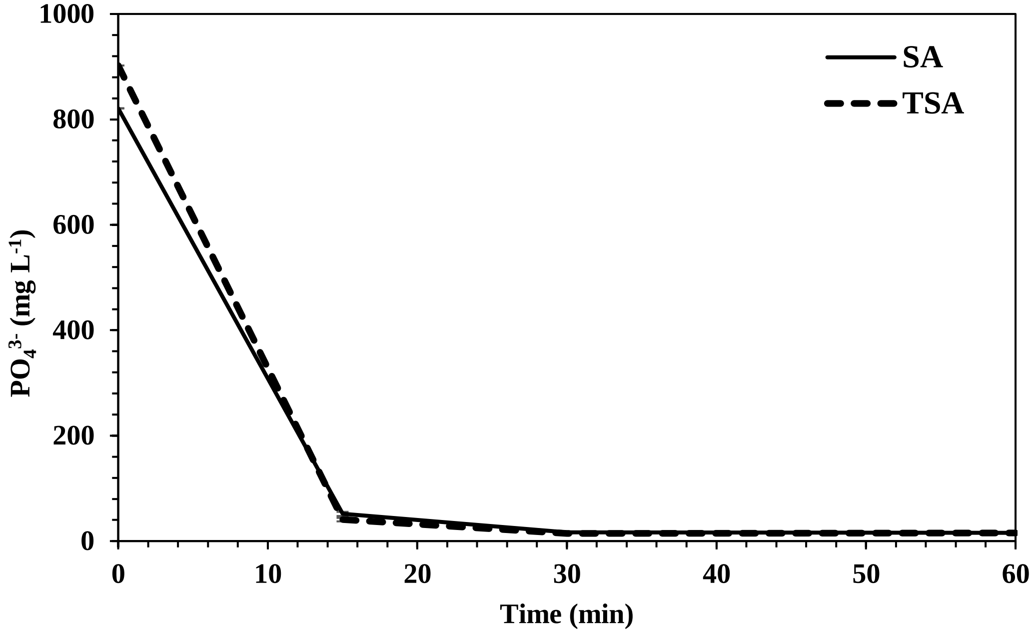
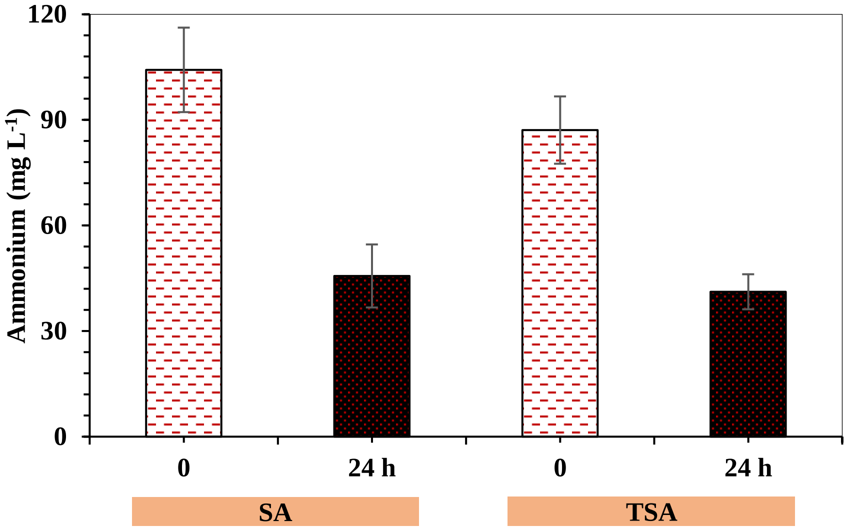
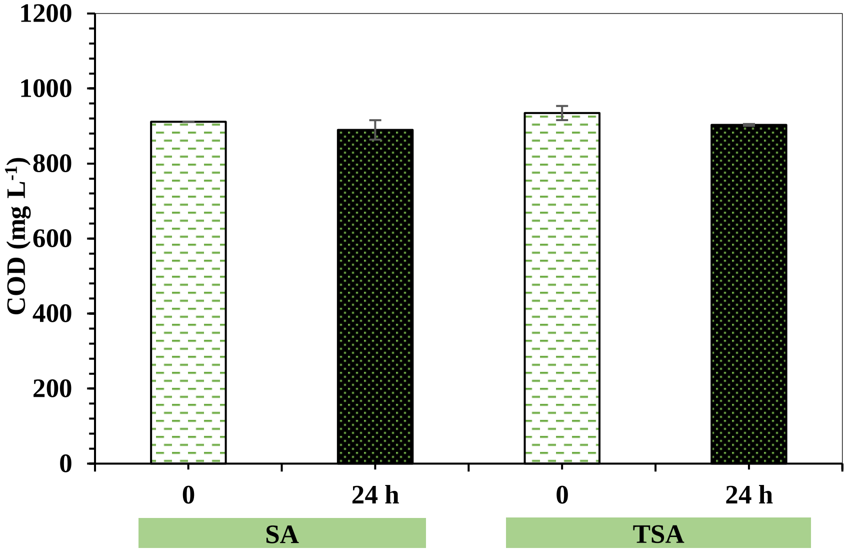


Figure 4-4. Adsorption of phosphate in mg L^{-1} from Sulfuric acid (SA) and Thermal-sulfuric acid (TSA) leachates at different time points.

4.3.2 Influence of co-existing ions

Adsorption capacity of an adsorbent for nutrient removal depends on water constraints such as anionic and cationic ions (Mu and Wang, 2016). Thus, the presence of anionic or cationic ions in leachate compete with phosphate molecules to get adsorbed onto the adsorbent through active surface binding centres (Darmograi et al., 2016). The capacity of thermally treated *P. oceanica* to adsorb other components from real wastewater such as NH_4^+, COD and NO_3^- was assessed in batch experiments using SA and TSA leachate. Fig. 4-5 shows the results for the aforementioned compounds following 24 h in contact with the adsorbent. The concentration of NH_4^+ and NO_3^- was reduced for both leachates, while no significant adsorption efficiency was observed towards COD.


Ammonium (mg L^{-1})
120
90
60
30
0
0
24 h
0
24 h
SA
TSA


COD (mg L^{-1})
1200
1000
800
600
400
200
0
0
24 h
0
24 h
SA
TSA

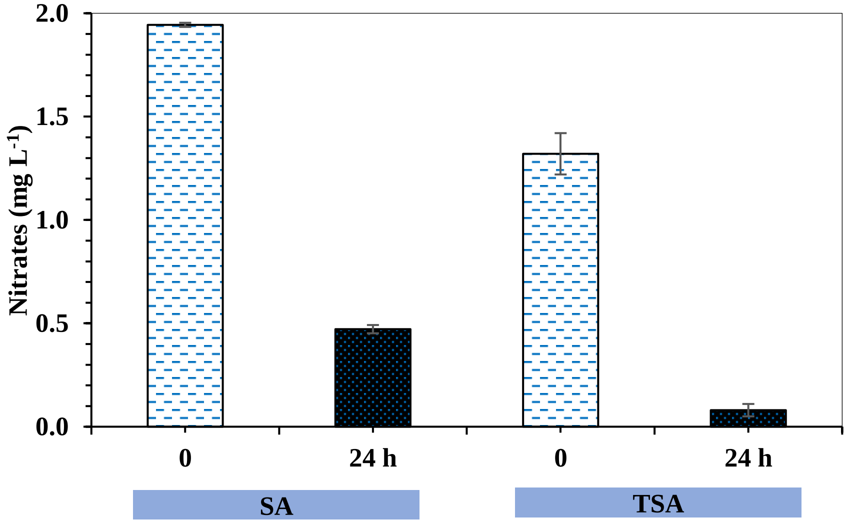

Nitrates (mg L^{-1})
2.0
1.5
1.0
0.5
0.0
0
24 h
0
24 h
SA
TSA

Figure 4-5. Adsorption of Ammonium (NH_4^+), Chemical Oxygen Demand (COD) and Nitrates (NO_3^-) in mg L^{-1} from Sulfuric acid (SA) and Thermal-sulfuric acid (TSA) leachates after 24 h time period.

Table 4-2 presents the influence of co-existing ions (mg L^{-1}) in anaerobic effluent wastewater. The concentration of ions in this solution after the adsorption process were analogous to the previous results for SA and TSA leachates. Moreover, these data are consistent with the results obtained in our previous work (Photiou et al., 2021) where the concentration of NO_3^- and NH_4^+ decreased through the adsorption process. The NH_4^+-N reduction was 56.1 and 52.7% (45.5 and 35.7 mg L^{-1}) for SA and TSA leachate and 41.3% (2 mg L^{-1}) for the anaerobic effluent wastewater, respectively. The main pollution issue associated with UWTP sludge treatment is the composition of the leachate, which is characterized by high levels of NH_4^+-N as well as high organic load (Liu et al., 2015). However, the concentration of NH_4^+, COD and NO_3^- extracted was very low in compared to the concentration of these components contained in commercial fertilizers (Romero et al., 2013). Thus, these results indicate that spent seagrass has high selectivity towards phosphate and lower adsorption efficiency towards other ions.

Table 4-2. Influence of co-existing ions (mg L^{-1}) in anaerobic effluent wastewater.

Time (h)	**NO_3^-**	**NH_4^+**	**COD**
0	0.53	4.09	161.3
24	0.35	2.40	136.8

4.4 Adsorption isotherm and kinetic studies

The equilibrium isotherm analysis of the adsorption process was evaluated by contacting different concentrations of seagrass residue (5 – 50 g L^{-1}) with real wastewater solution (anaerobic effluent) contained 62.62 mg L^{-1} phosphate for 24 h at neutral pH. The experimental data were applied to the linear Langmuir and Freundlich isotherm equations and the findings are demonstrated at Figs. 4-6 and 4-7. Adsorption results derived using different concentrations of seagrass residue demonstrated that both Langmuir and Freundlich isotherm exhibited similar fit predicting the process closely, with the first to be slightly better (Fig. 4-7). The constant parameters of both isotherm equations and the linear regression coefficients R^2 ($0 < R^2 < 1$) of measured and modelled adsorption results are summarized in Table 4-3. The experimental data fitted very well the Langmuir equation since the R^2 values calculated were very close to 1, indicating a linear regression coefficient (R^2) of 0.9957. More also shown in Table 4-3 the pseudo-second-order model better fits better the data than the pseudo-first-order model. This indicates a chemisorption process between phosphate and SG-TT. These results are not consistent with our previous work since the adsorption isotherm and kinetic studies were estimated in synthetic solutions (Photiou et al., 2021) compared to the current work that phosphate adsorption from real wastewater was tested. Organic compounds, colloids and other ions likely influence the mechanism of adsorption; most adsorption isotherm and kinetic studies has taken place using synthetic solution (Table 4-2). Therefore, this study's primary objectives were to examine phosphate adsorption on seagrass residues using real wastewater and then to test solid residues after adsorption as a fertilizer.

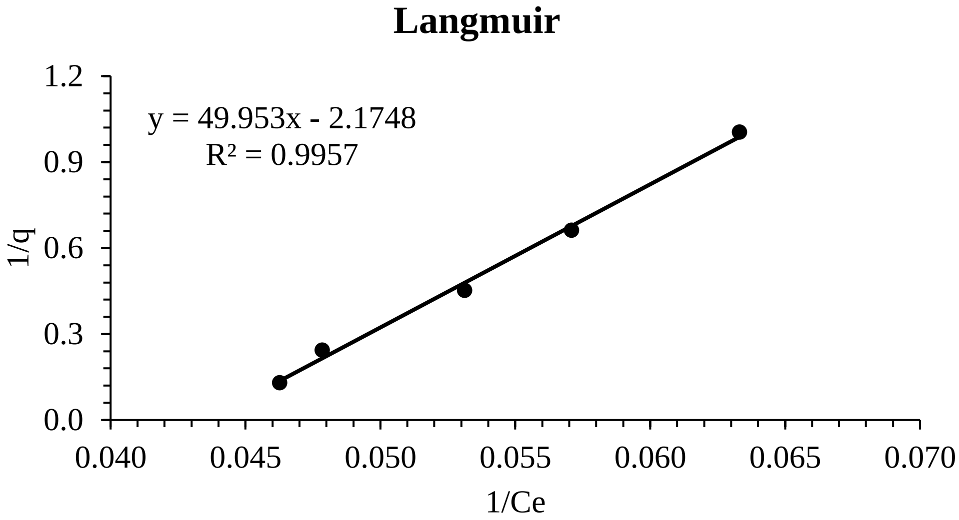


Figure 4-6. Langmuir isotherm plot for wastewater phosphate removal by the application of different concentrations of seagrass *P. oceanica* residues.

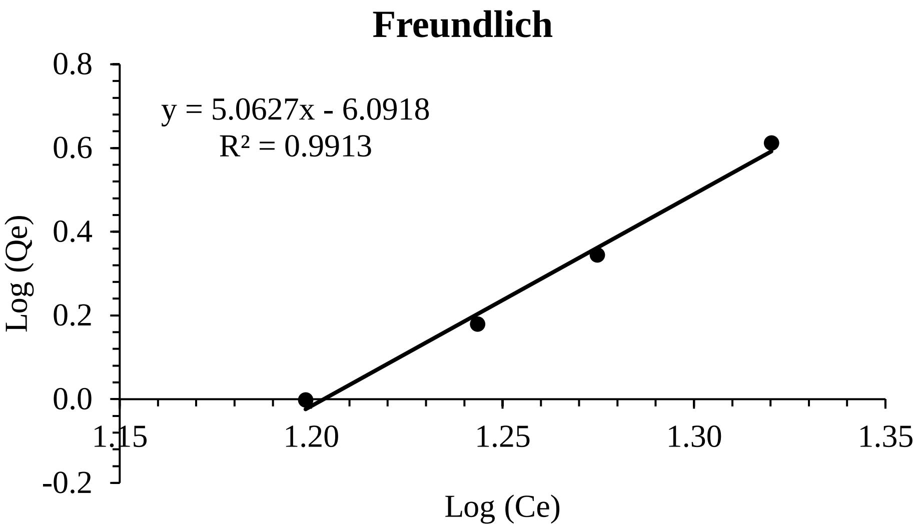


Figure 4-7. Freundlich isotherm plot for wastewater phosphate removal by the application of different concentrations of seagrass *P. oceanica* residues.

Table 4-3. Langmuir and Freundlich isotherms constants and kinetics.

		Isotherm constants	
Langmuir	Qo (mg g^{-1})	b (L mg^{-1})	R^2
	0.4598	0.043	0.9957
Freundlich	K (mg g^{-1})	n	R^2
	$8.0946e^{-7}$	0.1989	0.9913
		Kinetic parameters	
First Order	-	k_1	R^2
	-	0.0016	0.9957
Second Order	Qe	k_2	R^2
	2.4525	0.0928	1.0000

4.5 Assessing the applicability of end-product as soil conditioner

4.5.1 Testing with adsorbed phosphate from synthetic solution

Solid fraction remaining from the current procedure was tested in an agricultural application as soil conditioner, aiming to substantially reduce the waste emitted by the adsorption process. Different concentrations of the end product (0, 1, 2.5, 5, 10%) were amended with compost and tested in *Solanum lycopersicum* (tomato) seeds. Fig. 4-8 depicts the number of germinated tomato seeds, the root and shoot length for the concentrations examined. The data suggest that from the concentrations examined, the ratio 1:20 exhibited slightly better performance than control concerning the root (12.0%) and shoot (9.0%) length of the germinated tomato seeds. In addition, the total length of tomato seeds germinated using the 5% concentration was statistically significant different in compared to the control. Thus, the results confirmed that using a synthetic solution as a phosphate source could justify applying the end product in the agriculture field as a soil conditioner.

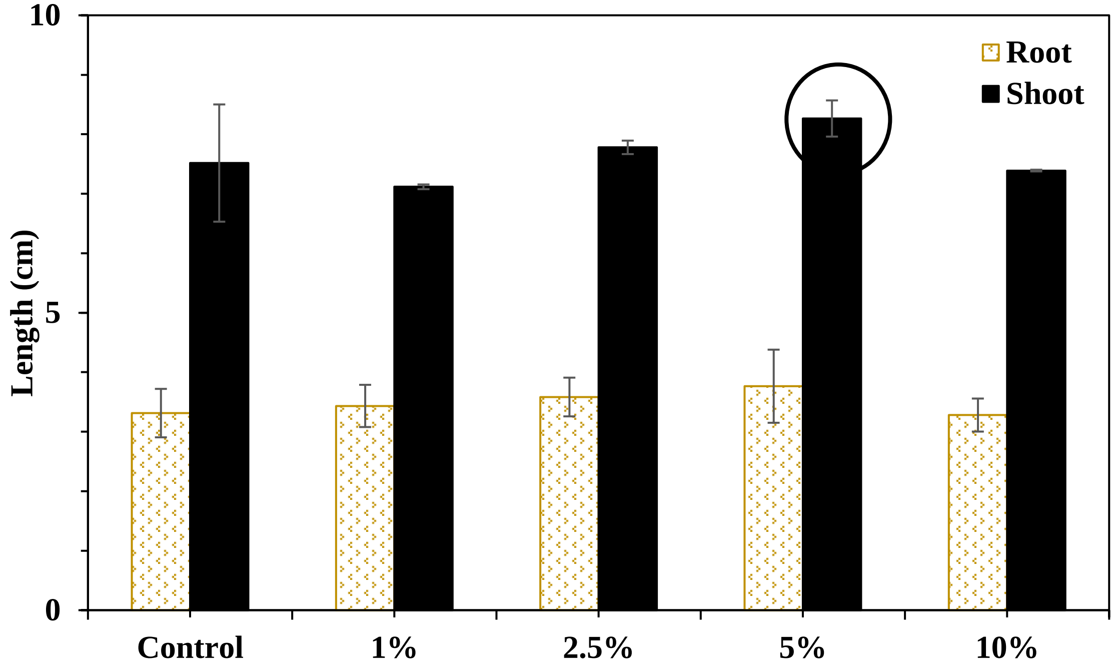


Figure 4-8. Effect of different concentrations of the end product (0, 1, 2.5, 5, 10%) from adsorption using synthetic phosphate on root and shoot length of germinated tomato seeds.

GI (%) consists of a parameter often used to characterize the phytotoxicity of a sample, so GI values above 100% evident the beneficial effect of the material examined in plants. GI was calculated to evaluate the possibility of using thermally treated *P. oceanica* loaded with phosphate as a soil conditioner. Fig. 4-9 illustrates the GI results for different end product concentrations (0, 1, 2.5, 5, and 10%) after an 8 d period. As follows from the figure shown below, GI is always equal or superior to 78% when synthetic phosphate was used as phosphate source, and thus the inhibition of seeds germination and growth was not an issue in this work. Specifically, the samples contained 2.5 and 5% of the end product exhibited superiors GI values (104.2 and 108.7%, respectively) comparing to the others, indicating that the application of the end product at these concentrations can enhance the germination of seeds. However, only the sample containing 5% of the end product showed significant statistically different results than the control.

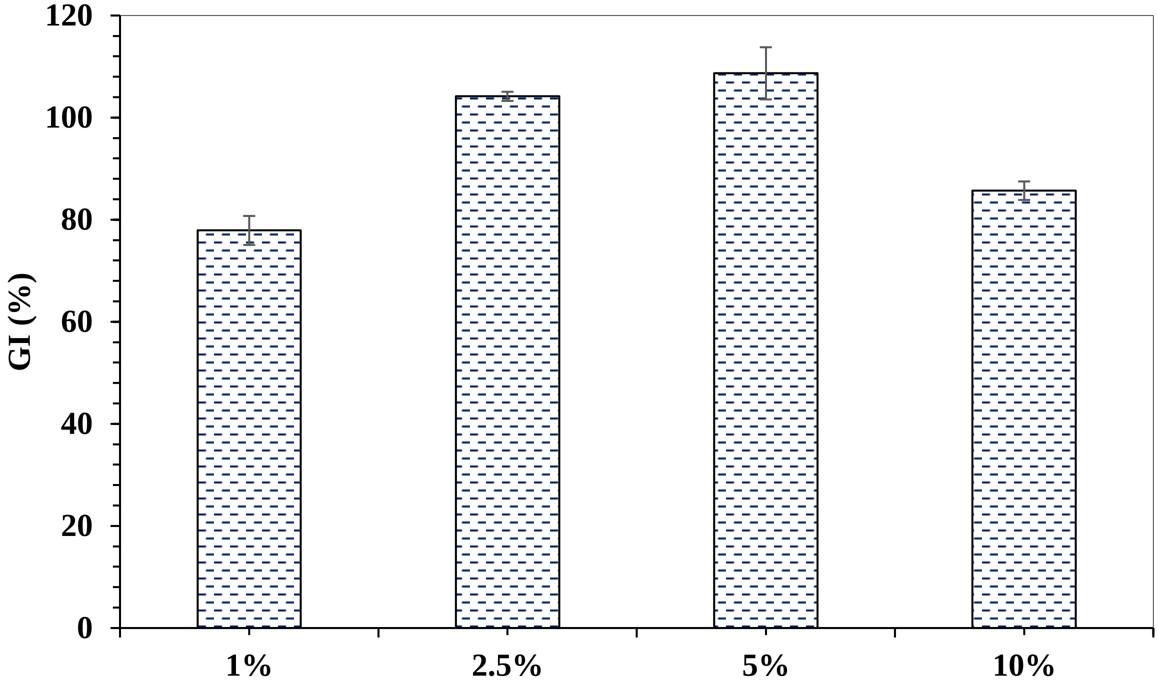


Figure 4-9. Germination index (GI (%)) of different concentrations of the end product (0, 1, 2.5, 5, 10%) after 7 d time period. The (% GI) of each test was calculated in compared to the seeds and root growth of the control samples.

4.5.2 Testing with adsorbed phosphate from anaerobic effluent

The end product of adsorption using anaerobic wastewater effluent as phosphate source, was evaluated by using the 5% concentration on *Sinapis alba* and *Lepidium sativum* seeds. These test species' selection was based on their rapid germination and growth of roots and shoots, which allow observations and scoring after 3 days. Fig. 4-10 demonstrates the root and shoot length of germinated *Sinapis alba* and *Lepidium sativum* seeds after the 3 days cultivation. From the data obtained, the root length of germinated *Sinapis alba* was increased by 6.8% compared to the control when the end product applied at the concentration of 5%, indicating the positive effect of seagrass addition in the roots of the plant. The increase of the *Sinapis alba* root length was statistically proved. The shoot length increased for both seeds, exhibiting 3.4 and 12.5% higher germination than the controls. However, for shoot length, no statistical difference was observed when compared to the control.

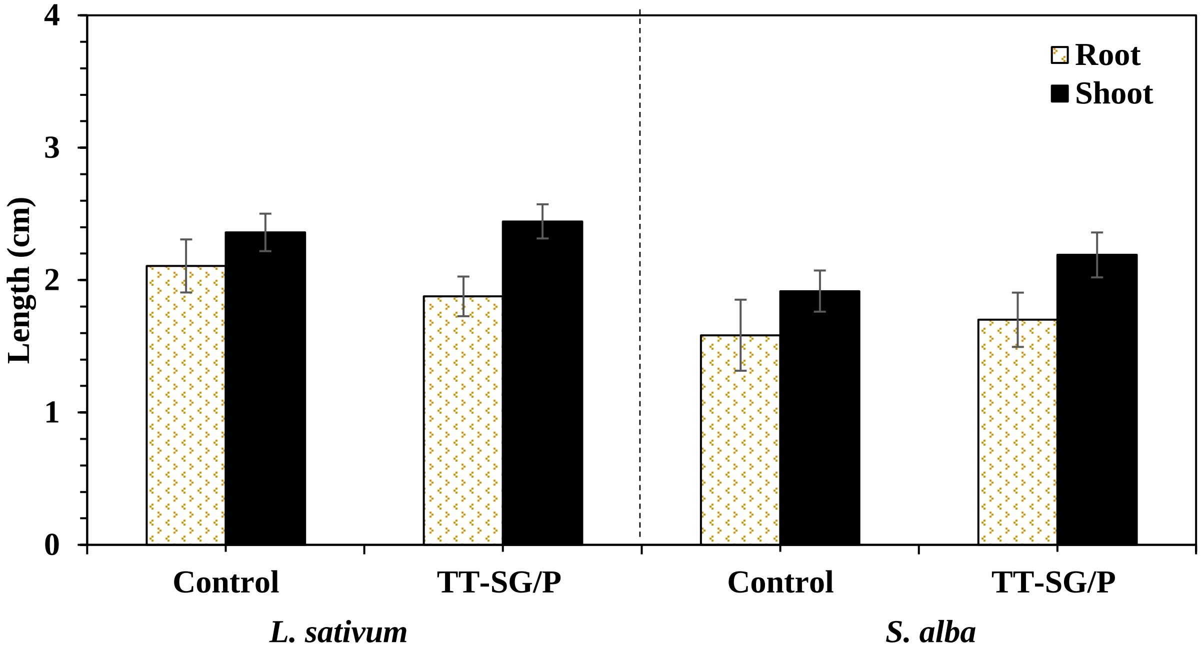


Figure 4-10. Effect of the end product from adsorption using phosphate from real wastewater on root and shoot length of germinated *Sinapis alba* and *Lepidium sativum* seeds.

Fig. 4-11 demonstrates the GI calculated after applying the phosphate adsorbed end product from real wastewater on germinated *Sinapis alba* and *Lepidium sativum* seeds. The GI was 96.7% when the end product was tested on *Lepidium sativum* seeds and 111.1% when tested on *Sinapis alba* seeds. These values indicate that no inhibition of seeds germination and growth occurred when the phosphate adsorbed end product from real wastewater was applied, and thus the exhibited GI values superior to 100% confirmed that the application of the phosphate adsorbed end product can enhance the germination of seeds.

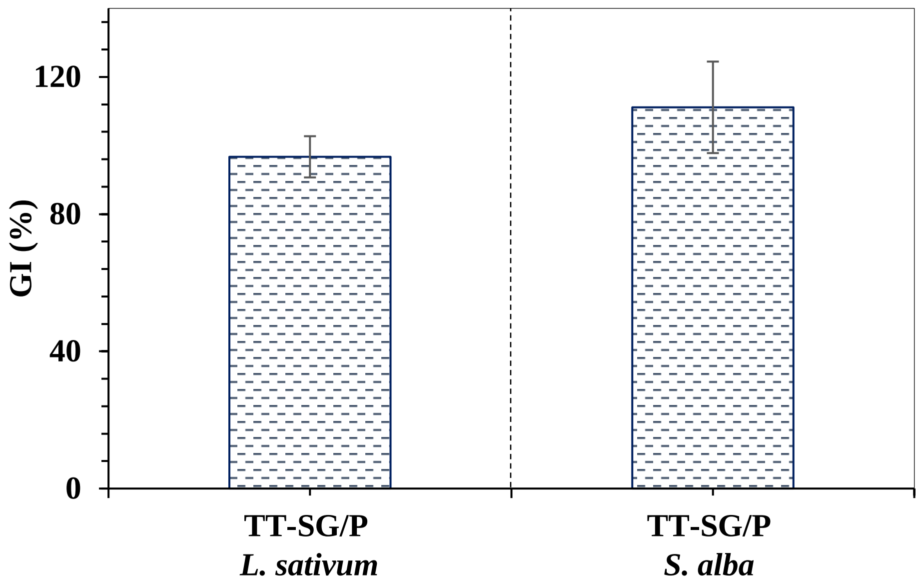


Figure 4-11. Germination index (GI (%)) of the end product from adsorption using phosphate from real wastewater of germinated *Sinapis alba* and *Lepidium sativum* seeds after 3 d time period.

4.5.3 Testing with adsorbed phosphate from leachate

The phosphate-adsorbed end product from leachates was evaluated using the 5% concentration on *Sinapis alba* and *Lepidium sativum* seeds. In comparison with the controls, the seed germination was decreased, exhibiting low germination for all plants when the end product applied at the concentration of 5% (Fig. 4-12), indicating phytotoxicity. Similar effects were observed for the shoot and root length in vitro, where seeds appeared affected following the addition of the end product. The leachate solution from DWAS contains organic compounds (soluble microbial products), heavy metals and a high concentration of iron (Vardanyan et al., 2018; Wu et al., 2020). Despite the relative low COD adsorption to thermally seagrass residue, the main organic compounds that are bound are detected around 330 nm, likely to be humic-like or fulvic-like compounds (Photiou et al. 2021). In addition, Vardanyan et al. (2018) found DWAS (from the same UWTP as the current study) contained 8685 mg total Iron per kg of DWAS. Therefore, the inhibition to the plant growth (Fig. 4-12) caused by SG-TT residue after exposure to DWAS leachate could be due to those compounds. Moreover, Solaiman et al. (2012) reported that biochar after the leachate phosphate adsorption process might not be suitable as soil amendments due to the binding of harmful compounds in biochar (Solaiman et al., 2012).

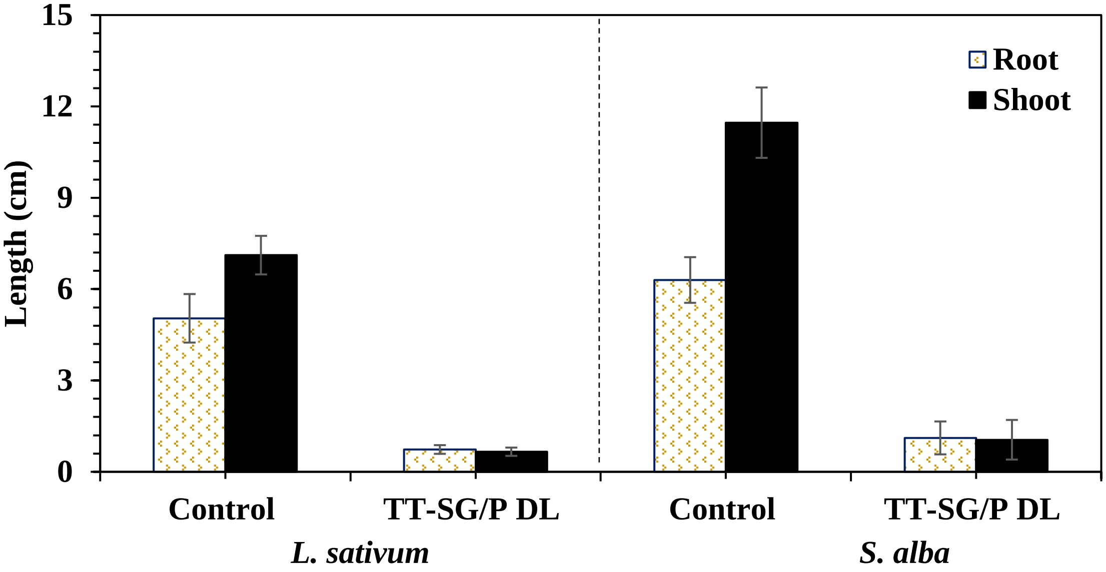


Figure 4-12. Effect of the end product from adsorption using leachate phosphate on root and shoot length of germinated *Sinapis alba* and *Lepidium sativum* seeds.

4.6 Techno-economical study and Challenges

Short cost estimation was conducted based on the valorisation of seagrass residues as adsorbent and the application of the end product as fertilizer. According to the Municipality's data in Cyprus, the collection and disposal of seagrass residues is approximately 70-80 € per tonne. Thus, these expenses could be considered a profit for the investing company. However, the cost for collection and transportation and the cost for converting seagrass residues to adsorbing material should be considered. The treatment process includes sieving, drying and heating of seagrass residues after transportation. As mentioned in our previous study (Photiou et al., 2021), the transportation and the treatment of 1 tonne of seagrass residue costs € 10-15 and € 50.36, respectively, without the estimation of the capital cost of seagrass treatment. According to these calculations, the net profit was estimated to be around 5 to 20 € per tonne of seagrass residue. Moreover, the application of the end product as a potential soil amendment could increase the estimated net profit considering that a commercial fertilizer costs 607.78 € per tonne on average (National Agricultural Statistics Services).

The phosphate concentration in DWAS is substantially high, and it can potentially be extracted using SA (Vardanyan et al., 2018). However, the cost for the extraction process needs to be calculated and can contribute significantly to the operational and capital cost of the phosphate recovery process. According to the United States Statista 2020, the price of 1 tonne SA is 33.13 €. In this work, 1 M H_2SO_4 was used for the chemical leaching of phosphate from DWAS. Based on the volume of 1 M H_2SO_4 used for the extraction process, it was found that 0.465 kg H_2SO_4 is required per kg of DWAS. Egle et al., (2015) reported that 0.50 kg H_2SO_4 per kg sewage sludge (TS) is required for 75–90% phosphate dissolution at pH 2, which is in line with the findings of the present work.

Furthermore, the current results showed that 0.045 kg phosphate is extracted per kg H_2SO_4, and thus, the extraction of 20.77 kg phosphate / t H_2SO_4 costs 33.13 €. The UWTPs in Cyprus are currently producing 901 tonnes of DWAS per month, which required disposal. The average disposal for 1 tonne of DWAS costs on average 128 €, much more than the chemical leaching applied in this study. However, in order for this process to be considered economically feasible, the value of the final product, the removal cost of other components present in the leachate such as metals and ions, the cost for the treatment of the residual sludge or liquid residues from the adsorption process need to be considered.

Recently Li et al. (2020) used proportional acidification to extract phosphate and organics from sludge. Then it has recovered struvite, produce short-chain fatty acids, and acidulated biological activated carbon as three cleaner products (Li et al., 2020). Based on the results of this study, more research can take place to recover short-chain fatty acids from the leached of DWAS after phosphate adsorption. Another alternative for the leached from DWAS is to be inserted into the activated sludge process since its relatively low volume will not influence the activated sludge process.

Regarding the residual sludge from leachate there are several options: Chen et al., (2001), found that acidification improves the dewaterability of activated sludge due to extracellular polymer released from sludge surface, which makes it easier to pack the sludge and reduces the water content of the sludge. It can also anaerobically co-digested with waste sludge or other type of waste with alkaline pH (Vardanyan et al. 2018). It can neutralized with lime and used as a solid stabilizer or mixed with alkaline soils. According to Quist-Jensen et al., (2018), incineration after acidification is the best option, which simultaneously produces energy as many European countries have banned the use of sludge in agriculture (Quist-Jensen et al., 2018). Following this, a more detailed economic analysis can be made based on a pilot-scale study to valid these estimations.

Chapter's conclusions

A zero-waste process based on *P. oceanica* residues has been applied to recover phosphate from wastewater and the production of a fertilizer substitute. Assessment of the saturation capacity of thermally treated *P. oceanica* confirmed the high capacity and selectivity towards phosphate. Different extraction methods of phosphate from DWAS were evaluated, indicating that sulfuric acid can efficiently solubilize phosphate from sludge. Adsorption experiments showed that SG-TT could be applied as adsorbents for Phosphate from synthetic and real wastewater solutions, with 76.0 and 98.3% adsorption efficiency, respectively. The concentration of NH_4^+ and NO_3^- was reduced for both leachates at around 50.0%, while no significant adsorption efficiency was identified towards COD. The remaining process solid residues were mixed with compost and were explored as fertilizer substitutes; the end material generated from anaerobic effluent or synthetic solutions imposed a beneficial effect on plant growth with germination index (GI) values 96.7 – 111.1%, for all types of seeds tested (*Solanum lycopersicum*, *Lepidium sativum*, and *Sinapis alba*). More specifically, when the end material generated from anaerobic effluent was used, the root length of germinated *Sinapis alba* was statistically increased by 6.8%, in compared to the control, indicating a positive effect on the root of plants. Nevertheless, when the final product (thermally treated *P. oceanica* exposed to phosphate leached from DWAS solution) used as a potential fertilizer this negatively affects the plant growth. Therefore, further research needs to be undertaken towards exploring the use of end product in the cultivation of plants with a tolerance to substances of high concentrations DWAS. In conclusion, it is evident that due to the considerably high adsorption capacity of seagrass residues and the end product generated from anaerobic effluent, *P. oceanica* biomass after adsorption can be used as a low-cost soil conditioner, but also as a promising material for treating real wastewater contaminated with inorganic phosphate. Furthermore, the use of modified biowastes as adsorbents could possibly be the key to solve two problems; phosphate recovery from wastewater and biowaste management, creating a phosphorus-based product that can potentially use as a biofertilizer.

5 Thermally treated eggshells in anaerobic digestion: testing in-situ phosphate recovery and buffering acidification in AD

Batch experiments were conducted to evaluate the recovery of phosphates from three different solutions as follows: (a) DWAS leachate using nitric acid, (b) DWAS leachate using sulfuric acid and (c) anaerobic effluent wastewater as well as the in-situ recovery of phosphates using EGSL-TT from the AD and the anaerobic effluents (AD effluent and wastewater leached from DWAS). This chapter also proposed the use of EGSL-TT in AD systems as a strategy to counteract the pH drop due to the high concentrations of VFAs and increase methane production. The innovation presented in this chapter is based on a new perspective regarding the use of final process products as soil conditioners after the adsorption process and on EGSL-TT, which can be effectively counteract excessive acidification and alleviate low pH in AD systems.

5.1 Adsorption of phosphate ions from anaerobic effluents and evaluation of end products as soil supplements

EGSL-TT were employed to adsorb phosphate from a) anaerobic effluent wastewater and b) acid leachates (NA and SA). Batch experiments were performed with the addition of 20 g L^{-1} EGSL-TT in both wastewater solutions and the initial phosphate concentration of the anaerobic effluent was 70.8 mg L^{-1} and 124.2 mg L^{-1}, 103.9 mg L^{-1} for acid leachates (SA and NA), respectively (see APPENDIX I). Except from NA leachate, the results from SA leachate and anaerobic effluent wastewater demonstrate that the highest phosphate removal was obtained within the first 20 min. Overall, the results highlighted that the EGSL-TT constitutes a great biomaterial for removing phosphate ions from real wastewater solutions, since each experiment conducted indicates that 78.4, 85.0, 97.2% (anaerobic effluent wastewater, NA leachate, and SA leachate) of the initial phosphate concentration was adsorbed by the end of the adsorption process.

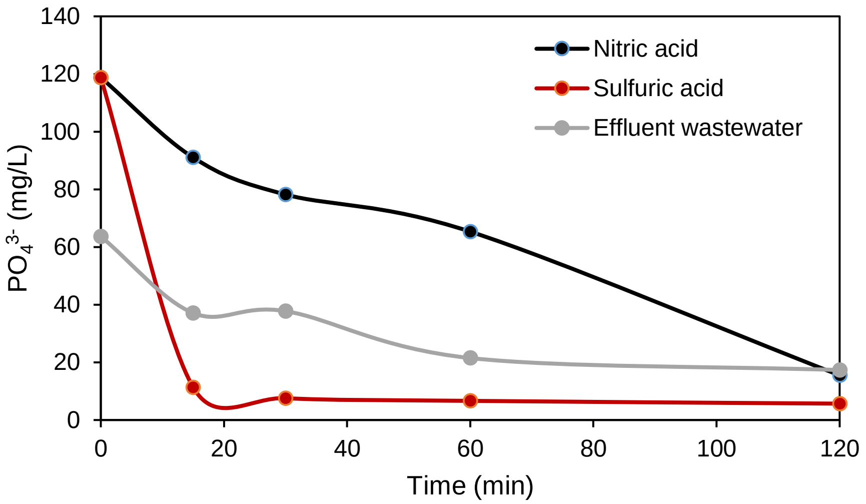


Figure 5-1. Wastewater solutions tested for phosphate recovery; (a) DWAS leachate using nitric acid, (b) DWAS leachate using sulfuric acid and (c) anaerobic effluent wastewater.

Given that the presence of coexisting anions might compete with phosphate for active adsorption sites and significantly reduce the phosphate removal performance by the adsorbents (Lee et al., 2022), the capacity of EGSL-TT to adsorb other components such as NH_4^+, NO_3^- and COD from real wastewater was assessed in batch experiments using wastewater effluent from anaerobic digesters. From the results obtained, EGSL-TT exhibited higher adsorption efficiency towards NO_3^- and NH_4^+, which were decreased substantially from 0.37 to 0.14 mg L^{-1} and 16.13 to 8.98 mg L^{-1}, respectively (see APPENDIX I). Lee et al., (2022), reported that the higher the molar concentration of a compound, the greater the effect of coexisting anions on phosphate adsorption, which follows the order $CO_3^{2-} \gg SO_4^{2-} > NO_3^- > Cl^-$. Similarly, Wei et al., (2020) indicated that divalent anions, such as CO_3^{2-} and SO_4^{2-} highly influence the phosphate adsorption as opposed to monovalent anions, such as NO_3^- or Cl^-. Thus, NO_3^- and Cl^- are considered to have no significant effect on the adsorption of phosphate, since the mechanisms of adsorption are unalike (phosphate adsorption forms the inner sphere complex, whereas NO_3^- and Cl^- adsorption is non-specific via an outer sphere complex) (Lee et al., 2022). However, due to the low COD compound removal from EGSL-TT (5.5%), these results indicate that the high selectivity of EGSL-TT towards phosphate and the relatively high selectivity towards NO_3^- and NH_4^+, could potentially result in an end product that contains the necessary nutrients for its application as low-cost fertilizer.

Despite the high phosphate adsorption capacity of EGSL-TT, desorption of phosphates is not completely reversible, and thus an alternative is to utilize the resulting material as a fertilizer. The end products of adsorption using anaerobic effluent wastewater and acid leachates as phosphate sources, were evaluated by using the 5% w/w (g of EGSL-TT/P per g of compost) on *Sinapis alba* and *Lepidium sativum* seeds. Fig. 5-2(a-b) demonstrates the GI calculated and the root and shoot length of germinated *Sinapis alba* and *Lepidium sativum* seeds after applying the phosphate adsorbed end product from anaerobic effluent wastewater. The GI reached 97.1% when the end product was tested on *Lepidium sativum* seeds and 122.7% when tested on *Sinapis alba* seeds (Fig. 5-6(a)). These values highlight that no inhibition of seeds germination and growth occurred when the solid product from anaerobic effluent wastewater was applied, and thus under these conditions, the exhibited GI values confirmed the possibility of the end product to be applied as a soil conditioner. Moreover, the shoot length of germinated *Sinapis alba* and *Lepidium sativum* seeds, exhibited 5.34 and 23.6% increase compared to the controls, indicating the positive effect of EGSL-TT addition in the shoots of the plant. The increase of the *Sinapis alba* shoot length was statistically proved. However, for root length, no statistical difference was observed when compared to the control (Fig. 5-2(b)). The studies of Radha and Karthikeyan, (2019) and Wazir et al., (2018) evaluated eggshell powder as fertilizer on potato and pea seeds. As reported, eggshell benefits the growth of potato and pea seeds. Both studies found a positive correlation between the growth of the plant and the concentration of eggshell used, which suggests an overall improvement of the mean plant height, the number of nodes, leaves, leaf area, branches and the tuber size of the plant.

Equally important were the results depicted in Fig. 5-2(c), which present the root and shoot length of germinated *Sinapis alba* and *Lepidium sativum* seeds after the application of the adsorption end-product from acid leachates (EGSL-TT/DL). The seed germination was decreased, exhibiting low GI for both plants (16.44 and 6.73% for *Sinapis alba* and *Lepidium sativum,* respectively). Similar effects were observed for the shoot and root length in vitro, where seeds appeared affected following the addition of the end product. In our previous work (Photiou and Vyrides, 2021), SG-TT *P. oceanica* after phosphate adsorption from acid leachates was tested as fertilizer substitutes on plant growth. The results attained were in line with the present study's findings, indicating that the leachate solution from DWAS imposed a negative effect on the germination of seeds and despite the relative low COD adsorption of EGSL-TT, other organic compounds such as humic or fulvic-like substances (Photiou and Vyrides, 2021), can cause the inhibition to the plant growth shown in Fig. 5-2(c).

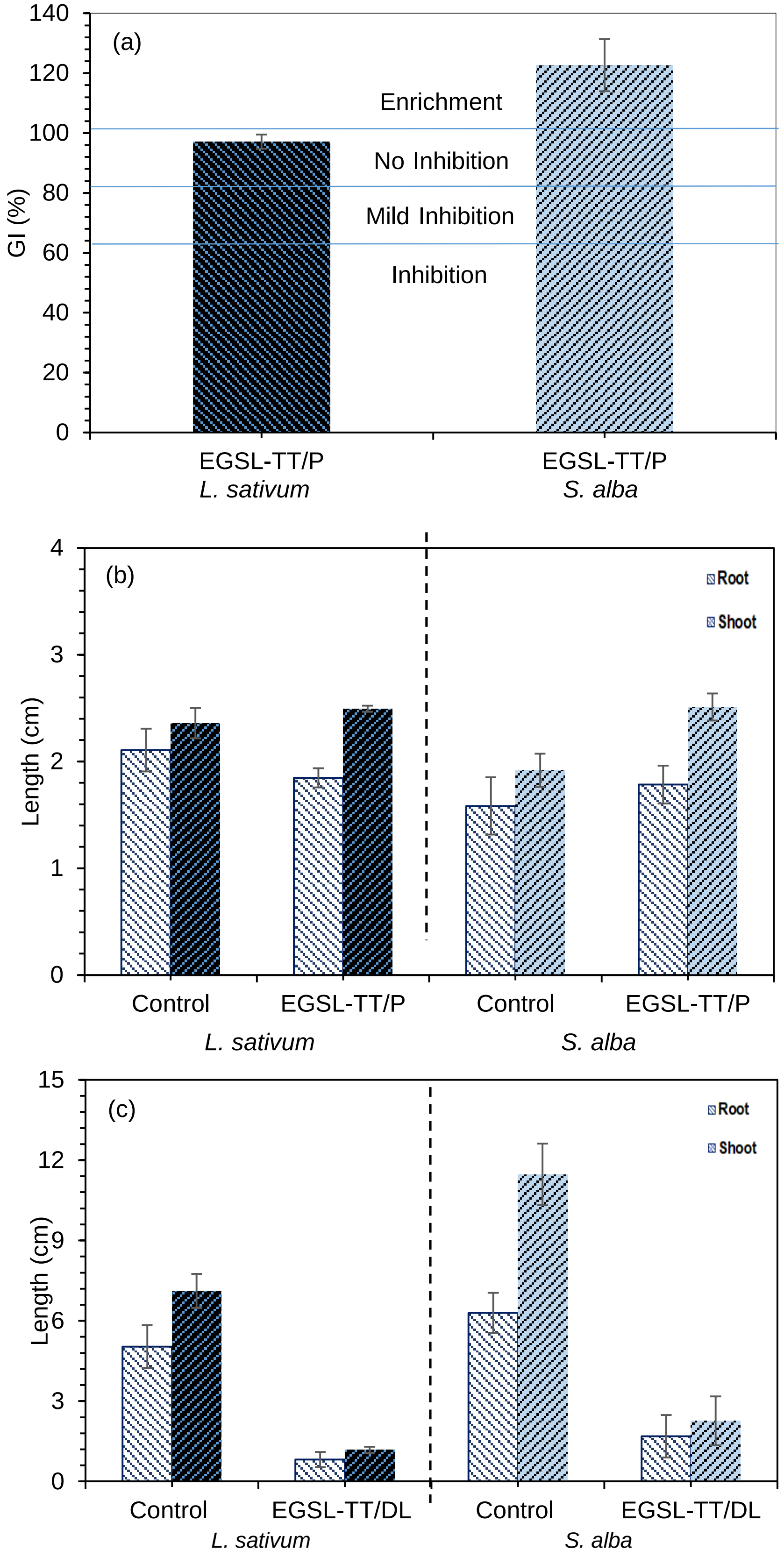

(a)
GI (%)
0
20
40
60
80
100
120
140
Enrichment
No Inhibition
Mild Inhibition
Inhibition
EGSL-TT/P
L. sativum
EGSL-TT/P
S. alba
(b)
Length (cm)
0
1
2
3
4
Root
Shoot
Control
EGSL-TT/P
Control
EGSL-TT/P
L. sativum
S. alba
(c)
Length (cm)
0
3
6
9
12
15
Root
Shoot
Control
EGSL-TT/DL
Control
EGSL-TT/DL
L. sativum
S. alba

Figure 5-2. Phytotoxicity trials on *Sinapis alba* and *Lepidium sativum* seeds after 3 d time period; **(a)** Germination index (GI (%)) and **(b)** shoot and root length of the end product from adsorption using phosphate from anaerobic effluent wastewater **(c)** shoot and root length of the end product from adsorption using phosphate from acid leachates.

5.2 Coupling EGSL-TT with anaerobic digestion (AD) systems

5.2.1 Influence of soluble carbonates (CO_2 flushing)

The adsorption capability of the adsorber depends on the equilibrium concentrations between the liquid and gaseous phase (Al Mamun and Torii, 2017). EGSL-TT was used as an adsorbent to demonstrate the effect of CO_2 or N_2 from the gas stream on the sorption capacity of phosphates and organic compounds. Fig. 5-3(a) shows the effect of CO_2 or N_2 on the sorption capacity of humic-like or fulvic-like compounds that are detected around 330 nm as well as in the range of 600-800 nm (Komatsu et al., 2020) and can be substantially removed following 24 h in contact with EGSL-TT. The exposure to N_2 contributed to the removal of higher humic-like compounds than the exposure with CO_2, and this can potentially alleviate inhibition of those compounds to anaerobic microorganisms. Fig. 5-3(b) depicts the effect of CO_2 or N_2 on the COD and phosphate removal after 24 h time period in contact with 20 g L^{-1} EGSL-TT. The initial average phosphate and COD concentration in liquid phase were 29.0 and 7489.0 mg L^{-1}, respectively. From the results obtained, the shake bottles containing the supernatant (anaerobic) liquid in contact with EGSL-TT and flushed with CO_2, highly influence the adsorption of phosphate ions, exhibiting low phosphate removal (20.6%). On the other hand, the phosphate removal was 95.7% at similar conditions but flushed with N_2 instead of CO_2. Similar results were observed in a 2023-study, where the dissolution of $CaCO_3$ and removal of HCO_3^- enabled CaP granulation from cow manure (Schott et al., 2023). In addition, both gases (N_2 and CO_2) do not seem to affect the adsorption of COD compounds from EGSL-TT (Fig. 5-3(b)).

The following chemical reactions describe the continuous chain of CO_2 in contact with EGSL-TT (CaO) running along in the flasks:

$$CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)} \quad (2)$$

$$CaO_{(s)} + H_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + H_2O_{(l)} \tag{3}$$

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)}, \tag{4}$$

$$Ca(OH)_{2(aq)} + H_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + H_2O_{(l),} \tag{5}$$

According to Lee et al., (2021), the high thermal treatment of the Ca-based adsorbents enhances the elution of Ca ions from the adsorbent, resulting in the presence of carbonates in the precipitates. During the experimentation phase, the pH was high due to the release of high concentration of OH^-, which provides the conditions for the formation of $Ca(OH)_2$. (equation 4) then H_2CO_3 can compete with phosphates for binding sites (equation 5). Thus, the decrease of adsorption capacity by 70.1% in the presence of H_2CO_3 was caused by the specific adsorption of bicarbonate forming inner-sphere complexes with Ca^{2+} hindering the formation of Ca-P precipitates. The main findings of this experiment are that in the presence of EGSL-TT (EGSL-TT), the bicarbonate had a higher trend to be adsorbed than phosphate anions, and the final pH significantly increased.

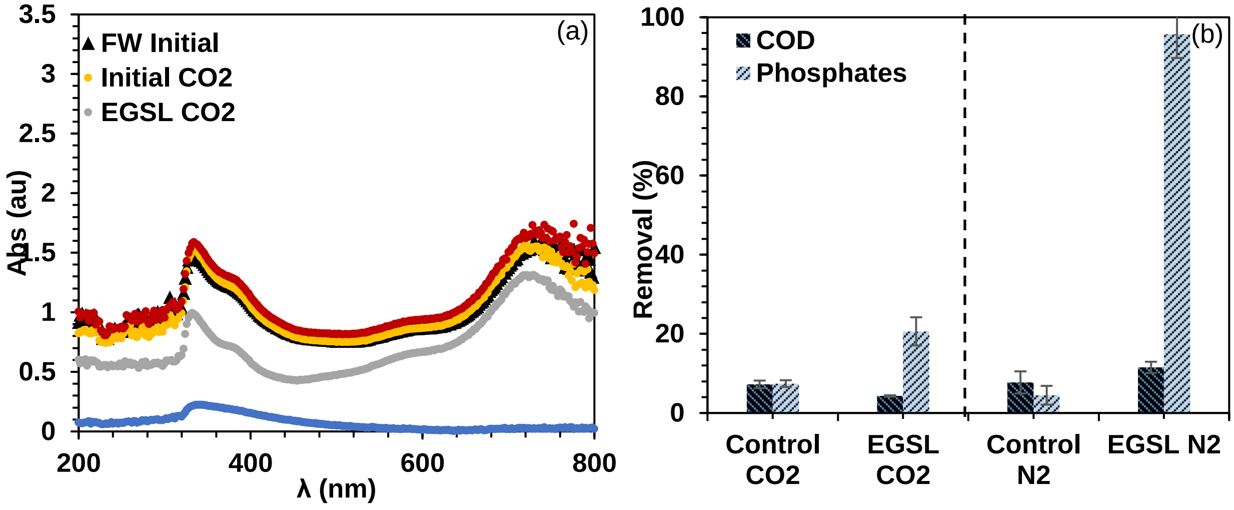


Figure 5-3. (a) UV/Vis spectrum and (b) Percentage removal of Phosphate and COD compounds (29.0 and 7489.0 mg L^{-1}, respectively) from food waste (FW) anaerobic liquid (control) and FW anaerobic liquid after 24 h time period in contact with 20 g L^{-1} EGSL-TT and flushed with two different gas streams (CO_2, N_2).

5.2.2 Anaerobic digestion (AD) performance

A series of three experiments was performed to assess the effect of EGSL-TT addition in the anaerobic fermentation systems. GS was initially adapted to mesophilic culture conditions (33°C) for 1 week prior to addition in the reactors. At the beginning of the experiments, flasks were flushed with N_2, and the pH value was adjusted to 7.8. No other adjustments were made through out the experiments and the pH was measured again at the end of each fermentation. The results obtained for the AD-FW and AD-CEL fermentations suggested that the volume of CH_4 formed was higher by 14.7 and 55.9%, respectively in fermentations inoculated with the addition of 20 g L^{-1} EGSL-TT, as compared to the production achieved in experiments inoculated only with FW and CEL (Fig. 5-4(a-b)). However, as shown in Fig. 5-4b, the sample EGSL-TT/DL- P produced after adsorption using leachate from DWAS exhibited lower methane yield compared to the corresponding control experiments, indicating that the leachate solution from DWAS contains organic compounds, heavy metals and other components (Wu et al., 2020), which negatively affect the AD systems.

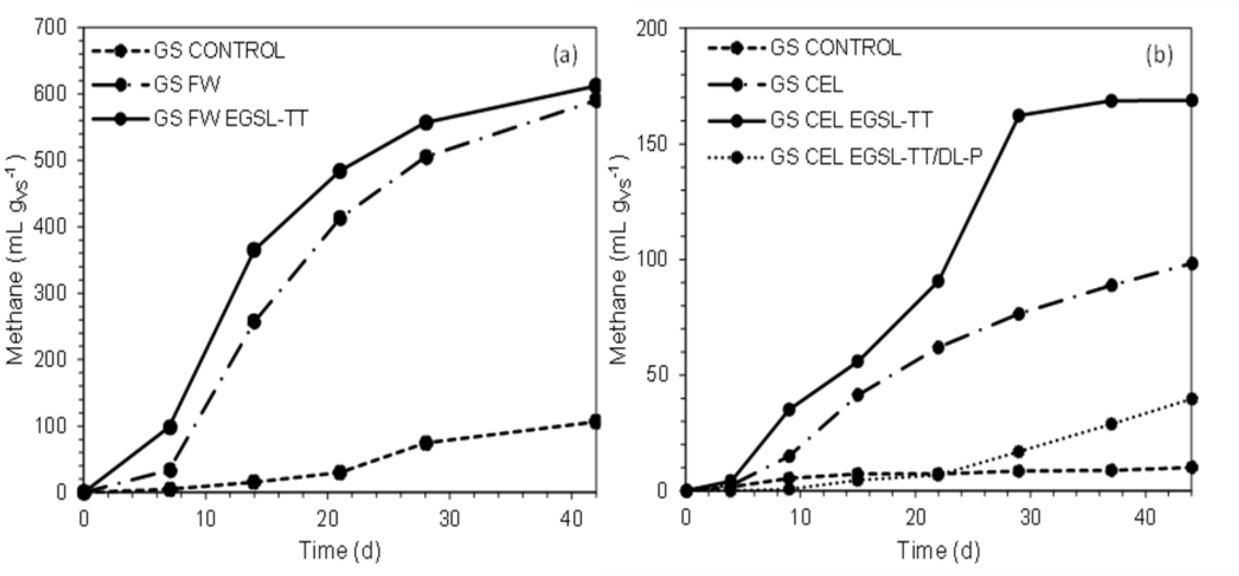


Figure 5-4. Anaerobic fermentations of (a) food waste (FW) and (b) cellulose (CEL) substrate with the addition of 20 g L^{-1} EGSL-TT in compared to each control (GS

CONTROL; without the addition of substrate and EGSL-TT, GS FW and GS CEL; without the addition of EGSL-TT).

In the following experiment, GS was exposed to relatively high concentrations of G substrate (4, 6, 8 g L^{-1}), and EGSL-TT at concentrations of 5 and 10 g L^{-1} were added as a strategy to counteract pH reduction due to VFAs production. The results exhibited in Fig. 5-5 showed that EGSL-TT amendment to AD reactors flushed with N_2, influenced the pH by contributing alkalinity and influencing the production and consumption of VFAs. The COD measurement results showed that high COD values (953.3 mg L^{-1}) correspond to reactors where the remained concentration of the organic matter was also high, and reduction of COD was achieved only in the reactors where EGSL-TT residues were present (261.2 -291.8 mg L^{-1}). As depicted in Fig. 5-5, at the end of the fermentation, the control bottle for 8 g L^{-1} G substrate generated around 2000 mg L^{-1} VFAs whereas the VFAs for the EGSL-TT assisted fermentations were less than 620 mg L^{-1}. Moreover, the pH value at the control was lower (5.63) than the reactors with EGSL-TT addition (7.09 - 7.13). Therefore, the low pH due to high concentrations of VFAs inhibited the anaerobic bottle at 8 g L^{-1} (control). In contrast, in the bottle that EGST-TT were added, this inhibition was not found, and the anaerobic bottles' performance was substantially higher. Moreover, the phosphate adsorption in EGSL-TT was evaluated in the anaerobic digester and the results showed that the initial concentration of phosphates in each flask where close to zero by the end of fermentation indicating that EGSL-TT has great adsorption properties.

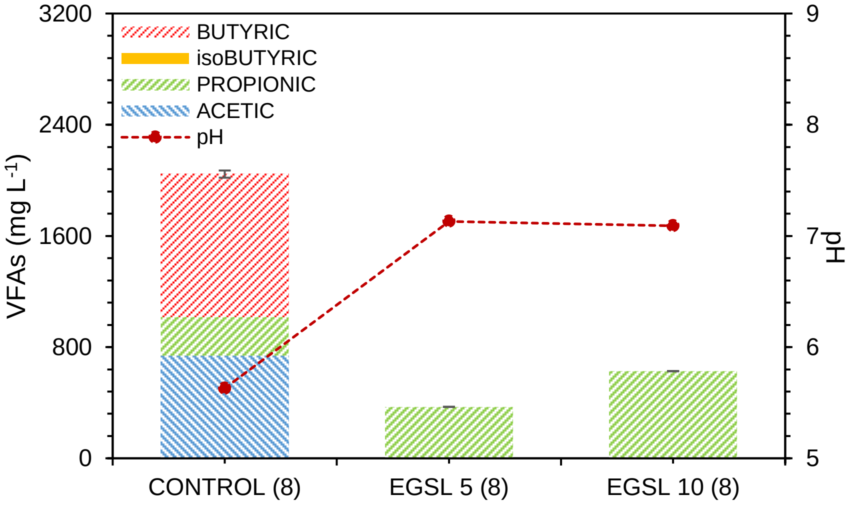


Figure 5-5. Volatile fatty acids (VFAs) and pH measurements during the anaerobic fermentations (AD-G) of glucose (G) substrate (4, 6, 8 g L^{-1}) with the addition of 5 and 10 g L^{-1} EGSL-TT in compared to each control (without EGSL-TT).

The results regarding the methane production during the final experiment are depicted in Fig. 5-6. EGSL-TT assisted fermentations at concentration of 10 g L^{-1} demonstrated the highest CH_4 production and the shortest lag phase in all G substrate concentrations in compared to 5 g L^{-1} ESGL-TT and each control. The difference was more profound in the bottles with the higher G concentration (8 g L^{-1}). Correspondingly, the control with 8 g L^{-1} was not retrieved until the end of the experiment, and the CH_4 composition was only 22.4%. In contrast, the addition of EGSL-TT exhibited substantially higher performance. Our findings pointed out the benefits of adding EGSL-TT in AD as a strategy to alleviate pH drops and increase AD's performance. Additionally, using EGSL-TT amendments in waste streams can contribute to a more local circular economy concept (Hart, 2021). Leininger and Ren, (2021), investigated the amendment of different FW biochar materials with AD reactors and reported high biogas yields, significant production rates, and short lag phases. However, the conversion process of biowaste to biochar is the most expensive component of the pyrolysis operation. Thus, thermally treated biowaste is a more economically feasible approach, which can obtain a similar outcome.

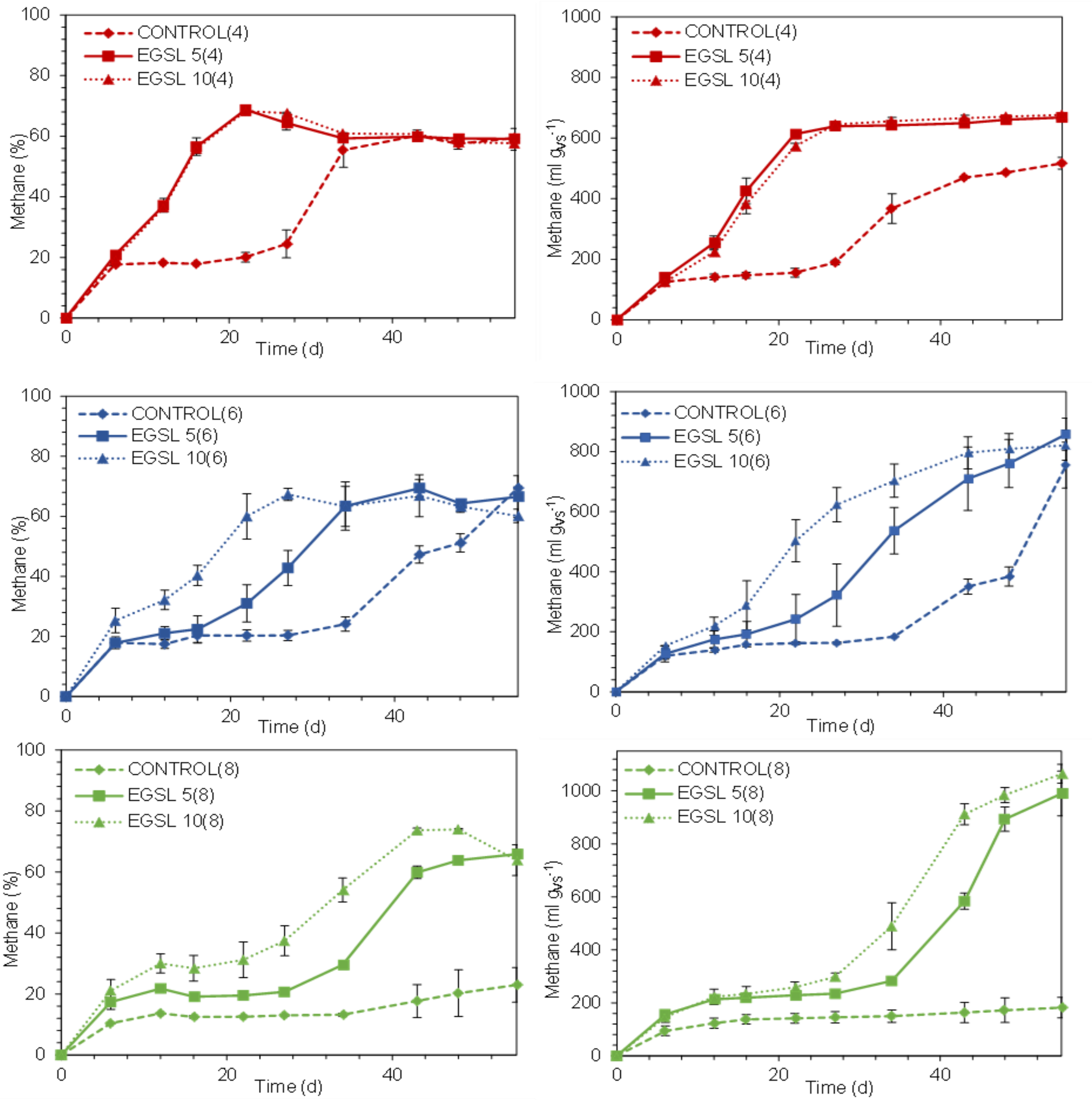


Figure 5-6. Anaerobic fermentations (AD-G) of glucose (G) substrate (4, 6, 8 g L^{-1}) with the addition of 5 and 10 g L^{-1} EGSL-TT in compared to each control (CONTROL; without the addition of EGSL-TT).

Chapter’s conclusions

The results highlighted that thermally treated eggshell addition in AD reactors (tested substrates were food waste, cellulose, and glucose) prevented the pH reduction due to high VFAs generation and resulted in substantially higher performance compared to the control. Soluble CO_2 had a higher adsorption affinity towards EGSL-TT than phosphates. If N_2 was used instead of CO_2, EGSL-TT showed high phosphate removal. Moreover, thermally treated eggshell constitutes an excellent biomaterial for phosphate recovery from anaerobic effluents. The high selectivity of EGSL-TT towards phosphate resulted in solid residue containing the necessary nutrients for agricultural applications. Phytotoxicity trials showed that the solid residue after phosphate recovery from anaerobic effluent positively affected plant growth.

6 Phosphate recovery from the effluent of a submerged anaerobic membrane bioreactor using columns of eggshell and seagrass residues

The combination of a submerged anaerobic membrane bioreactor (SAnMBR) and two biowaste adsorption columns (EGSL-TT and SG-TT) was investigated for the first time to assess the recovery of phosphates from wastewater. Low-strength wastewater relatively high in phosphate ion (reject wastewater from anaerobic sludge dewatering process) was fed into the SAnMBR and the COD results are presented below. Then, the effluent from anaerobic SAnMBR was continuously fed independently in two columns consisted of SG-TT and EGSL-TT residues. After adsorption, the solid end products were evaluated as soil conditioners. A fractionation analysis was also performed in order to practically define the different forms of phosphorus in each end product. The originality of this study resides in the recovery of phosphates from real wastewater using biowastes and in the creation of phosphorus-based products that can be directly applied as soil conditioners. Overall, this work aims to the development of new zero-waste technology for the treatment of wastewater after anaerobic process.

6.1 SAnMBR performance

Rejected wastewater from dewatering process was used as a feeding stream with an average COD and phosphates of 195.2 ± 15.6 and 23.5 ± 1.9 mg L^{-1}, respectively. Fig. 6-1 (A-D) depicts the inlet and outlet variation of COD, phosphates, pH and conductivity during the operational time of the SAnMBR. The pH value was relatively constant in the feed and effluent of the SAnMBR within a range of 7.2-8.3. The conductivity was close to 5 mS cm^{-1} for both influent and effluent wastewater. The soluble COD value was decreased gradually to relatively stable value of 97 mg L^{-1}. The anaerobic reactor coupled with a membrane system exhibited an instant decrease as indicated by a COD reduction of 50%, showing that SAnMBRs can also treat low strength wastewaters. The significantly lower final dissolved COD in the outlet stream of the AnMBR was attained due to the biodegradation of the wastewater's organic load, which was considered the main removal mechanism. Contrary to the high removal of organics in anaerobic reactors, from the results obtained, phosphate and ammonium were hardly removed, exhibiting low percentage efficiencies, 7 and 16%, respectively. This indicates that further treatment was needed to remove the phosphates if the effluent was to be reclaimed. As such, a two-column system was connected to the SAnMBR for the recovery of phosphates from the effluent.

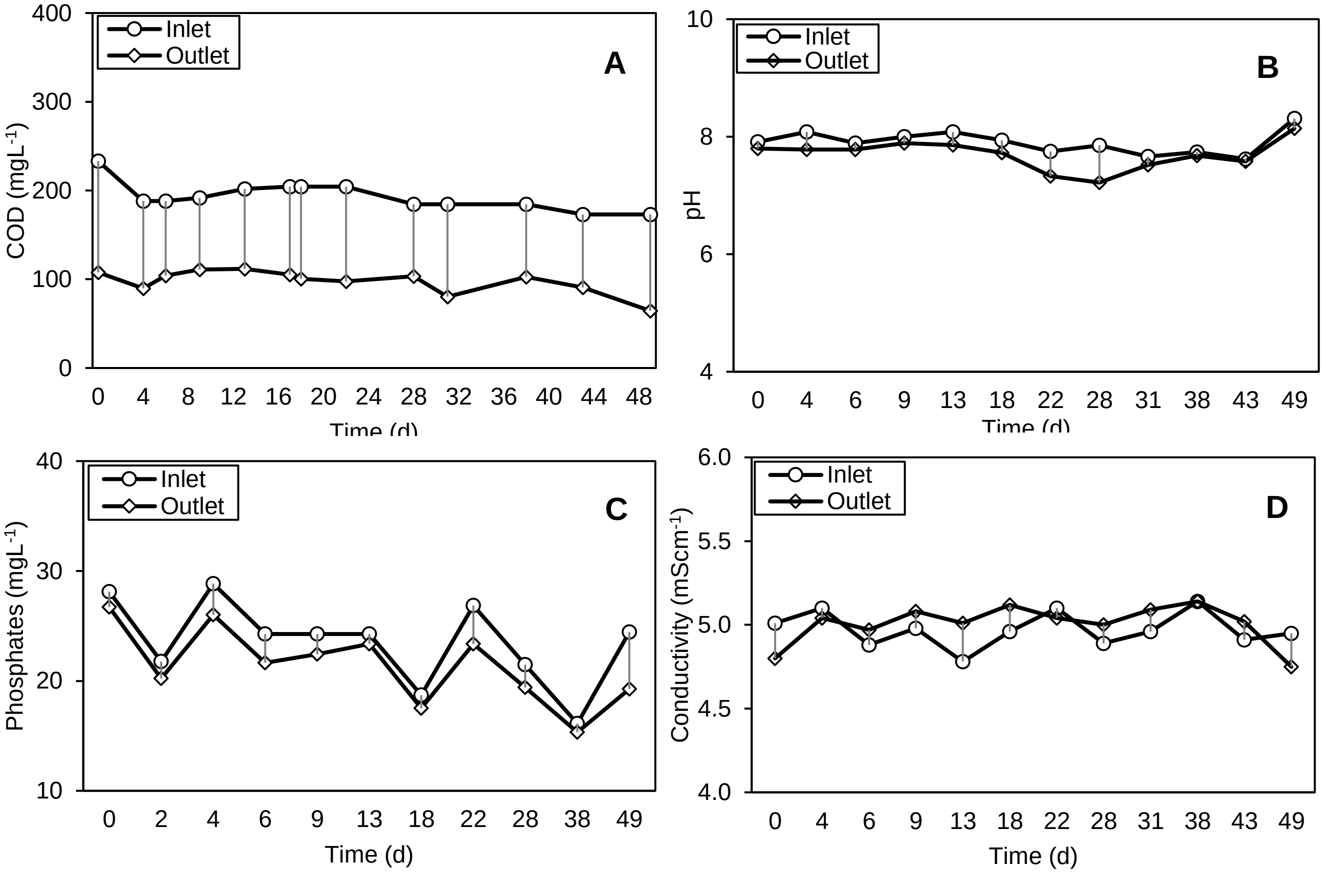


Figure 6-1. Variations of (A) COD, (B) pH, (C) phosphates and (D) conductivity in influent and effluent wastewater during the operational time of SAnMBR.

A series of processes are applied in an anaerobic reactor to produce biogas and the methane content varies depending on the composition of wastewater, the other constituents' concentration, as well as on the system's operating conditions. Reject wastewater had low organic load, which led to comparatively low production of methane (40%) compared to wastewater with higher organic loading rate (OLR) in shorter HRT. These conditions induced additional biomass multiplication and conversion of carbon to methane gas. Even so, the

SAnMBR biogas composition exhibited relatively stable performance under different HRTs, and this was evidence that the methanogenic activity was relatively consistent.

6.2 Column system performance

Following the operation of the SAnMBR system, the effluent wastewater was stored in a tank for the adsorption process. One-litre containers were filled with the SAnMBR effluent and then passed into both columns (EGSL and SG) using a feeding pump. The operational behaviour of the column system was finely explained by the phosphate concentration in both effluents. Fig. 6-2(A-D) depicts the EGSL and SG removal efficiency and concentration of phosphates in the EGSL and SG effluent at different flow rates (0.3-0.5 L d^{-1}). The removal efficiencies of EGSL and SG were above 94 - 99% and 74 - 95% for all the flow rates tested, respectively. It was observed that with the flow rate increasing to 0.5 L d^{-1}, both EGSL and SG phosphate removal was decreased and eventually the concentration of phosphates in both effluents was increased. High flow rates result to low residence time and high turbulence, which causes weak interactions between the adsorbate and the adsorbent. Contrastingly, low flow rates, ensure higher contact time and thus stronger adsorbate-adsorbent interaction. Ramirez et al., (2018) evaluated the hybrid adsorbent for phosphate recovery from a liquid solution with the use of a fixed bed column. In this study, different flow rates (1- 2.5 mL min^{-1}) were examined, and the best adsorption capacity was found at 1.0 mL min^{-1} flow rate. These results showed that high flow rates do not affect the adsorption capacity. In general, the increase in the flow rate loads more phosphate ions in the adsorbent in a shorter period. However, insufficient contact time of phosphate ions with the adsorbent can lead to faster withdrawal of these ions from the column system before establishing the adsorption stability.

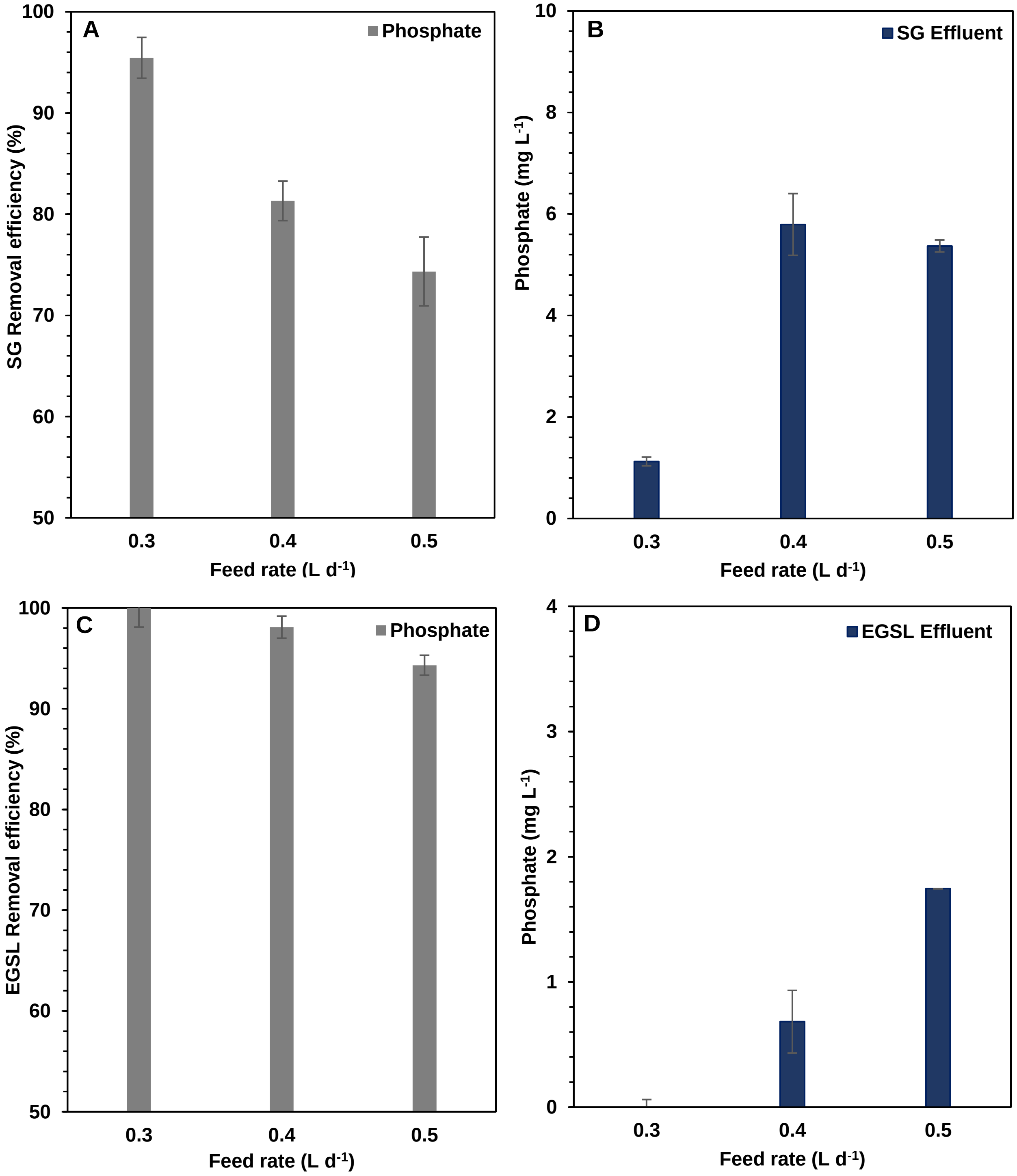


Figure 6-2. (A) SG removal efficiency (B) phosphate concentration in the SG effluent (C) EGSL removal efficiency (D) phosphate concentration in the EGS effluent at different flow rates (0.3-0.5 L d^{-1}) during the adsorption process.

The EGSL and SG effluents were also analyzed for COD, while the pH and conductivity were monitored during the process. Fig. 6-3(A) shows the COD content in the feeding and both effluents. The data obtained are similar for the two effluents indicating that EGSL and SG have low adsorption efficiency towards organic compounds. This can be confirmed from the UV-Vis spectrum illustrated in Fig. 6-3(C), where the absorbance of humic and fulvic-like compounds (at 330 nm) cannot be reduced after 24 h in-contact with the adsorption materials. Furthermore, Fig. 6-3(B, D) shows the pH and conductivity values through the adsorption process. As may be seen, the EGSL outlet has a higher pH value and lower conductivity levels in contrast to the feeding, probably due to its high content in alkali cations such as calcium.

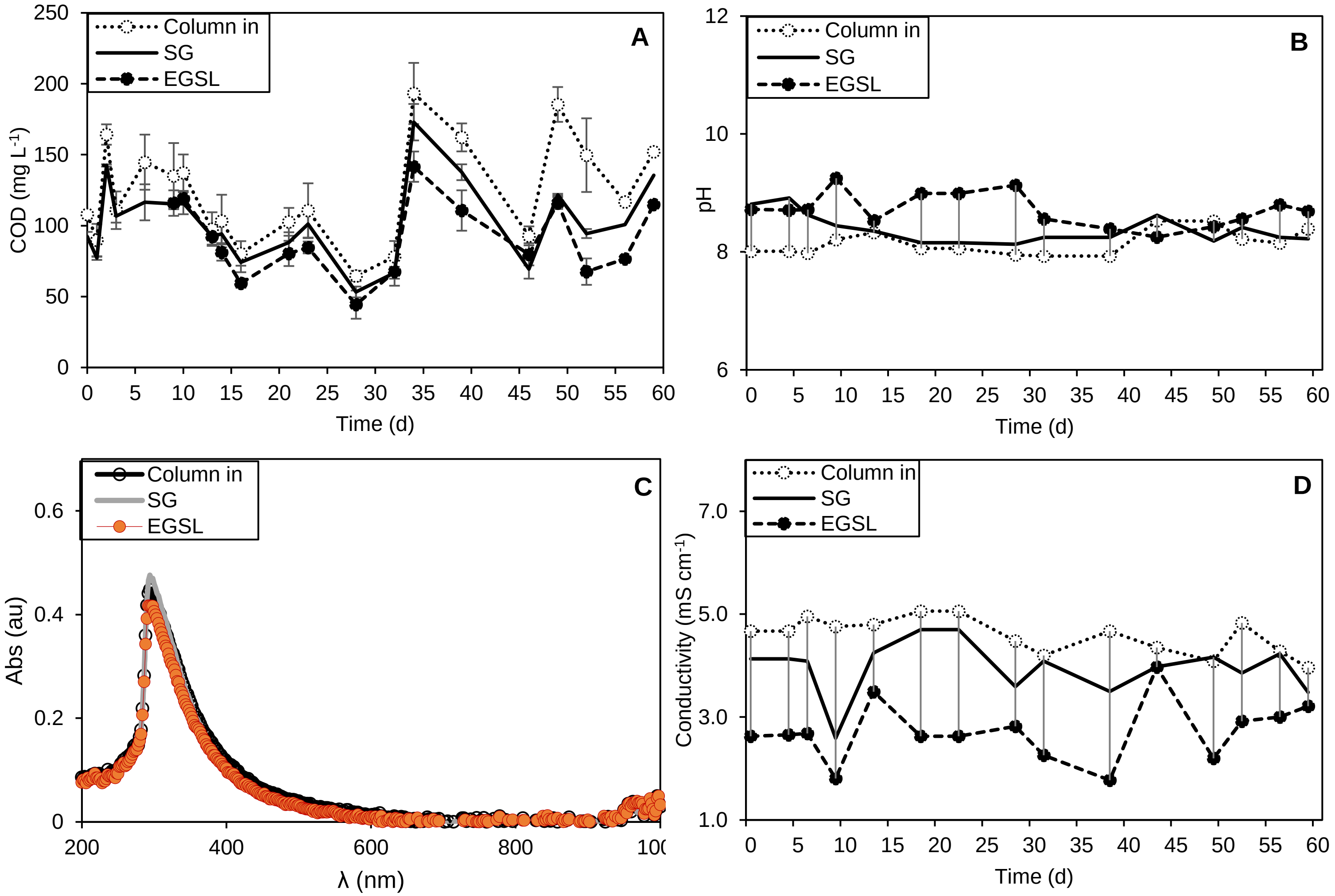


Figure 6-3. (A) COD variations (B) pH values (C) UV/Vis spectrum of organic compounds (D) conductivity values during the adsorption process for the feeding and both effluents (EGSL and SG).

The overall measurement results regarding the ammonium and phosphate concentration during the SAnMBR and column adsorption process of influents and effluents are summarized in Table S6-2 (see APPENDIX II). The data obtained indicate no significant reduction of the ammonium and phosphate concentration during the rejected wastewater treatment in SAnMBR. It is widely known that SAnMBRs can provide a low level of nutrient removal (Salazar-Peláez et al., 2011). Thus, an important implication of these findings is the need to incorporate more advanced processes to attain a degree of nutrients in the effluents in line with the legislation. As such, the column system was employed to treat SAnMBR effluent and more than 94% of phosphates could be removed through adsorption from both materials, with an effluent phosphate concentration of 0.1 - 1.3 mg L^{-1}. The removal of ammonium was lower, with an average of 16 – 25% for both adsorbents. Therefore, these results indicate that EGSL and SG residues have high selectivity regarding the phosphate ions and low efficiencies in adsorbing organic compounds and other ions.

6.3 Phytotoxicity assessment

The EGSL and SG end solid products after adsorption from SAnMBR anaerobic effluent were assessed by using the 5% w/w (g of EGSL or SG end product per g of compost) on *S. alba* and *L. sativum* seeds. Fig. 6-4(A-B) illustrates the root and shoot length (cm) and germination (%) as well as the calculated GI of germinated *S. alba* and *L. sativum* seeds after applying each end product. The results obtained, showed that the root and shoot length of the germinated *S. alba* and *L. sativum* seeds was increased in comparison to the control after the SG end product application. According to the diagram below, the root length was increased 35.7 and 6.4% for *S. alba* and *L. sativum* seeds, respectively. The shoot length was significantly improved with the addition of SG end product as soil conditioner, exhibiting 50.2 and 41.8% for *S. alba* and *L. sativum* seeds. Although the total length of both species was increased, the statistically significant difference in compared to the control was found in the *L. sativum* shoot and the *S. alba* root length. These findings match with the calculated GI (%) for the SG end product, which reached 138.5% when tested on *L. sativum* seeds and 182.9% on *S. alba* seeds. These data highlight the positive effect of SG end product on the plant as previously stated in the work of Photiou and Vyrides (2021).

The observations concerning the application of EGSL end product on *S. alba* and *L. sativum* seeds were of equal import as the aforementioned results. The seed germination and total length of the seeds were decreased compared to the controls, demonstrating low GI for both plants. Eggshells comprise mostly of calcium carbonate (94%). AP compounds (mainly $Ca_3(PO_4)_2$) are used in fertilizer manufacture as their main raw materials (Tan and Lagerkvist, 2011). However, Ca-associated AP phosphorus fertilizers consist slow-release phosphorus fertilizers in a long term due to their low solubility (Li et al., 2015). Assuming that, only a fragment of the presented apatite minerals in the parent material dissolves, resulting in low content of secondary phosphorus fractions. Hence, this could explain the poor germination of seeds in a 3-d period when EGSL end product was tested. More details regarding the fractionation of phosphorus in the end products can be found in Section 6.4.

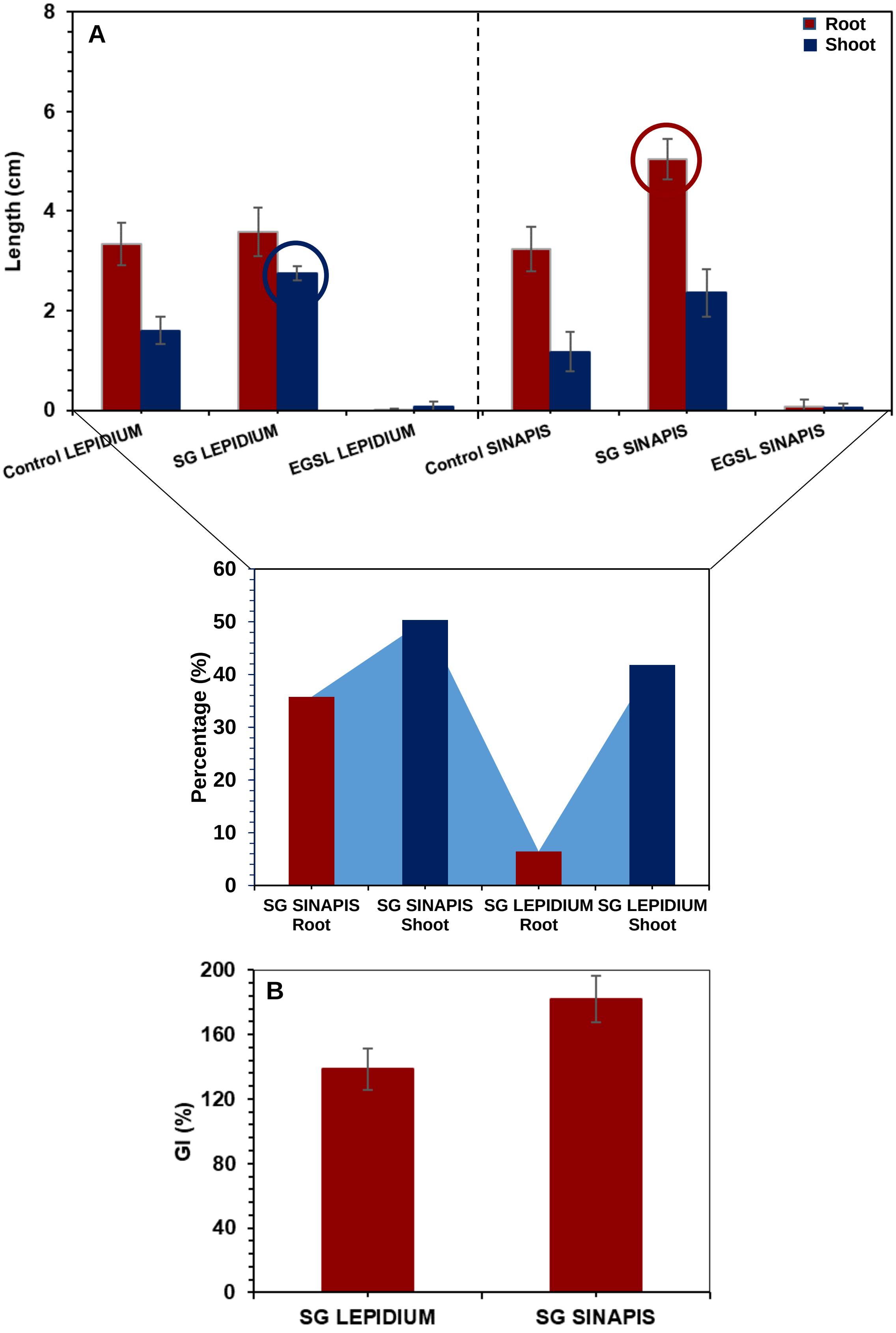

A
Root
Shoot
Length (cm)
0
2
4
6
8
Control LEPIDIUM
SG LEPIDIUM
EGSL LEPIDIUM
Control SINAPIS
SG SINAPIS
EGSL SINAPIS
Percentage (%)
0
10
20
30
40
50
60
SG SINAPIS Root
SG SINAPIS Shoot
SG LEPIDIUM Root
SG LEPIDIUM Shoot
B
GI (%)
0
40
80
120
160
200
SG LEPIDIUM
SG SINAPIS

Figure 6-4. Phytotoxicity trials on *S. alba* and *L. sativum* seeds after 3 d time period; (A) Shoot and root length (cm), shoot and root germination (%) in compared to the control and (B) Germination index (GI (%)) of SG and EGSL end products after adsorption using phosphate from SAnMBR effluent wastewater.

Among numerous nutrients, nitrogen and phosphorus are the most crucial nutrients for living organisms (Nidheesh et al., 2022). Wastewater consists of a valuable source of nutrients due to its high concentration and production rates. Hence, the nutrient recovery using biowastes and the creation of new products, contribute to a sustainable solution which combines the recovery of solid waste and the adequate purification of wastewater (Marcińczyk et al., 2022). Table 6-1 summarized the latest studies on nutrient removal (nitrates and phosphates) from both synthetic and wastewater solutions with the use of different biowaste. Interestingly, the removal efficiency of each material varies (25-98%) depending on the nutrient source. These findings highlight the need of using real wastewater as a nutrient source instead of synthetic solutions, which can provide data near the actual conditions that exist in industries. Furthermore, the main limitation of these studies is the conversion of nutrients into high-value products, which could be applied in agriculture. More specifically the majority of these studies (62.5%) have implemented desorption steps after the removal of phosphates or nitrates from the different solutions. Nevertheless, the studies focusing on the product's application found that depending on the adsorption material the end products can impose a positive effect on plant growth, resulting in the development of a zero-waste technology.

Table 6-1. Comparison between adsorption studies with the use of biowaste and final products a

Adsorbent	System	Adsorbent concentration (g L^{-1})	Nutrient source	Nutrient	Nutrient concentration (mg L^{-1})	Removal (%)	End products applications	Result	Ref.
Waste corn cobs	Batch	0.5	KNO_3	NO_3^-	20	49	Desorption	-	Kalaruban et al., (2016)
Fresh coconuts	Batch	0.5	KNO_3	NO_3^-	20	45	Desorption	-	Kalaruban et al., (2016)
Onion peel dust (OPD)	Batch	2	KNO_3	NO_3^-	100	79	Rice plant	Positive	Mondal et al., (2019)
Seagrass (SG) residues	Batch	20	Anaerobic wastewater	PO_4^{3-}	70.78	94	*Lepidium sativum* *Sinapis alba*	Positive	Photiou and Vyrides, (2021)
Seagrass (SG) residues	Batch	20	Leachate from dewatered sludge	PO_4^{3-}	821.9	98	*Lepidium sativum* *Sinapis alba*	Negative	Photiou and Vyrides, (2021)
Blue mussel (MSB) Oyster (OSB) shell	Batch	0.2	KH_2PO_4	PO_4^{3-}	20	>97	Desorption	-	Pap et al., (2022)
Blue mussel (MSB) Oyster (OSB) shell	Batch	0.2	Secondary wastewater	PO_4^{3-}	20	35-65	Desorption	-	Pap et al., (2022)
Hazelnut shells (HS)	Batch	10	KNO_3	NO_3^-	30	93	Desorption	-	Stjepanović et al., (2022)
Hazelnut shells (HS)	Batch	10	KNO_3	NO_3^-	30	54	Desorption	-	Stjepanović et al., (2022)
Hazelnut shells (HS)	Batch	10	Wastewater from the	NO_3^-	30	25	Desorption	-	Stjepanović et al., (2022)

			confectionery industry						
Hazelnut shells (HS)	Batch	10	Wastewater from the dairy industry	NO_3^-	30	27	Desorption	-	Stjepanović et al., (2022)
Calcined eggshell (CES)	Batch	1	Aquaculture wastewater	PO_4^{3-}	4.5	97	-	-	Tan et al., (2022)
Fir wood waste - seawater (SBC) powder	Batch	1	Aquaculture wastewater	PO_4^{3-}	1.82	95	Desorption	-	Zhang et al., (2022)
Fir wood waste - seawater (SBC) granule	Column	3.06	Aquaculture wastewater	PO_4^{3-}	1.82	73	Desorption	-	Zhang et al., (2022)
Eggshell (EGSL) residues	Column	68	Reject wastewater	PO_4^{3-}	29.68	>94	*Lepidium sativum* *Sinapis alba*	Negative	This study
Seagrass (SG) residues	Column	34	Reject wastewater	PO_4^{3-}	29.68	>74	*Lepidium sativum* *Sinapis alba*	Positive	This study

6.4 Phosphorus fractions in end products

The SMT protocol was applied to the end products after adsorption and the GS of the SAnMBR to determine the phosphorus species (TP, IP, OP, NAIP and AP) in the extracts. In theory, among the five phosphorus fractions, the following relationships exist: TP=OP+IP and IP=NAIP+AP. From the results obtained, it was obvious that IP was the major phosphorus fraction in EGSL and SG end products, accounting for 92.6 and 95.7% of TP, respectively. The percentage of the OP bound was relatively low (4.3-7.4%) for both samples in compared to the TP. The inorganically bound phosphorus consisted of 68.5% AP and 31.5% NAIP for SG end product. The same trend but with higher concentration of AP (87.4%) was found in the EGSL end product, while NAIP fraction accounted for 12.6%. AP dissolution depends on the pH and is considered a proton-consuming procedure (Brucker and Spohn, 2019) that can be applied as a slow-release P fertilizer (Li et al., 2015). Slow-release fertilizers contain nutrients in a form that is not immediately available to plants. Although the high proportions of AP in both end products can have many long-term benefits (uniform rate of plant growth, stronger root systems, less stress experience, better handling of disease and pest pressures), the high AP fraction (87.4%) in EGSL end product seems to require further time for the dissolution process, leading to low concentrations of potentially releasable and bioavailable phosphorus fractions. The remaining inorganic phosphorus was as NAIP fraction (mainly $AlPO_4$ and $FePO_4$), which consist of the most labile phosphorus formation. This fraction exhibits low bioavailability, resulting in limited applications as an industrial raw material or as a high-value fertilizer that can be utilized directly by plants (Pardo et al., 2004; Xie et al., 2011).

Higher differences between IP and OP fractions were found for the samples of GS from the SAnMBR in comparison to the end products, with the majority of phosphorus in GS being organically bound, accounting for 52.1%. The percentage of the IP was 48.4%, where 60.6% was NAIP fraction and 39.4% was AP minerals. Therefore, the NAIP and OP percentage fraction in GS was more than 81% of TP. He et al., (2016) studied the phosphorus (P) fractions in WAS and found similar results regarding the percentage of NAIP and OP, indicating that WAS can be used as a future substitution for phosphate rocks to recover phosphorus.

Chapter’s conclusions

SAnMBR effluent contains no solids and is bacteria-free; hence, it is an excellent source for resource recovery from this effluent. The SAnMBR low performance on phosphate removal suggests the need to incorporate processes for advanced treatment of the effluents. These findings indicate that feeding SAnMBR effluent high in phosphate to a column system consisting of SG-TT or eggshell residues can recover phosphate with high selectivity. The columns were operated in a continuous mode and the data obtained showed high phosphate recovery efficiencies from SAnMBR effluent (above 94 and 74% for EGSL and SG, respectively) for all the flow rates tested. Furthermore, the solid residues of EGSL and SG after adsorption showed opposite results probably due to the different fractionation of phosphates in the end products. More specifically, the SG end product imposed a positive effect on plant growth for *L. sativum* and *S. alba* seeds, while the EGSL end product negatively affected the germination of both seeds tested. Phosphorus fractionation of the end products after adsorption pointed out the majority of phosphorus was inorganically bounded. High proportions of AP require further time for the dissolution process. The fraction of AP minerals in the EGSL end product was higher (87.4%) compared to the SG end product, which indicates that the potentially releasable and bioavailable phosphorus fractions of the EGSL end product were at low concentrations leading to low germination of seeds. Overall, the results of this study suggest that the SG and EGSL could be effectively reclaimed as selective adsorbents towards phosphates in combination with a SAnMBR contributing to the development of a zero-waste technology.

7 SAnMBR followed by thermally treated biowaste and PAC adsorption processes for domestic wastewater treatment and resource recovery

The Chapter 7 aims to evaluate the performance of a SAnMBR system on treating domestic wastewater, which is a more common type of wastewater than rejected wastewater, for organic matter removal based on COD and the recovery of phosphates independently after the SAnMBR treatment with the use of SG-TT and EGSL-TT. Further COD removal from wastewater using PAC was also evaluated. A vast array of crucial parameters was measured throughout SAnMBR and followed adsorption reactors operations: PO_4^{3-}, NH_4^+, transmembrane pressure (TMP), phytotoxicity, pH, conductivity, gas composition and volume of biogas, volatile fatty acids, and VOC (by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS), which revealed the toxic organic compounds that can be removed during the treatment process. A fractionation analysis was finally performed to define the phosphate adsorption species in the solid products as well as a phytotoxicity test in the effluent.

7.1 SAnMBR treatment performance

The results depicted in Fig. 7-1(A-F) are evidence of the high-quality performance of the SAnMBR system. More specifically, Fig. 7-1(A) shows the methane production of SAnMBR for treating both synthetic and domestic wastewater. According to the latter figure, the SAnMBR treating synthetic and domestic wastewater exhibited 89.1 and 76.2%, respectively. Following the analysis of the feeding streams, synthetic solution had higher SCOD in contrast to the real domestic wastewater. Thus, these conditions led to increased biomass growth and the conversion of carbon to higher methane percentages. The COD removal profile during the operational time of the SAnMBR is shown in Fig. 7-1(B, F). SCOD removal for synthetic wastewater and TCOD removal of domestic wastewater were remarkable with average percentages of 82.3 and 87.8%, respectively. The COD removal efficiencies were high after the start-up process (Fig. 7-1(B)) and during the entire operational period an average effluent concentration of 58.9 ± 23 mg L^{-1} was obtained. These results were also confirmed by the turbidity of the samples before and after the treatment process (Fig. S7-3, APPENDIX III). MBR reactor is distinguished to produce high-quality effluent with low variability regardless the wide range of influent COD content of each wastewater. Huang et al., (2020) studied the treatment of real petrochemical wastewater (PW) with the use of an MBR and attained high removal efficiency (> 80%), which points out the extended applicability of such technology. The change in TMP was also monitored during the 61-d experiments. It is evident that during the treatment of synthetic wastewater, the HRT was stable at 36 h, which is in line with the TMP data. However, the HRT decrease to 24 h during the treatment of domestic wastewater (Phase III), resulted to an immediate increase of the TMP of the SAnMBR system (Figure 7-1(E)).

Nutrients recovery was lower regarding the phosphate and ammonium ions. The average phosphate removal for both wastewaters were ranged from 10.9 – 13.5%, while ammonium concentration of SAnMBR inlet and outlet streams were almost similar (Fig. 7-1(C, D)). During the anaerobic digestion of both wastewaters, a small increase of ammonium anions content (8.9%) was observed in the SAnMBR compared with influent, which was probably caused due to the ammonisation of the organically bound nitrogen. However, the cooperation of the SAnMBR system with adsorption reactors is mandatory to attain a high effluent quality, which is in line with the regulations regarding the nutrients' discharge limits.

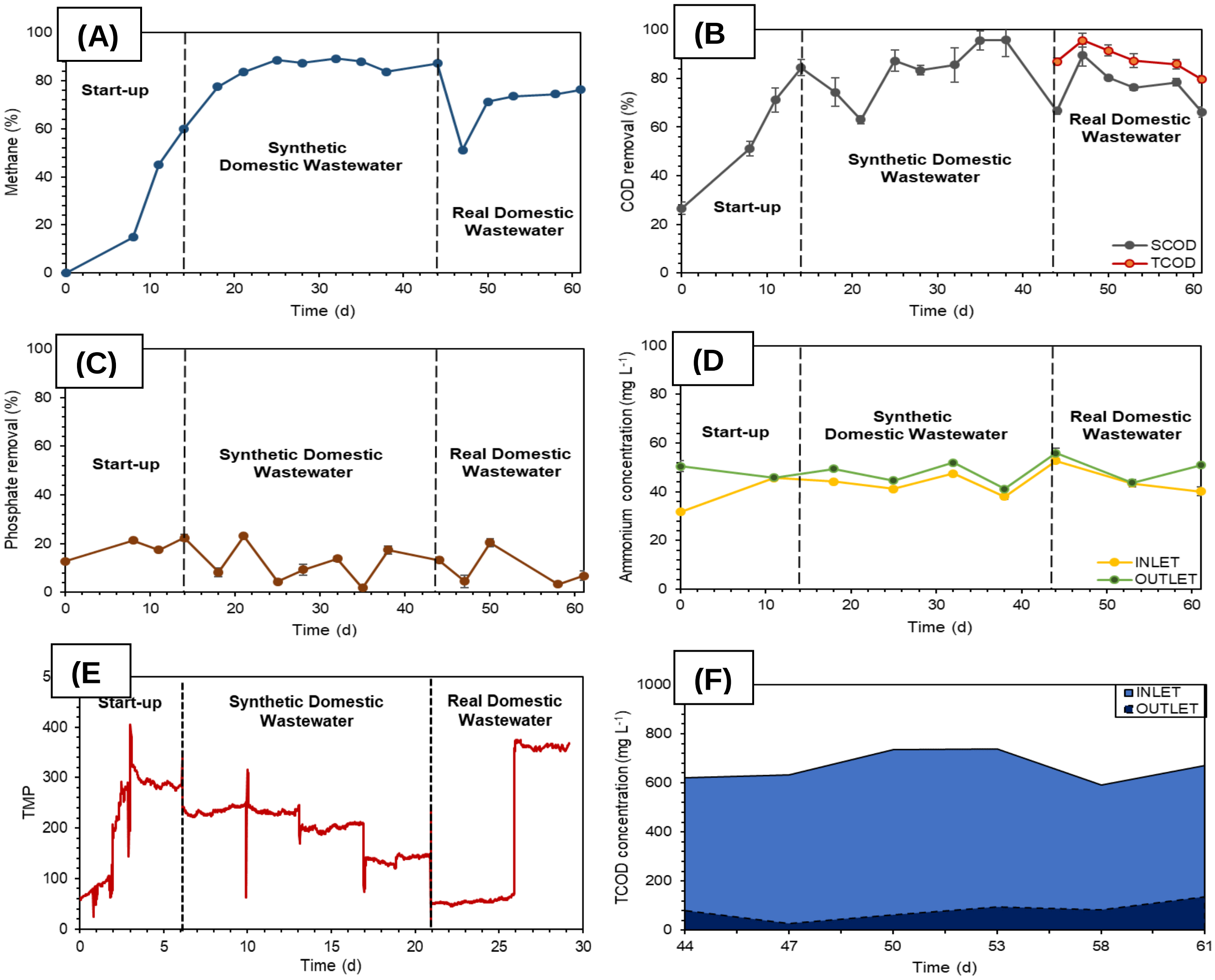


Figure 7-1(A-F). SAnMBR performance and monitor during the anaerobic treatment of synthetic (Phase I and II) and domestic wastewater (Phase III) (Parameters monitor; (A) Methane production (%), (B) COD removal (%), (C) Phosphate removal (%), (D) Ammonium removal (mg L^{-1}), (E) TMP changes, and (F) TCOD concentration (mg L^{-1}) of inlet and outlet during the treatment of domestic wastewater (Phase III)).

7.2 Adsorption reactors performance

The effluent from a SAnMBR treating synthetic and domestic wastewater were fed into reactors with thermally treated materials (EGSL and SG) in order to evaluate the use of biowaste as a post-treatment technique. To the author's knowledge, this is the first attempt to test the SAnMBR effluents for further treatment with biowaste materials. Fig. 7-2 depicts the phosphate removal from the EGSL and SG reactors at different flow rates, after the SAnMBR process treating (A) synthetic and (B) domestic wastewater. From the results obtained, the recovery of phosphates for both wastewaters tested were significantly high at lower flow rates. More specifically, the recovery percentage ranged from 71.8 - 99.9% and 60.5 - 78.0% for EGSL and SG, respectively. However, when the flow rate increased, the recovery efficiency of phosphate diminished as expected due to the short contact time of ions with the active sides of the materials. Ammonium ions were also present in both wastewater effluents due to the poor performance of the SAnMBR nutrients' removal (Fig. 7-3). Adsorption reactors consisting of EGSL and SG could further remove ammonium and COD from both wastewaters, only up to 2.0 - 4.9% and 13.0 - 21.0%, respectively, which points out the high selectivity of those materials towards phosphates. The same results were observed concerning the adsorption of ammonium and phosphate ions from PAC_A and PAC_B, which achieved a further removal within the range of 8.6 - 11.8%, respectively. In the study of Ruiz-Martinez et al., (2012), microalgae were applied to treat AnMBR effluent for phosphorus and ammonium removal. The results depicted that microalgae are capable of removing up to 98.0% of the phosphates and 67.2% of the ammonium ions, attaining a high-quality effluent.

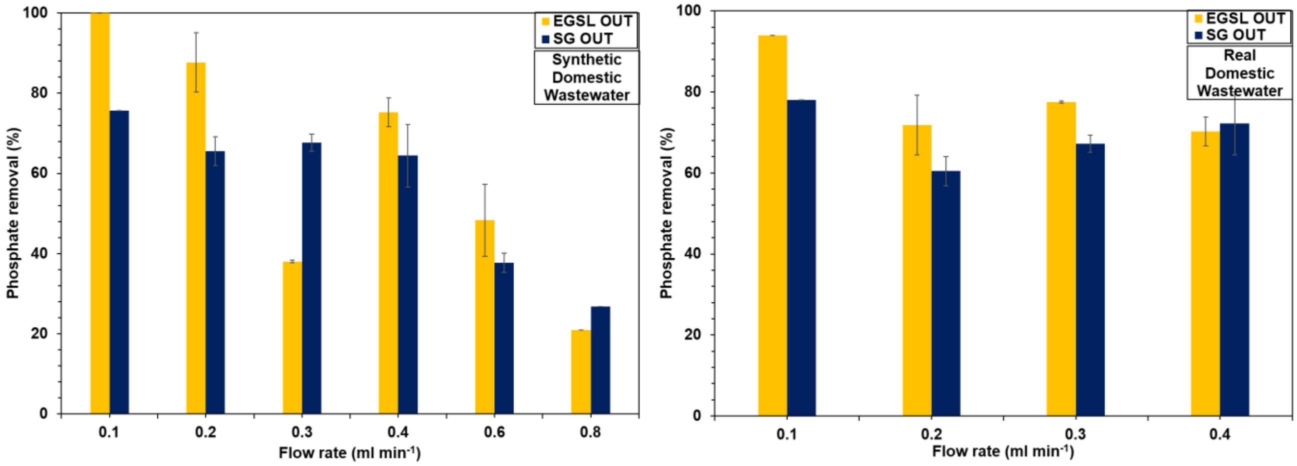


Figure 7-2(A-B). Phosphate removal (%) during the anaerobic treatment of (A) synthetic (Phase II) and (B) domestic wastewater (Phase III) in the SAnMBR at different flow rates.

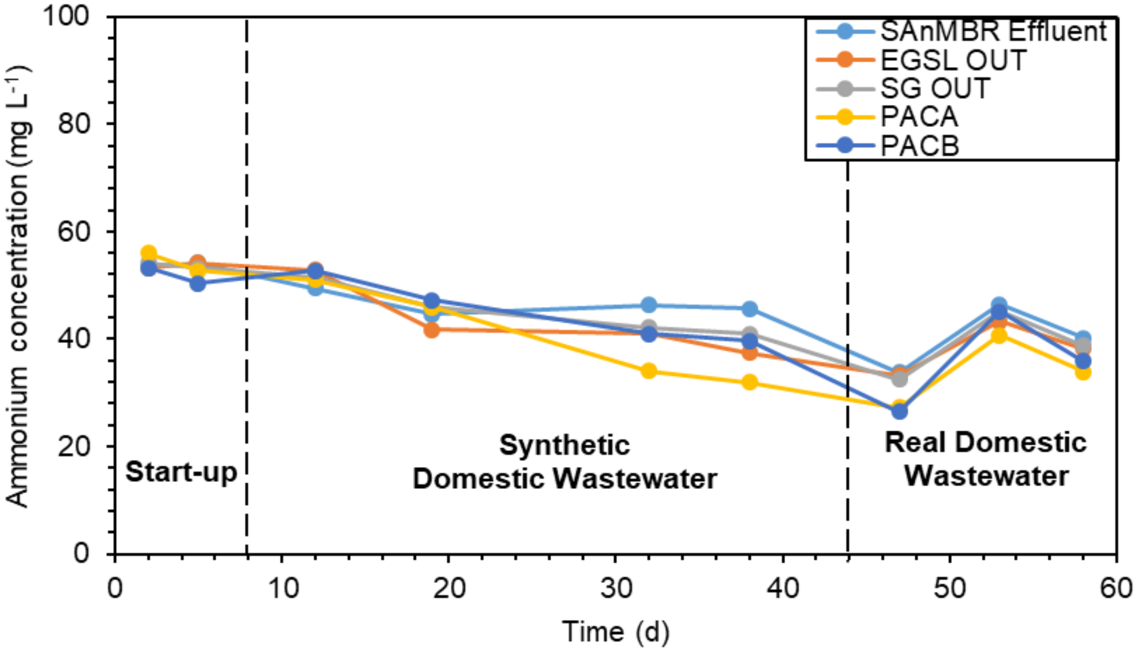


Figure 7-3. Ammonium concentration (mg L^{-1}) during the anaerobic treatment of synthetic (Phase II) and domestic wastewater (Phase III) in the SAnMBR for the: (1) synthetic/domestic effluent (2) eggshell effluent, (3) seagrass effluent and (4) effluent after PAC$_A$, and (5) effluent after PAC$_B$.

Fig. 7-4 presents the soluble COD concentrations during the anaerobic treatment of (A) synthetic (Phase II) and (B) domestic wastewater (Phase III) in the SAnMBR for the: (1) synthetic/domestic effluent (2) eggshell effluent, (3) seagrass effluent and (4) effluent after PAC_A, and (5) effluent after PAC_B. According to the respective figure, the incorporation of PAC seems to further improve the removal efficiency of COD, which was high after the start-up process (Fig. 7-4). During the entire operational period, an average COD effluent concentration of 20.2 ± 5.2 and 57.0 ± 13.3 mg L^{-1} was obtained after the PAC treatment of SAnMBR real domestic and synthetic domestic wastewater, respectively, which was far below the discharge limit (125 mg L^{-1}) enforced by the European legislation (91/271/EEC) on urban wastewater. More specifically, in Cyprus, a discharge limit below 70 mg L^{-1} is permissible for the recycled water to be used for irrigation purposes for specific crops. Overall, the applied PAC attained an additional removal of 60.5-78.3% of COD in both wastewaters, while the whole process reached a removal efficiency of 89.6 and 94.1% for domestic and synthetic wastewater, respectively.

VFAs are also rapidly produced during the anaerobic digestion of organic substrates at the acidogenesis and acetogenesis stages (Waqas et al., 2018). Fig. 7-5(A-B) presents the VFAs concentration after SAnMBR treatment in the two different systems at two-time points (day 21 for synthetic and on day 54 for real domestic wastewater). On day 21, the SAnMBR effluent was 239 mg L^{-1} and was reduced by around 36% and 58% when it was passed through EGSL and SG adsorption reactors, respectively (Fig. 7-5(A-B)). Then, the effluents from EGSL and SG reactors passed through PAC reactors, and the VFAs were further reduced by around 85 and 55 %, respectively. On day 54, the effluent from SAMBR treating real domestic wastewater was 35.5 mg L^{-1}, mainly propionic acid. The EGSL adsorption reactor had higher performance than the SG adsorption reactor (Fig. 7-5(B)) when exposed to SAMBR effluent. However, when the effluents from EGSL and SG passed through PAC reactors, the final effluent for both systems was 17.5 mg L^{-1}. Overall, the system of EGSL-PAC and SG-PAC showed VFAs removal around 50-90% and 50-71%, respectively. The high solubility in water (polar compounds), such as VFAs and low molecular organic compounds, makes them less adsorbable to PAC than higher molecular organic compounds (Vyrides et al. 2010).

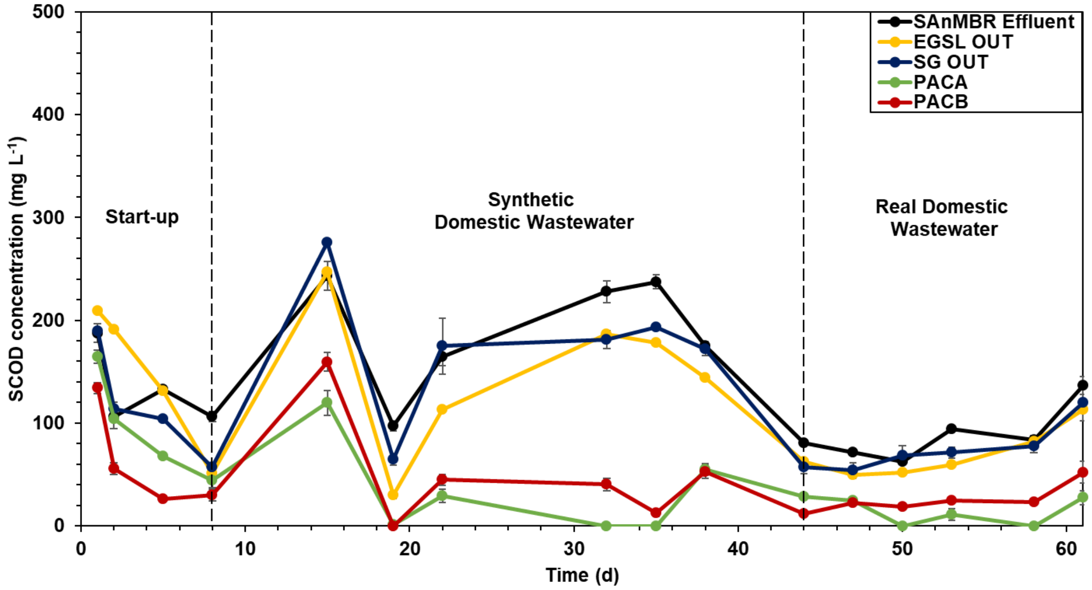


Figure 7-4. Soluble COD concentration (mg L^{-1}) during the anaerobic treatment of (A) synthetic for Phase I and II, and (B) domestic wastewater for Phase III in the SAnMBR for the: (1) synthetic/domestic effluent (2) eggshell effluent, (3) seagrass effluent and (4) effluent after PAC$_A$, and (5) effluent after PAC$_B$.

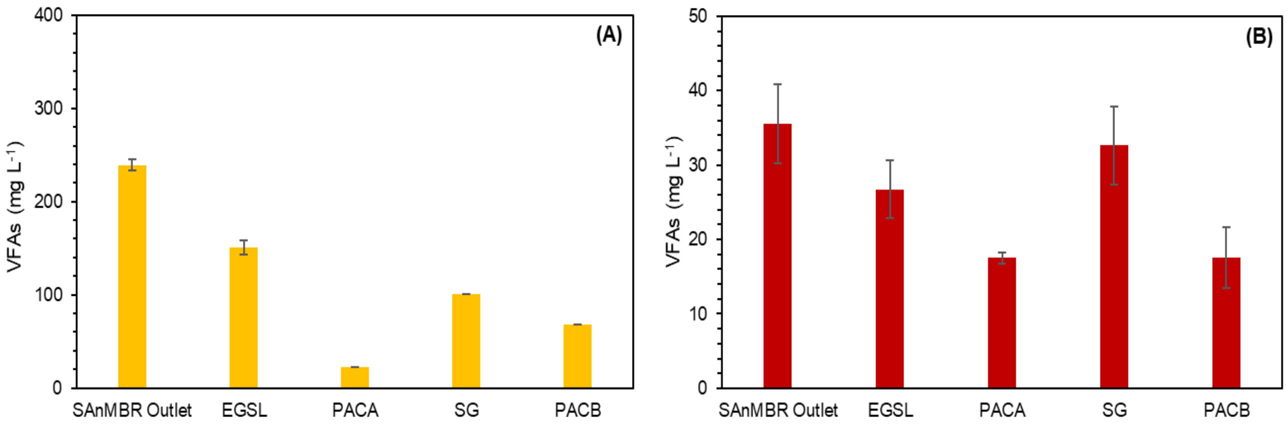


Figure 7-5. VFAs concentration (mg L^{-1}) during the anaerobic treatment of (A) synthetic (Phase II) and (B) domestic wastewater (Phase III) in the SAnMBR for the: (1) synthetic/domestic effluent (2) eggshell effluent, (3) seagrass effluent and (4) effluent after PAC$_A$, and (5) effluent after PAC$_B$.

7.3 Phytotoxicity assessment

Effective utilization of the liquid fraction remained after the phosphate adsorption process from the SAnMBR domestic effluent towards the growth and development of *Sinapis alba* and *Lepidium sativum* seeds are demonstrated in Fig. 7-6. After the adsorption process using EGSL, SG residues, and PAC, both effluents were mixed and evaluated, in contrast with SAnMBR samples before the adsorption treatment, for their potential toxicity on plant seeds. The results revealed that the SAnMBR outlet and the mixed effluent after the PAC treatment were significantly better regarding the *Sinapis alba* seeds, in compared to the untreated real domestic wastewater (inlet). The increase of the *Sinapis alba* growth was statistically proved. Similar results were observed on *Lepidium sativum* seeds when the PAC effluent was tested. However, the SAnMBR effluent treating domestic wastewater negatively affected the growth of seeds, exhibiting mild inhibition. Saddoud et al., 2007 studied the effect of AnMBR effluent produced after treating municipal wastewater on *Lepidium sativum* seeds. The calculated GI value was up to 87%, which considered non-phytotoxic on plant growth. In another study by Ravindran et al., (2016), treated wastewater from different domestic wastewater plants was evaluated for its phytotoxicity effect on selected crops. The results of this work were similar, indicating that SAnMBR treating domestic wastewater imposed positive effect on each crop with GI values above 80%.

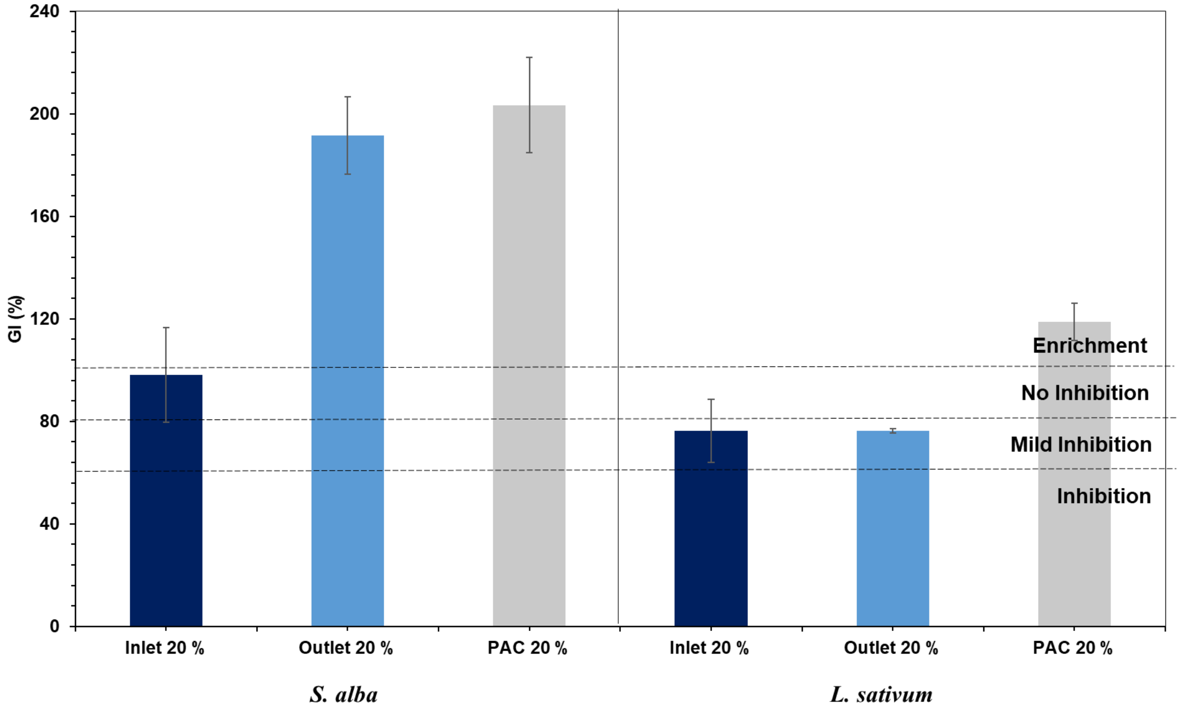


Figure 7-6. Phytotoxicity trials on *Sinapis alba* and *Lepidium sativum* seeds after a 3-d time period; Germination index (GI (%)) of 20% (v/v) diluted SAnMBR inlet and outlet, and effluent after PAC adsorption.

7.4 Phosphorus fractionation of the P-riched solid products

The solid fraction after adsorption from synthetic and domestic wastewater solutions were examined to determine the phosphorus species (TP, OP, IP, AP, NAIP) in the extracts. Phosphorus fractionation of solid products provides special benefits for comprehending the phosphorus path while the system's processes are being applied. According to the analysis of both solid products after the adsorption of synthetic and domestic SAnMBR effluents, the majority of the phosphorus was attained as an inorganically bound fraction, accounting for a range of 77.3 - 95.3% of the TP (Table 7-1).

Table 7-1. Phosphorus fractionation of the solid end products

Phosphate source	Synthetic wastewater		Domestic wastewater	
Products fractionation (%)	EGSL solid	SG solid	EGSL solid	SG solid
OP*	6.29	4.66	5.96	22.62
IP*	93.70	95.34	94.04	77.38
AP*	56.00	64.25	69.55	68.89
NAIP)*	44.00	35.75	30.45	31.11

* The following relationships exist: TP=OP+IP and IP=NAIP+AP

The elevated IP percentage confirms the high phosphorus' mobility and bioavailability in the final products (Huang et al., 2017). The OP percentage was relatively low for the EGSL solid products after phosphates adsorption from both wastewater effluents (6.0 - 6.3%) in compared to the TP fraction. However, a higher OP percentage was observed in the SG end product after the adsorption of the SAnMBR effluent treating domestic wastewater, which was accounted for 22.6% of the TP. The AP and NAIP fractions were similar for all the samples analysed and were consisted of 56.0 - 69.6% AP and 30.5 - 44.0% NAIP, respectively. Lee et al. (2022) studied the removal of phosphates from water using Ca-rich organic waste and analyzed the final product to determine the fractions of phosphorus. Their study identified inorganically bound phosphorus as the major fraction in the sediments, which is consistent with the results obtained in our study.

7.5 VOCs removal by the overall treatment

The degree of volatilization and biodegradation, as well as the mobility of compounds are influenced by the amount of VOCs adsorption on organic materials. The adsorption process can improve biodegradation through the reduction of toxic and non-biodegradable compounds from the solutions (Weber and Jones, 1986). Figure 7-7 shows the total VOCs content over time for five samples withdrawn during the process: (1) domestic wastewater inlet, (2) sample from SAnMBR, (3) SAnMBR effluent, (4) PAC_A effluent and (5) PAC_B effluent. The synthesis of domestic wastewater inlet included alcohols, sulfides, hydrocarbons, terpenes, phenols, aldehydes, amines, acids, ketones, esters, and others. The list of all detected wastewater VOCs is presented in Table S7-3 (APPENDIX III). According to Fig. 7-7, the normalized area of the total VOCs (Total Ai/Ais) was significantly decreased from the very first steps of the process. More specifically, the samples from the SAnMBR revealed a reduction of 45.5%, which was further reduced in the SAnMBR effluent by 3.7%. However, a small increase of the VOCs was observed while the SAnMBR effluent was passing through the PAC reactors. Najm et al., (1990) found that the rate of adsorption and PAC capacity are markedly reduced when humic substances are present in the water as a result of competition, which could probably explain the increase of VOCs after PAC treatment. Although the trend of total VOCs seems almost unaffected among PAC_A and PAC_B effluents, it appears that different chemical classes contribute to each case. In PAC_A effluent, an increase in hydrocarbons, acids, and aldehydes was observed, whereas in PAC_B a high decrease in aldehydes was noticed.

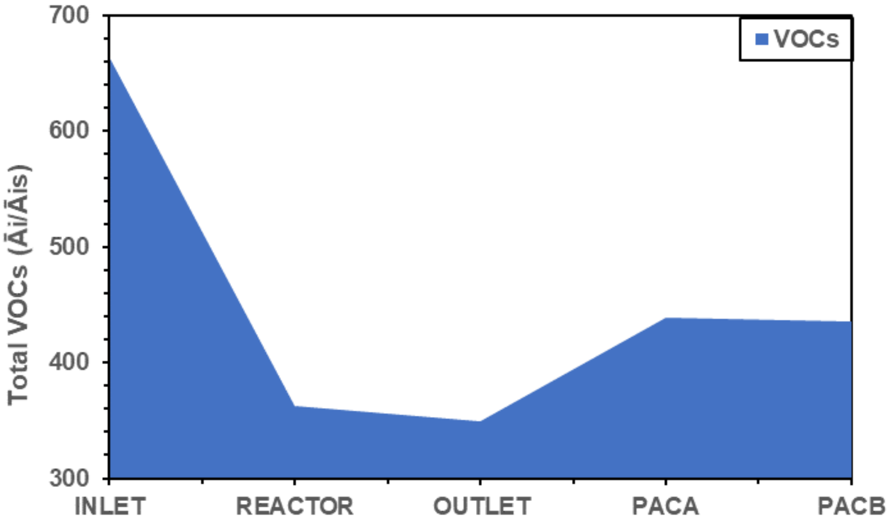
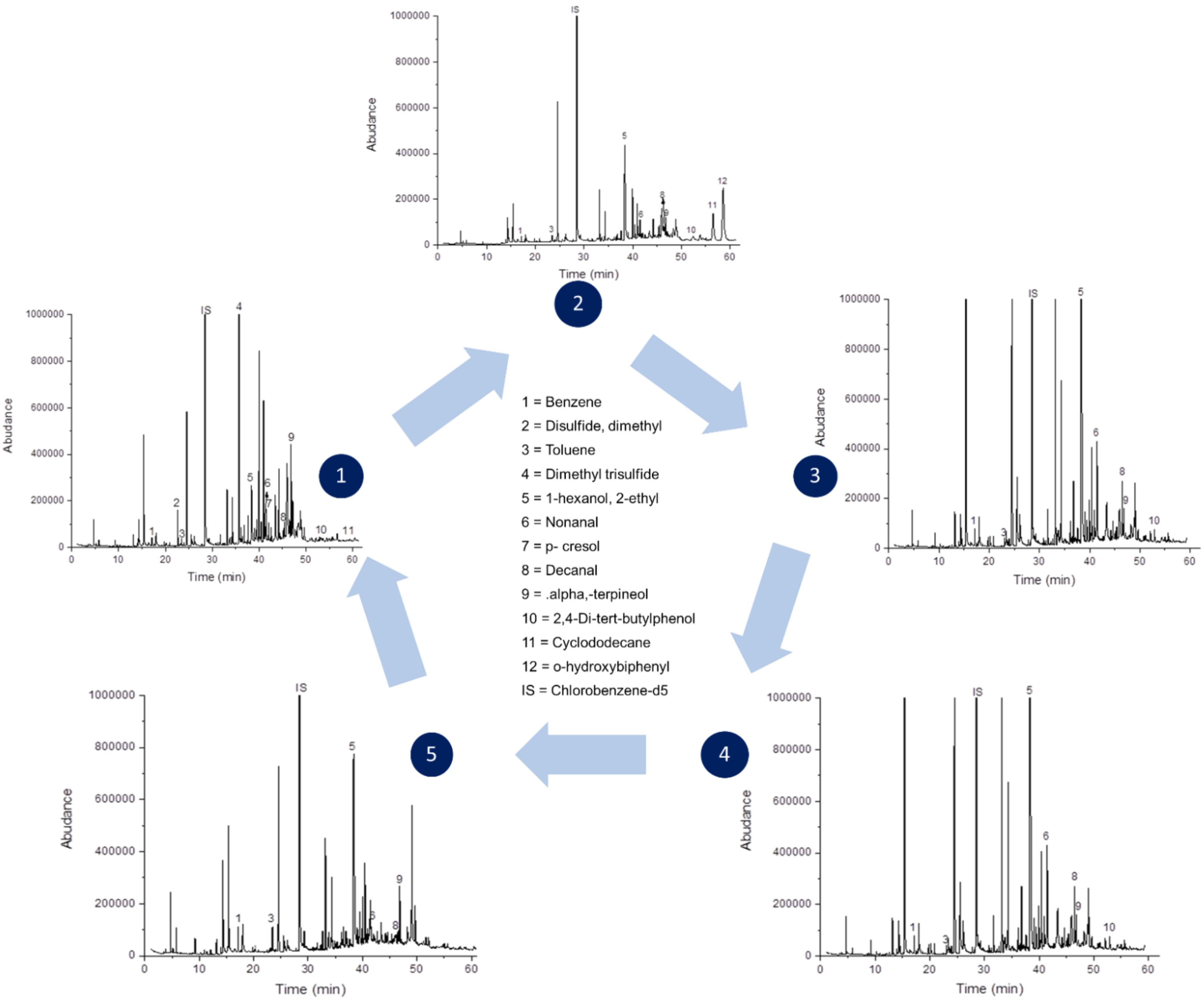


Figure 7-7. VOCs total area during the five procedure steps: (1) domestic wastewater inlet, (2) sample from SAnMBR, (3) SAnMBR effluent, (4) PAC_A effluent and (5) PAC_B effluent.

The most frequently detected compounds in the samples were benzene, toluene, nonanal, decanal, 2-ethylhexanol, alpha-terpineol, eucalyptol, phenol, p-cresol, o-hydroxybiphenyl, 2,4-Di-tert-butylphenol, cyclododecane, and the reduced organic sulfides of dimethyl disulfide and dimethyl trisulfide, which are considered known wastewater contaminants (Fig. 7-8). Volatile sulfide compounds (VSCs) are among the most frequently detected VOCs in wastewater and are characterized for their characteristic bad odours, even at low concentrations. Dimethyl trisulfide and dimethyl disulfide derive from food production and various wastes, due to the microbial decomposition of sulfur-containing organic matter (Sun et al., 2023). Although these compounds are usually detected abundantly than other VOCs in the domestic wastewater, as depicted in the TD-GC-MS chromatograms (Figure 7-8, marked as compounds 2 and 4), they were eliminated at the beginning of the process. Phenol and its alkyl-derivatives are moderately water-soluble pollutants, common to the wastewaters of various industries (oil and gas industry, paint manufacturing, pharmaceutical industries, etc.) (Selvasembian et al., 2022). They consist of hazardous compounds (e.g., o-hydroxybiphenyl, and 2,4-Di-tert-butylphenol) and after the SAnMBR treatment, the removal of such compounds was more than 56%. Among the most notable identified micropollutants was 2,4-Di-tert-butylphenol (2,4-DTBP), a common toxic secondary metabolite produced by various groups of organisms that is considered highly toxic and poor biodegradable (Feng et al., 2023). Moreover, the presence of diethyl phthalate (DEP) in the examined wastewater inlet is of high concern due to phthalates hazardous nature and industrial origin; therefore, their fate is under the microscope of researchers (Dargnat et al., 2009). An interesting chemical class usually present in wastewater is that of terpenes such as eucalyptol, camphor, linalool, levomenthol, and menthone that are originated from the numerous body care and cosmetic products (Lebedev et al., 2022). Also, the C_4-C_{10} aldehydes were all present in the wastewater, next to benzaldehyde (harmful to aquatic organisms). Decanal and nonanal are long chained aldehydes and their presence are likely due to cyanobacteria activity in wastewaters (Godayol et al., 2013). According to the TD-GC-MS analysis, both compounds were rapidly eliminated (>70%) during the process. On the other hand, 2-ethylhexanol shows a low solubility in water and a high octanol-water distribution coefficient, which enables to absorb on wastewater particle organic materials and end up in sludge. Considering this, the high values of 1-hexanol-2-ethyl can be justified due to the low biodegradation in the anaerobic digestion systems (Stamatelatou et al., 2011). Benzene and toluene were also detected at low levels in wastewater but remained constant through the whole process. Finally, the presence of coal and bitumen industries leads to the detection of multi-ringed thiophenes in wastewater samples (Lee and Brimblecombe, 2016).



1 = Benzene
2 = Disulfide, dimethyl
3 = Toluene
4 = Dimethyl trisulfide
5 = 1-hexanol, 2-ethyl
6 = Nonanal
7 = p- cresol
8 = Decanal
9 = .alpha,-terpineol
10 = 2,4-Di-tert-butylphenol
11 = Cyclododecane
12 = o-hydroxybiphenyl
IS = Chlorobenzene-d5

Figure 7-8. Indicative TD-GC-MS chromatograms of VOCs determined during the five procedure steps: (1) domestic wastewater inlet, sample from (2) SAnMBR, (3) SAnMBR effluent, (4) PAC_A effluent, and (5) PAC_B effluent.

7.6 Discussion

Domestic wastewater is the most prevalent type of wastewater worldwide, and conventional activated sludge processes are widely used for its treatment. However, this method has several challenges, including high-energy costs, significant waste sludge output, and substantial environmental impact. As an alternative, anaerobic treatment of domestic wastewater has been proposed. Studies (Robles et al., 2020, Ji et al., 2021) have shown that anaerobic digestion can effectively treat domestic wastewater, reaching up to 87% biodegradability and achieving COD effluent concentrations below discharge limits. Ji et al., (2021) used SAnMBR to treat real domestic wastewater. The process performance was evaluated by organic removal efficiency and biogas production, achieving 89% and 80% yield, respectively. An important implication of these studies is that MBR technology can be used for the treatment of real wastewater as efficiently as the conventional wastewater process.

Although numerous studies made significant steps towards the enhancement of wastewater anaerobic treatment solutions, very few address the treatment process to recover resources in addition to purifying various types of wastewater. Table 7-2 points out literature studies that used anaerobic treatment for domestic/municipal wastewater followed by a nutrient recovery process. The studies by Mavinic et al., (2007) and Huang et al., (2015) reported the anaerobic treatment of domestic wastewater followed by chemical precipitation for phosphate recovery. Lim et al., (2019) treated an anaerobic effluent for phosphorus, sulfides and ammonia recovery. Additionally, the studies that maintain to remove nutrients from the effluent after the anaerobic digestion of real wastewater, fail to properly recover and further evaluate the possible applications of nutritional products.

This study builds upon previous research on phosphate recovery from SAnMBR effluent using rejected wastewater generated during the dewatering of anaerobic sludge from UWTPs using biowaste columns (Photiou et al. 2023). The previous study (Photiou et al.

2023) faced challenges such as low biogas production, low volume of effluent fed into the column system, COD concentration exceeding discharge limits, and differences in phytotoxicity of the materials tested. The current study uses synthetic and real domestic wastewater with high organic content and higher volumes as feedstock, resulting in higher biogas production. To address excess COD content remaining after the biowastes adsorption system, PAC reactors were used, which resulted in final COD concentrations below the discharge limits. The liquid remaining after the process was evaluated for phytotoxicity, and high growth index percentages indicated that the treated wastewater could be used for irrigation purposes. The study takes a more holistic approach to wastewater treatment with a focus also on organic content and VOC reduction, biogas production, and phytotoxicity evaluation of the effluent.

In more detail the present work utilised thermally treated biowaste, which also consists of wastes, for the phosphate ions and PAC as adsorbent for further COD removal. The originality of this approach lies in the fact that the effluent obtained consists of high-quality water for re-use with pollutants content below the regulation’s discharge limits. The final products after adsorption using thermally treated biowaste can substantially be used as soil conditioners, leading to a holistic wastewater treatment with a zero-waste approach under the concept of the circular economy. In addition, the final products after adsorption that contained high concentration of inorganically bound phosphate can be used as a feedstock in the fertilized industry. The main recovery products of the tested system are a) treated wastewater that can be utilized for irrigation, b) biogas, and c) solid product high in inorganically bound phosphate. The system also contributed to the significant reduction of VOCs.

Table 7-2 Literature review regarding the anaerobic treatment of different types of domestic/municipal wastewater

#	Wastewater	Anaerobic treatment	Anaerobic effluent content (mg L^{-1})	Recover nutrient-Method	Final removal (%)	Reference
1	Anaerobic digestion supernatant	AD bioreactor	PO_4^{3-}: 84.0-133.0 NH_4^+: 989.0-1050.0	Phosphates-chemical precipitation	PO_4^{3-}: 90.0	Mavinic et al., (2007)
2	Anaerobic digestion supernatant	AD bioreactor	PO_4^{3-}: 211.0 NH_4^+: 389.0 COD: 308.0	Phosphates-chemical precipitation	PO_4^{3-}: 96.0	Huang et al., (2015)
3	Synthetic feed	Anaerobic Membrane Bioreactor	COD: 9.0-238.0	COD, phenols, nitrogen compounds-PAC	COD: 90.0	Mai et al., (2018)
4	Real domestic wastewater	Anaerobic Membrane Bioreactor	SO_4^-: 24.0 PO_4^{3-}: 4.2 NH_4^+: 0.05 COD: 71.0	Sulfide and phosphorus-coagulation, flocculation, sedimentation	COD: 88.0 PO_4^{3-}: 94.0	Lim et al., (2019)
	Real domestic wastewater			Ammonia-coagulation, flocculation, sedimentation, clinoptilolite ion-exchange column	NH_4^+: 99.5	Lim et al., (2019)
5	Municipal wastewater	SAnMBR	PO_4^{3-}: 5.1-10.5 NH_4^+: 20.0	Nitrogen and phosphorus- a mixed micro algal culture system	PO_4^{3-}: 97.8 NH_4^+: 67.2	Ruiz-Martinez et al. (2012)
6	Synthetic and Real domestic wastewater	SAnMBR	PO_4^{3-}: 23.0 NH_4^+: 50.2 COD: 80.0	Phosphates-Eggshell-PAC	PO_4^{3-}: 71.8-99.9 COD: 89.6-94.1	Present study
	Synthetic Real domestic wastewater				PO_4^{3-}: 60.5-78.0 COD: 89.6-94.1	Present study

Chapter's conclusions

The application of a SAnMBR for the treatment of municipal wastewater was examined. The process operated with the use of synthetic and real domestic wastewater. The results revealed that COD was effectively removed up to 82.3 and 87.8% for synthetic and domestic wastewater, respectively. Phosphate ions were also removed after the application of biowastes with percentages up to 71.8 - 99.9% and 60.5 - 78.0% for EGSL and SG, respectively, for all the tested flow rates. After PAC application, COD was further reduced with concentrations of 20.2 ± 5.2 and 57.0 ± 13.3 mg L^{-1} under all operating conditions, respectively. Phytotoxicity results revealed that the SAnMBR effluent achieved high GI values for both seeds tested compared to the untreated domestic wastewater. The solid fraction after adsorption from synthetic and domestic wastewater solutions showed that most of the phosphorus attained was inorganically bound. Finally, VOCs presented a significant decrease especially in VSCs, phenols, and aldehydes. In general, this technology might be viewed as a potential approach for treating a wide range of wastewater instead of the applied conventional systems as these products can be recovered in treated wastewater and be utilized for irrigation, supply biogas for energy, and a solid product high in inorganically bound phosphate that can be used as a raw material for fertilize product.

8 SUMMARY OF FINDINGS – CONCLUSIONS

Aligned with the concept of circular economy, this study proposes a novel approach (Fig. 1-14) aiming at a sustainable recovery of phosphates from real wastewater and DWAS using thermally treated biowaste-based materials and the evaluation of end products in the agricultural industry as soil conditioners. Thus, from a wide range of biowastes tested, the potential of SG-TT and EGSL-TT residues as a cost-effective solution for phosphate removal was highlighted. The residues showed exceptional adsorption capabilities in both synthetic and real wastewater sources. The thermal treatment of such materials transformed them into effective phosphate adsorbents. Optimal phosphate utilization using SG-TT and EGSL-TT occurred at 500ºC for 1 hr and at 900ºC for 30 min at neutral pH, approximately. The Freundlich equation efficiently predicted adsorption behavior for seagrass, while Langmuir equation was best fitted for eggshell adsorption. According to the results obtained the adsorption mechanisms were different for each material. EDS maps confirmed uniform phosphate distribution over the specimen's surface, while the presence of phosphate-based crystals indicated simultaneous physical and chemical adsorption for SG-TT samples. EGSL-TT mechanisms were examined in previous laboratory studies indicating that phosphates are collected in one or combination of the following three mechanisms: (a) adsorbed on the surface of CES900 particles, (b) reacting with calcium carbonate but forming amorphous phases, and/or (c) precipitating into calcium phosphate phases but forming amorphous material or crystals small enough (~1 nm), not detectable by XRD. The SG-TT and EGSL-TT adsorption of phosphates were minimally influenced by other components in real wastewater, exhibiting also high selectivity towards phosphates. As such, the findings underline the potential of these materials' high nutrition content and robust adsorption capacity.

DWAS were also used in adsorption batch experiments due to its high phosphate content. Sulfuric acid was efficient in solubilizing phosphate from DWAS. The SG-TT and EGSL-TT residues were suitable adsorbents achieving high adsorption efficiency. This study was also utilized SG-TT and EGSL-TT residues after adsorption from real wastewater and leachates to produce a fertilizer substitute. The findings were similar for both materials. More specifically, the solid residues after synthetic and real wastewaters (primary, anaerobic and reject wastewater) had a positive effect on plant growth, while the solid residues after adsorption from the leachate solution from DWAS imposed a negative effect on the germination of seeds. However, SG-TT and EGSL-TT are excellent biomaterials for recovering phosphate from anaerobic effluents, and the solid residue from this process contains essential nutrients for agricultural use.

EGSL-TT was also tested as an additive to AD, revealing that EGSL-TT prevented pH reduction and improved reactor performance. Soluble CO_2 had a higher affinity for EGSL-TT than phosphates, and N_2 replacement resulted in significant phosphate removal.

In the last chapters, a wholistic approach was implemented to improve the treatment procedure of real wastewater. SAnMBR effluent has potential for resource recovery due to its lack of solids and bacteria. However, it was not effective in removing phosphates, indicating the need for advanced treatment processes. This study proposed using a column system with SG-TT or eggshell residues to selectively recover phosphates from the rejected wastewater effluent. Continuous operation of these columns resulted in high phosphate recovery efficiencies. Similar results were obtained in the experiment where SAnMBR was used for treating municipal wastewater. Effective COD removal rates above 82.3% were achieved. With the addition of biowastes the substantial removal of phosphate ions was also ranging from 71.8% to 99.9% for EGSL and 60.5% to 78.0% for SG. The PAC addition further reduced COD concentrations, resulting in high-quality effluent. This was also confirmed by the phytotoxicity assessments, which showed high GI values for SAnMBR effluent, outperforming untreated wastewater. Moreover, VOCs exhibited a significant decrease, indicating the efficacy of this technology in wastewater treatment. Thus, this approach holds promise for treating diverse types of wastewater and the recovered products can be utilized for irrigation, biogas production, and as a solid feedstock for the fertilizer industry.

9 Recommendations

One area of investigation that could be pursued is conducting scale-up experiments and pilot studies to evaluate the feasibility of implementing the phosphate recovery process on a larger scale. To achieve potential industrial applications, it will be essential to gain an understanding of the practical challenges and performance of the adsorption system under real-world conditions.

Another crucial area of future research could involve investigating the efficiency and long-term stability of other bio-based adsorbents as well as other industrial wastes such as bypass dust from cement industry, which has high Ca content. Furthermore, conducting a comprehensive economic analysis and life cycle assessment could be a valuable way to evaluate the cost-effectiveness and environmental impacts of the proposed phosphate recovery process. This will assist in identifying potential barriers and opportunities for large-scale implementation and will be a crucial component of future research.

Another potential area of research could involve exploring additional avenues for the valorization of adsorbed phosphates recovered from bio-based adsorbents. Investigating their potential as raw materials for fertilizer production, soil amendments, or other valuable products could enhance the circular economy concept and further promote sustainable resource management. Moreover, exploring the integration of the phosphate recovery process into existing wastewater treatment plants, particularly anaerobic digestion facilities, could also be an area of interest. Developing efficient and practical systems for simultaneous wastewater treatment and phosphate recovery could enhance the overall resource recovery potential. Considering the combination of multiple treatment technologies or synergistic approaches to optimize phosphate recovery and overall wastewater treatment efficiency may also be a promising area of exploration that will improve the overall phosphorus removal performance. In addition, by conducting field trials and applying the phosphate recovery process in real-world wastewater treatment scenarios will provide valuable insights into the process's performance under different conditions and provide opportunities for collaboration with wastewater treatment facilities.

Finally, exploring the potential policy implications and regulatory considerations associated with adopting phosphate recovery technologies could be a crucial area of investigation. Engaging policymakers and stakeholders will be essential to ensure the integration of these sustainable practices into future waste management strategies.

REFERENCES

APHA. Standard Methods for the Examination of Water and Wastewater 20th Edition 1998, 4500-NO_2-B Colorimetric Method. Stand. Methods Exam. Water Wastewater. 1992, 552, 4-86.

Ábalos, M., Prieto, X., and Bayona, J. M. 2002. Determination of volatile alkyl sulfides in wastewater by headspace solid-phase microextraction followed by gas chromatography-mass spectrometry. Journal of Chromatography A, 963(1-2), 249-257. https://doi.org/10.1016/S0021-9673(02)00543-5

Acelas, N.Y., López, D.P., Wim Brilman, D.W.F., Kersten, S.R.A., Kootstra, A.M.J., 2014. Supercritical water gasification of sewage sludge: Gas production and phosphorus recovery. Bioresource Technology 174, 167-175. https://doi.org/10.1016/j.biortech.2014.10.003

Adelagun, R. O. A. 2016. Technological options for phosphate removal and recovery from aqua system: A review. Chemical Sciences Review and Letters, 5, 19-34. ISSN 2278-6783

Aditya, S., Stephen, J., Radhakrishnan, M., 2021. Utilization of eggshell waste in calcium-fortified foods and other industrial applications: A review. Trends Food Sci. Technol. 115, 422-432. https://doi.org/10.1016/j.tifs.2021.06.047

Afroze, S., Sen, T.K., 2018. A Review on Heavy Metal Ions and Dye Adsorption from Water. Agricultural Solid Waste Adsorbents. https://doi.org/10.1007/s11270-018-3869-z

Ahmad, W., Sethupathi, S., Munusamy, Y., Kanthasamy, R., 2021. Valorization of raw and calcined chicken eggshell for sulfur dioxide and hydrogen sulfide removal at low temperature. Catalysts 11, 1-20. https://doi.org/10.3390/catal11020295

Al Mamun, M.R., Torii, S., 2017. Enhancement of Methane Concentration by Removing Contaminants from Biogas Mixtures Using Combined Method of Absorption and Adsorption. Int. J. Chem. Eng. 2017. https://doi.org/10.1155/2017/7906859

Alazaiza, M. Y., Albahnasawi, A., Ali, G. A., Bashir, M. J., Nassani, D. E., Al Maskari, T., ... and Abujazar, M. S. S. 2022. Application of natural coagulants for pharmaceutical removal from water and wastewater: A review. Water, 14(2), 140.

https://doi.org/10.3390/w14020140

Ali, A. 2015. Phosphate Removal from Water and Wastewater by Membrane Operations. In: Drioli, E., Giorno, L. (eds) Encyclopedia of Membranes. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-40872-4_2182-1

Allouche, F., Mameri, N., Guibal, E., 2011. Pb (II) biosorption on Posidonia oceanica biomass. Chem. Eng. J. 168, 1174-1184. https://doi.org/10.1016/j.cej.2011.02.005

Almatouq, A., Ahmed, M. E., Khajah, M., and Al-Yaseen, R. (2022). Assessment of Volatile Organic Compounds Removal in Kuwait Wastewater Treatment Plants. International Journal of Environmental Science and Development, 13(6), 287-291. https://doi.org/10.18178/ijesd.2022.13.6.1406

Anastasakis, K., and Ross, A.B., 2015. Hydrothermal liquefaction of four brown macro-algae commonly found on the UK coasts: An energetic analysis of the process and comparison with bio-chemical conversion methods. Fuel, 139, 546-553. https://doi.org/10.1016/j.fuel.2014.09.006

Angelidaki, I., Alves, M., Bolzonella, D., Borzacconi, L., Campos, J.L., Guwy, A.J., Kalyuzhnyi, S., Jenicek, P., Van Lier, J.B., 2009. Defining the biomethane potential (BMP) of solid organic wastes and energy crops: A proposed protocol for batch assays. Water Sci. Technol. 59, 927-934. https://doi.org/10.2166/wst.2009.040

Antoniou, C. V., Koukouraki, E. E., Diamadopoulos, E., 2007. Analysis of Volatile and Semivolatile Organic Compounds in Municipal Wastewater Using Headspace Solid-Phase Microextraction and Gas Chromatography. Water Environment Research, Vol. 79, pp. 921-930 (10 pages)

APHA. Standard Methods for the Examination of Water and Wastewater, 22nd Edition. American Public Health Association (APHA), Washington, DC, USA. 2012.

Asimakopoulos, G., Baikousi, M., Salmas, C., Bourlinos, A.B., Zboril, R., Karakassides, M.A., 2021. Advanced Cr(VI) sorption properties of activated carbon produced via pyrolysis of the "Posidonia oceanica" seagrass. J Hazard Mater 405, 124274. https://doi.org/10.1016/j.jhazmat.2020.124274

Aslan, M., Ari, H., Gülen, H., Yildiz, H., Saatçi, Y., 2013. Treatment of Slaughterhouse Wastewaters by Anaerobic Submerged Membrane Bioreactor, Turkish Journal of

Science and Technology.

Awogbemi, O., Inambao, F., Onuh, E.I., 2020. Modification and characterization of chicken eggshell for possible catalytic applications. Heliyon 6, e05283. https://doi.org/10.1016/j.heliyon.2020.e05283

Aydin, M., Cavas, L., Merdivan, M., 2012. An alternative evaluation method for accumulated dead leaves of Posidonia oceanica (L.) Delile on the beaches: removal of uranium from aqueous solutions 489-496. https://doi.org/10.1007/s10967-012-1782-2

Baek, K., Kim, B. K., and Yang, J. W. 2004. Removal of phosphorous using micellar-enhanced ultrafiltration with cationic surfactant: Effects of surrounding pH. Fresenius Environmental Bulletin, 13(2), 105-111.

Bahrodin, M. B., Zaidi, N. S., Hussein, N., Sillanpää, M., Prasetyo, D. D., and Syafiuddin, A. 2021. Recent advances on coagulation-based treatment of wastewater: Transition from chemical to natural coagulant. Current Pollution Reports, 7(3), 379-391. https://doi.org/10.1007/s40726-021-00191-7

Balata, G., Tola, A., 2018. Cost-opportunity analysis of the use of Posidonia oceanica as a source of bio-energy in tourism-oriented territories. The case of Alghero. J. Clean. Prod. 172, 4085-4098. https://doi.org/10.1016/j.jclepro.2017.02.072

Baldisserotto, C., Demaria, S., Arcidiacono, M., Benà, E., Giacò, P., Marchesini, R., and Pancaldi, S. 2023. Enhancing Urban Wastewater Treatment through Isolated Chlorella Strain-Based Phytoremediation in Centrate Stream: An Analysis of Algae Morpho-Physiology and Nutrients Removal Efficiency. Plants, 12(5), 1027. https://doi.org/10.3390/plants12051027

Banerjee, M., Basu, R.K., Das, S.K., 2018. Cr(VI) adsorption by a green adsorbent walnut shell: Adsorption studies, regeneration studies, scale-up design and economic feasibility. Process Saf. Environ. Prot. 116, 693-702. https://doi.org/10.1016/j.psep.2018.03.037

Banks, C.J., Lo, H.M., 2003. Assessing the effects of municipal solid waste incinerator bottom ash on the decomposition of biodegradable waste using a completely mixed anaerobic reactor. Waste Manag. Res. 21, 225-234.

https://doi.org/10.1177/0734242X0302100306

Biswas, B.K., Inoue, K., Ghimire, K.N., Harada, H., Ohto, K., Kawakita, H., 2008. Bioresource Technology Removal and recovery of phosphorus from water by means of adsorption onto orange waste gel loaded with zirconium 99, 8685-8690. https://doi.org/10.1016/j.biortech.2008.04.015

Biswas, B.K., Inoue, K., Ghimire, K.N., Ohta, S., Harada, H., Ohto, K., Kawakita, H., 2007. The adsorption of phosphate from an aquatic environment using metal-loaded orange waste 312, 214-223. https://doi.org/10.1016/j.jcis.2007.03.072

Biswas, B.K., Inoue, K., Harada, H., Ohto, K., Kawakita, H., 2009. Leaching of phosphorus from incinerated sewage sludge ash by means of acid extraction followed by adsorption on orange waste gel. J. Environ. Sci. 21, 1753-1760. https://doi.org/10.1016/S1001-0742(08)62484-5

Bui, X. T., Dang, B. T., Nguyen, T. T., Nguyen, V. T., Tran, D. P., Nguyen, P. T., ... and Show, P. L. 2021. Influence of organic loading rates on treatment performance of membrane bioreactor treating tannery wastewater. Environmental Technology and Innovation, 24, 101810. https://doi.org/10.1016/j.eti.2021.101810

Bunce, J. T., Ndam, E., Ofiteru, I. D., Moore, A., and Graham, D. W. 2018. A review of phosphorus removal technologies and their applicability to small-scale domestic wastewater treatment systems. Frontiers in Environmental Science, 6, 8. https://doi.org/10.3389/fenvs.2018.00008

Cataldo, S., Chiodo, V., Crea, F., Maisano, S., Milea, D., Pettignano, A., 2018. Biochar from byproduct to high value added material - A new adsorbent for toxic metal ions removal from aqueous solutions. J. Mol. Liq. 271, 481-489. https://doi.org/10.1016/j.molliq.2018.09.009

Cendrine Dargnat, Marie-Jeanne Teil, Marc Chevreuil, Martine Blanchard, Phthalate removal throughout wastewater treatment plant: Case study of Marne Aval station (France), Science of The Total Environment, Volume 407, Issue 4,2009, Pages 1235-1244, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2008.10.027.

Cengiz, S., Cavas, L., 2010. A promising evaluation method for dead leaves of Posidonia oceanica (L.) in the adsorption of methyl violet. Mar. Biotechnol. 12, 728-736.

https://doi.org/10.1007/s10126-010-9260-8

Charalambous, P., Shin, J., Shin, S.G., Vyrides, I., 2020. Anaerobic digestion of industrial dairy wastewater and cheese whey: Performance of internal circulation bioreactor and laboratory batch test at pH 5-6. Renew. Energy 147, 1-10. https://doi.org/10.1016/j.renene.2019.08.091

Chen, Y., Long, J., Chen, S., Xie, Y., Xu, Z., Ning, Z., ... and Li, H., 2022. Multi-step purification of electrolytic manganese residue leachate using hydroxide sedimentation, struvite precipitation, chlorination and coagulation: Advanced removal of manganese, ammonium, and phosphate. Science of The Total Environment, 805, 150237. https://doi.org/10.1016/j.scitotenv.2021.150237

Chen, Y., Yang, H., Gu, G., 2001. Effect of acid and surfactant treatment on activated sludge dewatering and settling. Water Res. 35, 2615-2620. https://doi.org/10.1016/S0043-1354(00)00565-0

Chon-Lin Lee, Peter Brimblecombe, Anthropogenic contributions to global carbonyl sulfide, carbon disulfide and organosulfides fluxes, Earth-Science Reviews, Volume 160,2016, Pages 1-18, ISSN 0012-8252, https://doi.org/10.1016/j.earscirev.2016.06.005.

Chowdhury, R.B., Moore, G.A., Weatherley, A.J., Arora, M., 2017. Key sustainability challenges for the global phosphorus resource, their implications for global food security, and options for mitigation. J. Clean. Prod. 140, 945-963. https://doi.org/10.1016/j.jclepro.2016.07.012

Christian, S., Grant, S., McCarthy, P., Wilson, D., Mills, D., 2011. The first two years of full-scale anaerobic membrane bioreactor (AnMBR) operation treating high-strength industrial wastewater. Water Pract Technol 6. https://doi.org/10.2166/wpt.2011.032

Cieslik, B., Konieczka, P., 2017. A review of phosphorus recovery methods at various steps of wastewater treatment and sewage sludge management. The concept of "no solid waste generation" and analytical methods. J. Clean. Prod. 142, 1728-1740. https://doi.org/10.1016/j.jclepro.2016.11.116

Cordell, D., Drangert, J.O., White, S., 2009. The story of phosphorus: Global food security and food for thought. Glob. Environ. Chang. 19, 292-305. https://doi.org/10.1016/j.gloenvcha.2008.10.009

Correll, D.L., 1999. Phosphorus: A rate limiting nutrient in surface waters. Poult. Sci. 78, 674-682. https://doi.org/10.1093/ps/78.5.674

Darmograi, G., Prelot, B., Geneste, A., De Menorval, L.C., Zajac, J., 2016. Removal of three anionic orange-type dyes and Cr(VI) oxyanion from aqueous solutions onto strongly basic anion-exchange resin. The effect of single-component and competitive adsorption. Colloids Surfaces A Physicochem. Eng. Asp. 508, 240-250. https://doi.org/10.1016/j.colsurfa.2016.08.063

De Gisi, S., Lofrano, G., Grassi, M., and Notarnicola, M., 2016. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. Sustainable Materials and Technologies, 9, 10-40. http://dx.doi.org/10.1016/j.susmat.2016.06.002

Demirbas, A., Edris, G., and Alalayah, W. M., 2017. Sludge production from municipal wastewater treatment in sewage treatment plant. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 39(10), 999-1006. https://doi.org/10.1080/15567036.2017.1283551

Deng, H., Lu, J., Li, G., Zhang, G., Wang, X., 2011. Adsorption of methylene blue on adsorbent materials produced from cotton stalk. Chem. Eng. J. 172, 326-334. https://doi.org/10.1016/j.cej.2011.06.013

Deng, L., and Dhar, B. R., 2023. Phosphorus recovery from wastewater via calcium phosphate precipitation: A critical review of methods, progress, and insights. Chemosphere, 138685. https://doi.org/10.1016/j.chemosphere.2023.138685

Deng, L., Guo, W., Ngo, H. H., Zhang, X., Chen, C., Chen, Z., and Wang, Q., 2022. Recent advances in attached growth membrane bioreactor systems for wastewater treatment. Science of the Total Environment, 808, 152123. https://doi.org/10.1016/j.scitotenv.2021.152123

Du, R., Hu, Y., Nitta, S., Ji, J., and Li, Y. Y., 2022. Material mass balance and elemental flow analysis in a submerged anaerobic membrane bioreactor for municipal wastewater treatment towards low-carbon operation and resource recovery. Science of The Total Environment, 852, 158586. http://dx.doi.org/10.1016/j.scitotenv.2022.158586

Dural, M.U., Cavas, L., Papageorgiou, S.K., Katsaros, F.K., 2011. Methylene blue adsorption on activated carbon prepared from *Posidonia oceanica (L.)* dead leaves: Kinetics and equilibrium studies. Chem. Eng. J. 168, 77-85. https://doi.org/10.1016/j.cej.2010.12.038

Egle, L., Rechberger, H., Zessner, M., 2015. Overview and description of technologies for recovering phosphorus from municipal wastewater. Resour. Conserv. Recycl. 105, 325-346. https://doi.org/10.1016/j.resconrec.2015.09.016

Elmorsi, R.R., El-wakeel, S.T., El-dein, W.A.S., Lotfy, H.R., Rashwan, W.E., Nagah, M., Shaaban, S.A., Ahmed, S.A.S., El-sherif, I.Y., Abou-el-sherbini, K.S., 2019. Adsorption of Methylene Blue and Pb 2 + by using acid-activated Posidonia oceanica waste. Sci. Rep. 1-12. https://doi.org/10.1038/s41598-019-39945-1

Fang, C., Zhang, T., Li, P., Jiang, R.F., Wang, Y.C., 2014. Application of magnesium modified corn biochar for phosphorus removal and recovery from swine wastewater. Int. J. Environ. Res. Public Health 11, 9217-9237. https://doi.org/10.3390/ijerph110909217

Faridi, H., Arabhosseini, A., 2018. Application of eggshell wastes as valuable and utilizable products: A review. Res. Agric. Eng. 64, 104-114. https://doi.org/10.17221/6/2017-RAE

Fouzi, A., Trache, D., Klapötke, T.M., 2019. International Journal of Biological Macromolecules Microcrystalline cellulose from Posidonia oceanica brown algae: Extraction and characterization. Int. J. Biol. Macromol. 138, 837-845. https://doi.org/10.1016/j.ijbiomac.2019.07.176

Fox, R.A., Stuckey, D.C., 2015. The effect of sparging rate on transmembrane pressure and critical flux in an AnMBR. J Environ Manage 151, 280-285. https://doi.org/10.1016/j.jenvman.2014.08.011

Fritzen, R.R., Domingues Benetti, A., 2021. Phosphorus removal in domestic wastewater treatment plant by calcined eggshell. Water Sci. Technol. 84, 995-1010. https://doi.org/10.2166/wst.2021.263

Galib, M., Elbeshbishy, E., Reid, R., Hussain, A., Lee, H.S., 2016. Energy-positive food wastewater treatment using an anaerobic membrane bioreactor (AnMBR). J Environ Manage 182, 477-485. https://doi.org/10.1016/j.jenvman.2016.07.098

Galinha, C. F., Sanches, S., and Crespo, J. G., 2018. Membrane bioreactors. In Fundamental modelling of membrane systems (pp. 209-249). Elsevier. https://doi.org/10.1016/B978-0-12-813483-2.00006-X

Gao, Q., Wang, C. Z., Liu, S., Hanigan, D., Liu, S. T., and Zhao, H. Z., 2019. Ultrafiltration membrane microreactor (MMR) for simultaneous removal of nitrate and phosphate from water. Chemical engineering journal, 355, 238-246. https://doi.org/10.1016/j.cej.2018.08.137

Gao, Y., Xu, C., 2012. Synthesis of dimethyl carbonate over waste eggshell catalyst. Catal. Today 190, 107-111. https://doi.org/10.1016/j.cattod.2011.12.004

Gautam, R. K., Valente, R., Abbas, H., Bui, A., More, N., Gray, S., and Navaratna, D., 2022. Recovery of biomethane from a submerged anaerobic membrane bioreactor treating domestic wastewater blended with semi-solid organic wastes discharged from residential establishments. Environmental Technology and Innovation, 27, 102763. https://doi.org/10.1016/j.eti.2022.102763

Gebretsadkan, A. A., Bernstein, R., and Gross, A., 2022. Adsorption of ammonium from AnMBR effluent using activated hydrochar as potential fertilizer. Conference paper.

Geissler, B., Mew, M. C., and Steiner, G., 2019. Phosphate supply security for importing countries: Developments and the current situation. Science of the Total Environment, 677, 511-523. https://doi.org/10.1016/j.scitotenv.2019.04.356

Gizaw, A., Zewge, F., Kumar, A., Mekonnen, A., and Tesfaye, M., 2021. A comprehensive review on nitrate and phosphate removal and recovery from aqueous solutions by adsorption. AQUA—Water Infrastructure, Ecosystems and Society, 70(7), 921-947. https://doi.org/10.2166/aqua.2021.146

Godayol, A., Marcé, R.M., Borrull, F., Anticõ, E., Sanchez, J.M., 2013. Development of a method for the monitoring of odor-causing compounds in atmospheres surrounding wastewater treatment plants. J Sep Sci 36, 1621-1628. https://doi.org/10.1002/jssc.201300046

Gomez-Rico, M. F., Fullana, A., and Font, R., 2008. Volatile organic compounds released from thermal drying of sewage sludge. Water Pollution IX, 425-433. https://doi.org/10.2495/WP080411

Gokyay, O., and Alshami, K., 2017. Effects of reject water on a large-scale wastewater treatment plant in Istanbul. Conference Paper.

Guezguez, I., Mhenni, F., 2008. Sorption of Yellow 59 on *Posidonia oceanica*, a non-conventional biosorbent: Comparison with activated carbons 9, 197-204. https://doi.org/10.1016/j.indcrop.2008.05.002

Guida, S., Rubertelli, G., Jefferson, B., and Soares, A., 2021. Demonstration of ion exchange technology for phosphorus removal and recovery from municipal wastewater. Chemical Engineering Journal, 420, 129913. https://doi.org/10.1016/j.cej.2021.129913

Hafuka, A., and Kimura, K., 2022. Phosphorus recovery by adsorption from the membrane permeate of an anaerobic membrane bioreactor digesting waste-activated sludge. Membranes, 12(1), 99. https://doi.org/10.3390/membranes12010099

Han, Q., Wang, J., Goodman, B.A., Xie, J., Liu, Z., 2020. High adsorption of methylene blue by activated carbon prepared from phosphoric acid treated eucalyptus residue. Powder Technol. 366, 239-248. https://doi.org/10.1016/j.powtec.2020.02.013

Haoran Feng, Min Liu, Taotao Tang, Ye Du, Bing Yao, Chengyu Yang, Changjie Yuan, Ying Chen, Insights into the efficient ozonation process focusing on 2,4-di-tert-butylphenol - A notable micropollutant of typical bamboo papermaking wastewater: Performance and mechanism, Journal of Hazardous Materials, Volume 443, Part B, 2023, 130346. https://doi.org/10.1016/j.jhazmat.2022.130346

Huang H, Liu J, Ding L, Recovery of phosphate and ammonia nitrogen from the anaerobic digestion supernatant of activated sludge by chemical precipitation, Journal of Cleaner Production, 2015, https://doi.org/10.1016/j.jclepro.2015.04.117.

Huang, R., Fang, C., Lu, X., Jiang, R., Tang, Y., 2017. Transformation of Phosphorus during (Hydro)thermal Treatments of Solid Biowastes: Reaction Mechanisms and Implications for P Reclamation and Recycling. Environ Sci Technol. https://doi.org/10.1021/acs.est.7b02011

Huang, S., Pooi, C.K., Shi, X., Varjani, S., Ng, H.Y., 2020. Performance and process simulation of membrane bioreactor (MBR) treating petrochemical wastewater. Science of the Total Environment 747. https://doi.org/10.1016/j.scitotenv.2020.141311

Humayro, A., Harada, H., Naito, K., 2021. Adsorption of Phosphate and Nitrate Using Modified Spent Coffee Ground and Its Application as an Alternative Nutrient Source for Plant Growth. J. Agric. Chem. Environ. 10, 80-90. https://doi.org/10.4236/jacen.2021.101006

Ittisupornrat, S., Phihusut, D., Kitkaew, D., Sangkarak, S., and Phetrak, A., 2019. Performance of dissolved organic matter removal from membrane bioreactor effluent by magnetic powdered activated carbon. Journal of environmental management, 248, 109314. https://doi.org/10.1016/j.jenvman.2019.109314

Jack, J., Huggins, T.M., Huang, Y., Fang, Y., Ren, Z.J., 2019. Production of magnetic biochar from waste-derived fungal biomass for phosphorus removal and recovery. J. Clean. Prod. 224, 100-106. https://doi.org/10.1016/j.jclepro.2019.03.120

Ji, J., Du, R., Ni, J., Chen, Y., Hu, Y., Qin, Y., ... and Li, Y. Y., 2022. Submerged anaerobic membrane bioreactor applied for mainstream municipal wastewater treatment at a low temperature: Sludge yield, energy balance and membrane filtration behaviors. Journal of Cleaner Production, 355, 131831. https://doi.org/10.1016/j.jclepro.2022.131831

Jung, K.W., Jeong, T.U., Hwang, M.J., Kim, K., Ahn, K.H., 2015. Phosphate adsorption ability of biochar/Mg-Al assembled nanocomposites prepared by aluminum-electrode based electro-assisted modification method with MgCl2 as electrolyte. Bioresour. Technol. 198, 603-610. https://doi.org/10.1016/j.biortech.2015.09.068

Jung, Y. J., Koh, H. W., Shin, W. T., and Sung, N. C., 2006. A novel approach to an advanced tertiary wastewater treatment: Combination of a membrane bioreactor and an oyster-zeolite column. Desalination, 190(1-3), 243-255. https://doi.org/10.1016/j.desal.2005.02.088

Karaca, S., Ejder, M., Ac, M., 2006. Adsorptive removal of phosphate from aqueous solutions using raw and calcinated dolomite 128, 273-279. https://doi.org/10.1016/j.jhazmat.2005.08.003

Karunanithi, R., Szogi, A.A., Bolan, N., Naidu, R., Loganathan, P., Hunt, P.G., Vanotti, M.B., Saint, C.P., Ok, Y.S., Krishnamoorthy, S., 2015. Phosphorus recovery and reuse from waste streams, Advances in Agronomy. Elsevier Ltd. https://doi.org/10.1016/bs.agron.2014.12.005

Kehrein, Philipp, Mark Van Loosdrecht, Patricia Osseweijer, Marianna Garfí, Jo Dewulf, and John Posada. "A critical review of resource recovery from municipal wastewater treatment plants-market supply potentials, technologies and bottlenecks." Environmental Science: Water Research and Technology 6, no. 4, 2020: 877-910. https://doi.org/10.1039/c9ew00905a

Khiari, R., Belgacem, M.N., 2017. Potential for using multiscale Posidonia oceanica waste: current status and prospects in material science, Lignocellulosic Fibre and Biomass-Based Composite Materials. Elsevier Ltd. https://doi.org/10.1016/B978-0-08-100959-8.00021-4

Khiari, R., Mhenni, M.F., Belgacem, M.N., Mauret, E., 2010. Bioresource Technology Chemical composition and pulping of date palm rachis and Posidonia oceanica - A comparison with other wood and non-wood fibre sources. Bioresour. Technol. 101, 775-780. https://doi.org/10.1016/j.biortech.2009.08.079

Kim, H.; Murthy, S.; McConnell, L.L.; Peot, C.; Ramirez, M.; Strawn, M., 2002. Characterization of wastewater and solids odors using solid phase microextraction at a large wastewater treatment plant. Water Science and Technology, 46(10), 9-16. doi:10.2166/wst.2002.0277

Kim, I. T., Lee, Y. E., Jeong, Y., and Yoo, Y. S., 2020. A novel method to remove nitrogen from reject water in wastewater treatment plants using a methane-and methanol-dependent bacterial consortium. Water Research, 172, 115512. https://doi.org/10.1016/j.watres.2020.115512

Kizito, S., Luo, H., Wu, S., Ajmal, Z., Lv, T., Dong, R., 2017. Phosphate recovery from liquid fraction of anaerobic digestate using four slow pyrolyzed biochars: Dynamics of adsorption, desorption and regeneration. J. Environ. Manage. 201, 260-267. https://doi.org/10.1016/j.jenvman.2017.06.057

Koh, K. Y., Zhang, S., and Chen, J. P., 2020. Improvement of ultrafiltration for treatment of phosphorus-containing water by a lanthanum-modified aminated polyacrylonitrile membrane. ACS omega, 5(13), 7170-7181. https://dx.doi.org/10.1021/acsomega.9b03573?ref=pdf

Komatsu, K., Onodera, T., Kohzu, A., Syutsubo, K. and Imai, A., 2020. Characterization of dissolved organic matter in wastewater during aerobic, anaerobic, and anoxic treatment processes by molecular size and fluorescence analyses. Water Research, 171, p.115459. https://doi.org/10.1016/j.watres.2019.115459

Kong, X., Wei, Y., Xu, S., Liu, J., Li, H., Liu, Y., Yu, S., 2016. Inhibiting excessive acidification using zero-valent iron in anaerobic digestion of food waste at high organic load rates. Bioresour. Technol. 211, 65-71. https://doi.org/10.1016/j.biortech.2016.03.078

Köse, T.E., Kvanc, B., 2011. Adsorption of phosphate from aqueous solutions using calcined waste eggshell 178, 34-39. https://doi.org/10.1016/j.cej.2011.09.129

Kotowska, U., alikowski, M. and Isidorov, V., 2011. HS-SPME/GC-MS analysis of volatile and semi-volatile organic compounds emitted from municipal sewage sludge. Environmental Monitoring and Assessment, 184(5), pp.2893-2907.

Koul, B., Yadav, D., Singh, S., Kumar, M., and Song, M., 2022. Insights into the domestic wastewater treatment (DWWT) regimes: a review. Water, 14(21), 3542. https://doi.org/10.3390/w14213542

Krika, F., Azzouz, N., Ncibi, M.C., 2015. Adsorptive removal of cadmium from aqueous media using Posidonia oceanica biomass: equilibrium, dynamic and thermodynamic studies. Int. J. Environ. Sci. Technol. https://doi.org/10.1007/s13762-013-0483-x

Kumar, P. S., Korving, L., van Loosdrecht, M. C., and Witkamp, G. J., 2019. Adsorption as a technology to achieve ultra-low concentrations of phosphate: Research gaps and economic analysis. Water Research X, 4, 100029. https://doi.org/10.1016/j.wroa.2019.100029

Kurniawan, S. B., Abdullah, S. R. S., Imron, M. F., Said, N. S. M., Ismail, N. I., Hasan, H. A., ... and Purwanti, I. F., 2020. Challenges and opportunities of biocoagulant/bioflocculant application for drinking water and wastewater treatment and its potential for sludge recovery. International journal of environmental research and public health, 17(24), 9312. http://dx.doi.org/10.3390/ijerph17249312

Lebedev, A. T., Detenchuk, E. A., Latkin, T. B., Bavcon Kralj, M., and Trebše, P., 2022. Aqueous Chlorination of D-Limonene. Molecules, 27(9), 2988. https://doi.org/10.3390/molecules27092988

Lee, J.I., Kang, J.K., Oh, J.S., Yoo, S.C., Lee, C.G., Jho, E.H., Park, S.J., 2021. New insight to the use of oyster shell for removing phosphorus from aqueous solutions and fertilizing rice growth. J. Clean. Prod. 328, 129536. https://doi.org/10.1016/j.jclepro.2021.129536

Lee, J.I., Kim, J.M., Yoo, S.C., Jho, E.H., Lee, C.G., Park, S.J., 2022. Restoring phosphorus from water to soil: Using calcined eggshells for P adsorption and subsequent application of the adsorbent as a P fertilizer. Chemosphere 287, 132267. https://doi.org/10.1016/j.chemosphere.2021.132267

Lee, J.I., Oh, J.S., Yoo, S.C., Jho, E.H., Lee, C.G., Park, S.J., 2022. Removal of phosphorus from water using calcium-rich organic waste and its potential as a fertilizer for rice growth. J Environ Chem Eng 10. https://doi.org/10.1016/j.jece.2022.107367

Lee, Y., Cho, J., Seo, Y., Lee, J. W., and Ahn, K. H., 2002. Modeling of submerged membrane bioreactor process for wastewater treatment. Desalination, 146(1-3), 451-457. https://doi.org/10.1016/S0011-9164(02)00543-X

Lehtinen, J., and Veijanen, A., 2011. Odour Monitoring by Combined TD-GC-MS-Sniff Technique and Dynamic Olfactometry at the Wastewater Treatment Plant of Low H2S Concentration. Water, Air, and Soil Pollution, 218(1-4), 185-196. https://doi.org/10.1007/s11270-010-0634-3

Li, B., Huang, H., Sun, Z., Zhao, N., Munir, T., Yu, W., Young, B., 2020. Minimizing heavy metals in recovered struvite from swine wastewater after anaerobic biochemical treatment: Reaction mechanisms and pilot test. J. Clean. Prod. 272, 122649. https://doi.org/10.1016/j.jclepro.2020.122649

Li, R., Wang, J.J., Zhang, Z., Awasthi, M.K., Du, D., Dang, P., Huang, Q., Zhang, Y., Wang, L., 2018. Recovery of phosphate and dissolved organic matter from aqueous solution using a novel CaO-MgO hybrid carbon composite and its feasibility in phosphorus recycling. Sci. Total Environ. 642, 526-536. https://doi.org/10.1016/j.scitotenv.2018.06.092

Liang, Z., Wang, J., Zhang, Y., Han, C., Ma, S., Chen, J., Li, G., and An, T., 2020. Removal of volatile organic compounds (VOCs) emitted from a textile dyeing wastewater treatment plant and the attenuation of respiratory health risks using a pilot-scale biofilter. Journal of Cleaner Production, 253, 120019. https://doi.org/10.1016/j.jclepro.2020.120019

Lide, D.R. ed., 2004. CRC handbook of chemistry and physics (Vol. 85). CRC press.

Lim, Kahao, Patrick J. Evans, and Prathap Parameswaran. "Long-term performance of a pilot-scale gas-sparged anaerobic membrane bioreactor under ambient temperatures for holistic wastewater treatment." Environmental science and technology 53.13., 2019: 7347-7354. https://doi.org/10.1021/acs.est.8b06198

Liu, Z., Dang, Y., Li, C., Sun, D., 2015. Inhibitory effect of high NH4+-N concentration on anaerobic biotreatment of fresh leachate from a municipal solid waste incineration plant. Waste Manag. 43, 188-195. https://doi.org/10.1016/j.wasman.2015.06.031

Liu, J., Kang, X., Luan, X., Gao, L., Tian, H., and Liu, X., 2020. Performance and membrane fouling behaviors analysis with SVR-LibSVM model in a submerged anaerobic membrane bioreactor treating low-strength domestic sewage. Environmental Technology and Innovation, 19, 100844. https://doi.org/10.1016/j.eti.2020.100844

Liu, W., Iordan, C. M., Cherubini, F., Hu, X., and Fu, D., 2021. Environmental impacts assessment of wastewater treatment and sludge disposal systems under two sewage discharge standards: a case study in Kunshan, China. Journal of Cleaner Production, 287, 125046. https://doi.org/10.1016/j.jclepro.2020.125046

Lorick, D., Macura, B., Ahlström, M., Grimvall, A., and Harder, R., 2020. Effectiveness of struvite precipitation and ammonia stripping for recovery of phosphorus and nitrogen from anaerobic digestate: a systematic review. Environmental Evidence, 9, 1-20. https://doi.org/10.1186/s13750-020-00211-x

Luo, D., Wang, L., Nan, H., Cao, Y., Wang, H., Kumar, T. V., and Wang, C., 2023. Phosphorus adsorption by functionalized biochar: A review. Environmental Chemistry Letters, 21(1), 497-524. https://doi.org/10.1007/s10311-022-01519-5

Luyckx, L., Geerts, S., Van Caneghem, J., 2020. Closing the phosphorus cycle: Multi-criteria techno-economic optimization of phosphorus extraction from wastewater treatment sludge ash. Sci. Total Environ. 713, 135543. https://doi.org/10.1016/j.scitotenv.2019.135543

MacDonald, G. K., Bennett, E. M., Potter, P. A., and Ramankutty, N., 2011. Agronomic phosphorus imbalances across the world's croplands. Proceedings of the National Academy of Sciences, 108(7), 3086-3091. https://doi.org/10.1073/pnas.1010808108

Mai, D. T., Kunacheva, C., and Stuckey, D. C. 2018. A review of posttreatment technologies for anaerobic effluents for discharge and recycling of wastewater. Critical Reviews in Environmental Science and Technology, 48(2), 167-209. https://doi.org/10.1080/10643389.2018.1443667

Mani, S., Tabil, L.G. and Sokhansanj, S., 2004. Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. Biomass and bioenergy, 27(4), pp.339-352. https://doi.org/10.1016/j.biombioe.2004.03.007

Martin, B. D., Parsons, S. A., and Jefferson, B., 2009. Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles. Water Science and Technology, 60(10), 2637-2645. https://doi.org/10.2166/wst.2009.686

Mavinic, D. S., et al. "Phosphorus recovery from anaerobic digester supernatants using a pilot-scale struvite crystallization process." Journal of Environmental Engineering and Science 6.5, 2007: 561-571. https://doi.org/10.1139/S07-007

Mayer, B. K., Baker, L. A., Boyer, T. H., Drechsel, P., Gifford, M., Hanjra, M. A., ... and Rittmann, B. E., 2016. Total value of phosphorus recovery. Environmental science and technology, 50(13), 6606-6620. https://doi.org/10.1021/acs.est.6b01239

Metcalf, E. and Eddy, E., 2003. Wastewater Engineering: Treatment and Reuse. McGraw Hill Inc., New York.

Meyer, S. S., and Wilderer, P. A., 2004. Reject water: Treating of process water in large wastewater treatment plants in Germany—A case study. Journal of Environmental Science and Health, Part A, 39(7), 1645-1654. https://doi.org/10.1081/ESE-120037866

Monclús, H., Sipma, J., Ferrero, G., Rodriguez-Roda, I., Comas, J., 2010. Biological nutrient removal in an MBR treating municipal wastewater with special focus on biological phosphorus removal. Bioresour Technol 101, 3984-3991. https://doi.org/10.1016/j.biortech.2010.01.038

Monea, M.C., Löhr, D.K., Meyer, C., Preyl, V., Xiao, J., Steinmetz, H., Schönberger, H., Drenkova-Tuhtan, A., 2020. Comparing the leaching behavior of phosphorus, aluminum and iron from post-precipitated tertiary sludge and anaerobically digested sewage sludge aiming at phosphorus recovery. J. Clean. Prod. 247, 119129. https://doi.org/10.1016/j.jclepro.2019.119129

Mor, S., Chhoden, K. and Ravindra, K., 2016. Application of agro-waste rice husk ash for the removal of phosphate from the wastewater. Journal of Cleaner Production, 129, pp.673-680. https://doi.org/10.1016/j.jclepro.2016.03.088

Mu, B., Wang, A., 2016. Adsorption of dyes onto palygorskite and its composites: A review. J. Environ. Chem. Eng. 4, 1274-1294. https://doi.org/10.1016/j.jece.2016.01.036

Mucha, Z., and Mikosz, J., 2021. Technological characteristics of reject waters from aerobic sludge stabilization in small and medium-sized wastewater treatment plants with biological nutrient removal. International Journal of Energy and Environmental Engineering, 12(1), 69-76. https://doi.org/10.1007/s40095-020-00358-w

Muhammad, A., Soares, A., and Jefferson, B., 2019. The impact of background wastewater constituents on the selectivity and capacity of a hybrid ion exchange resin for phosphorus removal from wastewater. Chemosphere, 224, 494-501. https://doi.org/10.1016/j.chemosphere.2019.01.085

Murakami, F.S., Rodrigues, P.O., De Campos, C.M.T., Silva, M.A.S., 2007. Physicochemical study of $CaCO_3$ from eggshells. Cienc. e Tecnol. Aliment. 27, 658-662. https://doi.org/10.1590/S0101-20612007000300035

Nageeb, M., 2013. Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater. InTech. doi: 10.5772/54048

Najm, I. N., Snoeyink, V. L., Suidan, M. T., Lee, C. H., and Richard, Y., 1990. Effect of particle size and background natural organics on the adsorption efficiency of PAC.

Journal-American Water Works Association, 82(1), 65-72. https://doi.org/10.1002/j.1551-8833.1990.tb06907.

Ncibi, M.C., 2008. Adsorptive removal of anionic and non-ionic surfactants from aqueous phase using *Posidonia oceanica* (L.) marine biomass. J. Chem. Technol. Biotechnol. 83, 1163-1169. https://doi.org/10.1002/jctb

Ncibi, M.C., Mahjoub, B., Seffen, M., 2014. Biosorption of Phenol onto *Posidonia oceanica* (L.) Seagrass in Batch System: Equilibrium and Kinetic Modelling 84, 495-500.

Nobaharan, K., Bagheri Novair, S., Asgari Lajayer, B., and van Hullebusch, E. D., 2021. Phosphorus removal from wastewater: The potential use of biochar and the key controlling factors. Water, 13(4), 517. https://doi.org/10.3390/w13040517

Obotey Ezugbe, E., and Rathilal, S., 2020. Membrane technologies in wastewater treatment: a review. Membranes, 10(5), 89. http://dx.doi.org/10.3390/membranes10050089

Oladoja, N.A., Adelagun, R.O.A., Ahmad, A.L., Ololade, I.A., 2015. Accept dust. Process Saf. Environ. Prot. https://doi.org/10.1016/j.psep.2015.09.006

Oladoja, N.A., Ahmad, A.L., Adesina, O.A., Adelagun, R.O.A., 2012. Low-cost biogenic waste for phosphate capture from aqueous system. Chem. Eng. J. 209, 170-179. https://doi.org/10.1016/j.cej.2012.07.125

Oliveira, D.A., Benelli, P., Amante, E.R., 2013. A literature review on adding value to solid residues: Eggshells. J. Clean. Prod. 46, 42-47. https://doi.org/10.1016/j.jclepro.2012.09.045

Ownby, M., Desrosiers, D. A., and Vaneeckhaute, C., 2021. Phosphorus removal and recovery from wastewater via hybrid ion exchange nanotechnology: a study on sustainable regeneration chemistries. npj Clean Water, 4(1), 6. https://doi.org/10.1038/s41545-020-00097-9

Owodunni, A. A., Ismail, S., Kurniawan, S. B., Ahmad, A., Imron, M. F., and Abdullah, S. R. S., 2023. A review on revolutionary technique for phosphate removal in wastewater using green coagulant. Journal of Water Process Engineering, 52, 103573. https://doi.org/10.1016/j.jwpe.2023.103573

Özacar, M., and Şengil, İ. A., 2003. Enhancing phosphate removal from wastewater by using polyelectrolytes and clay injection. Journal of Hazardous Materials, 100(1-3), 131-146. https://doi.org/10.1016/S0304-3894(03)00070-0

Panagiotou, E., Kafa, N., Koutsokeras, L., Kouis, P., Nikolaou, P., Constantinides, G., Vyrides, I., 2018. Turning calcined waste eggshells and wastewater to Brushite: Phosphorus adsorption from aqua media and anaerobic sludge leach water. J. Clean. Prod. 178, 419-428. https://doi.org/10.1016/j.jclepro.2018.01.014

Paradelo, R., Conde-Cid, M., Cutillas-Barreiro, L., Arias-Estevez, M., Nóvoa-Munoz, J.C., Álvarez-Rodríguez, E., Fernández-Sanjurjo, M.J. and Núñez-Delgado, A., 2016. Phosphorus removal from wastewater using mussel shell: investigation on retention mechanisms. Ecological engineering, 97, pp.558-566. https://doi.org/10.1016/j.ecoleng.2016.10.066

Photiou, P., Kallis, M., Samanides, C.G., Vyrides, I., Padoan, E., Montoneri, E., Koutinas, M., 2021a. Integrated Chemical Biochemical Technology to Reduce Ammonia Emission from Fermented Municipal Biowaste. ACS Sustain. Chem. Eng. https://doi.org/10.1021/acssuschemeng.1c00689

Photiou, P., Vyrides, I., 2022. Calcined eggshells in anaerobic digestion: buffering acidification in AD and evaluating end products from phosphate adsorption as soil conditioners. J. Env. Chem. Eng. 107957, ISSN 2213-3437. https://doi.org/10.1016/j.jece.2022.107957

Photiou, P., Koutsokeras, L., Constantinides, G., Koutinas, M., Vyrides, I., 2021. Phosphate removal from synthetic and real wastewater using thermally treated seagrass residues of *Posidonia oceanica*. J. Clean. Prod. 278, 123294. https://doi.org/10.1016/j.jclepro.2020.123294

Photiou, P., Poulizou M., and Vyrides I., 2023. Recovery of phosphates from anaerobic MBR effluent using columns of eggshell and seagrass residues and their final use as a fertilizer." Sustain. Chem. Pharm. 33, 101039. https://doi.org/10.1016/j.scp.2023.101039

Photiou, P., Vyrides, I., 2021. Recovery of phosphate from dewatered anaerobic sludge and wastewater by thermally treated *P. oceanica* residues and its potential application as a fertilizer. J. Environ. Manage. 298, 113441.

https://doi.org/10.1016/j.jenvman.2021.113441

Pitiriciu, M., and Tansel, B., 2021. Volatile organic contaminants (VOCs) emitted from sewer networks during wastewater collection and transport. Journal of Environmental Management, 285, 112136. https://doi.org/10.1016/j.jenvman.2021.112136

Pourhakkak, P., Taghizadeh, M., Taghizadeh, A., and Ghaedi, M., 2021. Adsorbent. In Interface Science and Technology (Vol. 33, pp. 71-210). Elsevier. https://doi.org/10.1016/B978-0-12-818805-7.00009-6

Preisner, M., and Smol, M., 2022. Investigating phosphorus loads removed by chemical and biological methods in municipal wastewater treatment plants in Poland. Journal of Environmental Management, 322, 116058. https://doi.org/10.1016/j.jenvman.2022.116058

Putra, A. A., Watari, T., Maki, S., Hatamoto, M., and Yamaguchi, T., 2020. Anaerobic baffled reactor to treat fishmeal wastewater with high organic content. Environmental Technology and Innovation, 17, 100586. https://doi.org/10.1016/j.eti.2019.100586

Quina, M.J., Soares, M.A.R., Quinta-Ferreira, R., 2017. Applications of industrial eggshell as a valuable anthropogenic resource. Resour. Conserv. Recycl. 123, 176-186. https://doi.org/10.1016/j.resconrec.2016.09.027

Quist-Jensen, C.A., Wybrandt, L., Løkkegaard, H., Antonsen, S.B., Christensen, M.L., 2020. Pilot-scale study for phosphorus recovery by sludge acidification and dewatering. Environ. Technol. (United Kingdom) 41, 2928-2934. https://doi.org/10.1080/09593330.2019.1588385

Quist-Jensen, C.A., Wybrandt, L., Løkkegaard, H., Antonsen, S.B., Jensen, H.C., Nielsen, A.H., Christensen, M.L., 2018. Acidification and recovery of phosphorus from digested and non-digested sludge. Water Res. 146, 307-317. https://doi.org/10.1016/j.watres.2018.09.035

Radha, T., Karthikeyan, G., 2019. Hen Eggshell Waste As Fertilizer for the Growth of Phaseolus Vulgaris (Cow Pea Seeds). Res. J. Life Sci. Bioinformatics, Pharm. Chem. Sci. 5, 398-406 (9). https://doi.org/10.26479/2019.0501.35

Rahman TU, Roy H, Islam MR, Tahmid M, Fariha A, Mazumder A, Tasnim N, Pervez MN, Cai Y, Naddeo V, et al. The Advancement in Membrane Bioreactor (MBR) Technology toward Sustainable Industrial Wastewater Management. Membranes. 2023; 13(2):181. https://doi.org/10.3390/membranes13020181

Rathod, M., Mody, K., and Basha, S., 2014. Efficient removal of phosphate from aqueous solutions by red seaweed, *Kappaphycus alverezii*. Journal of Cleaner Production, 84, 484-493. http://dx.doi.org/10.1016/j.jclepro.2014.03.064

Ravindran, B., Kumari, S.K.S., Stenstrom, T.A., Bux, F., 2016. Evaluation of phytotoxicity effect on selected crops using treated and untreated wastewater from different configurative domestic wastewater plants. Environmental Technology (United Kingdom) 37, 1782-1789. https://doi.org/10.1080/09593330.2015.1132776

Reddy, A. S., and Nair, A. T., 2022. The fate of microplastics in wastewater treatment plants: An overview of source and remediation technologies. Environmental Technology and Innovation, 102815. https://doi.org/10.1016/j.eti.2022.102815

Renfrew, D., Vasilaki, V., McLeod, A., Lake, A., Danishvar, S. and Katsou, E., 2022. Where is the greatest potential for resource recovery in wastewater treatment plants?. Water Research, 220, p.118673. https://doi.org/10.1016/j.watres.2022.118673

Robalds, A., Dreijalte, L., Bikovens, O., Klavins, M., 2016. A novel peat-based biosorbent for the removal of phosphate from synthetic and real wastewater and possible utilization of spent sorbent in land application. Desalin. Water Treat. 57, 13285-13294. https://doi.org/10.1080/19443994.2015.1061450

Robles, Á., Jiménez-Benítez, A., Giménez, J. B., Durán, F., Ribes, J., Serralta, J., ... and Seco, A., 2022. A semi-industrial scale AnMBR for municipal wastewater treatment at ambient temperature: performance of the biological process. Water Research, 215, 118249. https://doi.org/10.1016/j.watres.2022.118249

Romero, C., Ramos, P., Costa, C., Carmen Márquez, M., 2013. Raw and digested municipal waste compost leachate as potential fertilizer: Comparison with a commercial fertilizer. J. Clean. Prod. 59, 73-78. https://doi.org/10.1016/j.jclepro.2013.06.044

Rout, P. R., Shahid, M. K., Dash, R. R., Bhunia, P., Liu, D., Varjani, S., and Surampalli,

R. Y., 2021. Nutrient removal from domestic wastewater: A comprehensive review on conventional and advanced technologies. Journal of Environmental Management, 296, 113246. https://doi.org/10.1016/j.jenvman.2021.113246

Saddoud, A., Ellouze, M., Dhouib, A., Sayadi, S., 2007. Anaerobic membrane bioreactor treatment of domestic wastewater in Tunisia. Desalination 207, 205-215. https://doi.org/10.1016/j.desal.2006.08.005

Safarova, V. I., Sapelnikova, S. V., Djazhenko, E. V., Teplova, G. I., Shajdulina, G. F., and Kudasheva, F. K., 2004. Gas chromatography-mass spectrometry with headspace for the analysis of volatile organic compounds in wastewater. Journal of Chromatography B, 800(1-2), 325-330. https://doi.org/10.1016/j.jchromb.2003.10.070

Saleh, I. A., Zouari, N., and Al-Ghouti, M. A., 2020. Removal of pesticides from water and wastewater: Chemical, physical and biological treatment approaches. Environmental Technology and Innovation, 19, 101026. https://doi.org/10.1016/j.eti.2020.101026

Salkunić, A., Vuković, J., and Smiljanić, S., 2022. Review of Technologies for the Recovery of Phosphorus from Waste Streams. Chemical and Biochemical Engineering Quarterly, 36(2), 91-116. https://doi.org/10.15255/CABEQ.2022.2066

Salkunić, A., Vuković, J., and Smiljanić, S., 2022. Review of Technologies for the Recovery of Phosphorus from Waste Streams. Chemical and Biochemical Engineering Quarterly, 36(2), 91-116. https://doi.org/10.15255/CABEQ.2022.2066

Santos, A.F., Arim, A.L., Lopes, D. V., Gando-Ferreira, L.M., Quina, M.J., 2019. Recovery of phosphate from aqueous solutions using calcined eggshell as an eco-friendly adsorbent. J. Environ. Manage. 238, 451-459. https://doi.org/10.1016/j.jenvman.2019.03.015

Sarker, P., Liu, X., Hata, N., Takeshita, H., Miyamura, H., and Maruo, M., 2023. Thermally modified bamboo-eggshell adsorbent for phosphate recovery and its sustainable application as fertilizer. Environmental Research, 231, 115992. https://doi.org/10.1016/j.envres.2023.115992

Schott, C., Yan, L., Gimbutyte, U., Cunha, J. R., van der Weijden, R. D., and Buisman, C., 2023. Enabling efficient phosphorus recovery from cow manure: Liberation of phosphorus through acidification and recovery of phosphorus as calcium phosphate granules. Chemical Engineering Journal, 460, 141695. https://doi.org/10.1016/j.cej.2023.141695

Selvasembian, R., Mal, J., Rani, R., Sinha, R., Agrahari, R., Joshua, I., and Pradhan, N., 2022. Recent progress in microbial fuel cells for industrial effluent treatment and energy generation: Fundamentals to scale-up application and challenges. Bioresource technology, 346, 126462. https://doi.org/10.1016/j.biortech.2021.126462

Sen, T.K., Afroze, S., Ang, H.M., 2011. Equilibrium, Kinetics and Mechanism of Removal of Methylene Blue from Aqueous Solution by Adsorption onto Pinecone Biomass of Pinus radiata 499-515. https://doi.org/10.1007/s11270-010-0663-y

Shabnam, N., Ahn, Y., Maksachev, A., Lee, J.H., Huang, C.P., Kim, H., 2019. Application of red mud based ceramic media for phosphate uptake from water and evaluation of their effects on growth of Iris latifolia seedling. Sci. Total Environ. 688, 724-731. https://doi.org/10.1016/j.scitotenv.2019.06.267

Shahid, M. K., Kashif, A., Rout, P. R., Aslam, M., Fuwad, A., Choi, Y., and Kumar, G., 2020. A brief review of anaerobic membrane bioreactors emphasizing recent advancements, fouling issues and future perspectives. Journal of Environmental Management, 270, 110909. https://doi.org/10.1016/j.jenvman.2020.110909

Shiba, N.C., Ntuli, F., 2017. Extraction and precipitation of phosphorus from sewage sludge. Waste Manag. 60, 191-200. https://doi.org/10.1016/j.wasman.2016.07.031

Siciliano, A., Limonti, C., Curcio, G. M., and Molinari, R., 2020. Advances in struvite precipitation technologies for nutrients removal and recovery from aqueous waste and wastewater. Sustainability, 12(18), 7538. http://dx.doi.org/10.3390/su12187538

Sikosana, M. L., Sikhwivhilu, K., Moutloali, R., and Madyira, D. M., 2019. Municipal wastewater treatment technologies: A review. Procedia Manufacturing, 35, 1018-1024. https://doi.org/10.1016/j.promfg.2019.06.051

Solaiman, Z.M., Murphy, D. V., Abbott, L.K., 2012. Biochars influence seed germination and early growth of seedlings. Plant Soil 353, 273-287. https://doi.org/10.1007/s11104-011-1031-4

Smol M, Preisner M, Bianchini A, Rossi J, Hermann L, Schaaf T, Kruopienė J, Pamakštys K, Klavins M, Ozola-Davidane R, et al. Strategies for Sustainable and Circular Management of Phosphorus in the Baltic Sea Region: The Holistic Approach of the InPhos Project. Sustainability. 2020; 12(6):2567. https://doi.org/10.3390/su12062567

Stamatelatou, K., Pakou, C., Lyberatos, G., 2011. Occurrence, Toxicity, and Biodegradation of Selected Emerging Priority Pollutants in Municipal Sewage Sludge, in: Comprehensive Biotechnology, Second Edition. Elsevier Inc., pp. 473-484. https://doi.org/10.1016/B978-0-08-088504-9.00496-7

Stepova, K., Fediv, I., Mažeikienė, A., Šarko, J., and Mažeika, J., 2023. Adsorption of Ammonium Ions and Phosphates on Natural and Modified Clinoptilolite: Isotherm and Breakthrough Curve Measurements. Water, 15(10), 1933. https://doi.org/10.3390/w15101933

Strydom, C.A., Hudson-Lamb, D.L., Potgieter, J.H. and Dagg, E., 1995. The thermal dehydration of synthetic gypsum. Thermochim. Acta, 269, 631-638. https://doi.org/10.1016/0040-6031(95)02521-9

Stuckey, D.C., 2012. Recent developments in anaerobic membrane reactors. Bioresource technology, 122, pp.137-148. https://doi.org/10.1016/j.biortech.2012.05.138

Sukmana, H., Bellahsen, N., Pantoja, F., and Hodur, C., 2021. Adsorption and coagulation in wastewater treatment–Review. Progress in Agricultural Engineering Sciences, 17(1), 49-68. https://doi.org/10.1556/446.2021.00029

Sun, D., Hale, L., Kar, G., Soolanayakanahally, R., Adl, S., 2018. Phosphorus recovery and reuse by pyrolysis: Applications for agriculture and environment. Chemosphere 194, 682-691. https://doi.org/10.1016/j.chemosphere.2017.12.035

Sun, E., Zhang, Y., Xiao, Q., Li, H., Qu, P., Yong, C., ... and Hunter, C., 2022. Formable porous biochar loaded with La-Fe (hydr) oxides/montmorillonite for efficient removal of phosphorus in wastewater: process and mechanisms. Biochar, 4(1), 53. https://doi.org/10.1007/s42773-022-00177-8

Sun, J., Xin, X., Sun, S., Du, Z., Yao, Z., Wang, M., and Jia, R., 2023. Experimental and theoretical investigation on degradation of dimethyl trisulfide by ultraviolet/peroxymonosulfate: Reaction mechanism and influencing factors. Journal of Environmental Sciences, 127, 824-832. https://doi.org/10.1016/j.jes.2022.07.025

Tambat, V. S., Tseng, Y. S., Kumar, P., Chen, C. W., Singhania, R. R., Chang, J. S., ... and Patel, A. K., 2023. Effective and sustainable bioremediation of molybdenum pollutants from wastewaters by potential microalgae. Environmental Technology and Innovation, 30, 103091. https://doi.org/10.1016/j.eti.2023.103091

Tang, Y., Gao, J., Liu, C., Chen, X. and Zhao, Y., 2019. Dehydration pathways of gypsum and the rehydration mechanism of soluble anhydrite-$CaSO_4$. ACS omega, 4(4), 7636-7642. https://doi.org/10.1021/acsomega.8b03476

Torbatinejad, N.M., Annison, G., Rutherfurd-Markwick, K., Sabine, J.R., 2007. Structural constituents of the seagrass Posidonia australis. J. Agric. Food Chem. 55, 4021-4026. https://doi.org/10.1021/jf063061a

Usman, M. O., Aturagaba, G., Ntale, M., and Nyakairu, G. W., 2022. A review of adsorption techniques for removal of phosphates from wastewater. Water Science and Technology, wst2022382. https://doi.org/10.2166/wst.2022.382

Vandeginste, V., 2021. Food waste eggshell valorization through development of new composites: A review. Sustain. Mater. Technol. 29, e00317. https://doi.org/10.1016/j.susmat.2021.e00317

Van der Roest, H. F., Lawrence, D. P., and Van Bentem, A. G. N., 2002. Membrane bioreactors for municipal wastewater treatment. IWA Publishing.

Vardanyan, A., Kafa, N., Konstantinidis, V., Shin, S.G. and Vyrides, I., 2018. Phosphorus dissolution from dewatered anaerobic sludge: Effect of pHs, microorganisms, and sequential extraction. Bioresource technology, 249, pp.464-472. https://doi.org/10.1016/j.biortech.2017.09.188

Vieyra, F.E.M., Palazzi, V.I., de Pinto, M.I.S. and Borsarelli, C.D., 2009. Combined UV-Vis absorbance and fluorescence properties of extracted humic substances-like for characterization of composting evolution of domestic solid wastes. Geoderma, 151(3-4), pp.61-67. https://doi.org/10.1016/j.geoderma.2009.03.006

Vinardell, S., Astals, S., Peces, M., Cardete, M. A., Fernández, I., Mata-Alvarez, J., and

Dosta, J., 2020. Advances in anaerobic membrane bioreactor technology for municipal wastewater treatment: A 2020 updated review. Renewable and Sustainable Energy Reviews, 130, 109936. https://doi.org/10.1016/j.rser.2020.109936.

Visvanathan, C., and Roy, P. K., 1997. Potential of nanofiltration for phosphate removal from wastewater. Environmental technology, 18(5), 551-556.

Vu, M. T., Vu, H. P., Nguyen, L. N., Semblante, G. U., Johir, M. A. H., and Nghiem, L. D., 2020. A hybrid anaerobic and microalgal membrane reactor for energy and microalgal biomass production from wastewater. Environmental Technology and Innovation, 19, 100834. https://doi.org/10.1016/j.eti.2020.100834

Vyrides, I., Andronikou, M., Kyprianou, A., Modic, A., Filippeti, A., Yiakoumis, C., Samanides, C.G., 2018. CO_2 conversion to CH_4 using Zero Valent Iron (ZVI) and anaerobic granular sludge: Optimum batch conditions and microbial pathways. J. CO_2 Util. 27, 415-422. https://doi.org/10.1016/j.jcou.2018.08.023

Vyrides, I., Conteras, P. A., and Stuckey, D. C., 2010. Post-treatment of a submerged anaerobic membrane bioreactor (SAMBR) saline effluent using powdered activated carbon (PAC). Journal of Hazardous Materials, 177(1-3), 836-841. https://doi.org/10.1016/j.jhazmat.2009.12.109

Vyrides, I., Stuckey, D.C., 2009. Saline sewage treatment using a submerged anaerobic membrane reactor (SAMBR): Effects of activated carbon addition and biogas-sparging time. Water Res 43, 933-942. https://doi.org/10.1016/j.watres.2008.11.054

Wahab, M.A., Hassine, R. Ben, Jellali, S., 2011. Posidonia oceanica (L.) fibers as a potential low-cost adsorbent for the removal and recovery of orthophosphate. J. Hazard. Mater. 191, 333-341. https://doi.org/10.1016/j.jhazmat.2011.04.085

Waheed, M., Yousaf, M., Shehzad, A., Inam-Ur-Raheem, M., Khan, M.K.I., Khan, M.R., Ahmad, N., Abdullah, Aadil, R.M., 2020. Channelling eggshell waste to valuable and utilizable products: A comprehensive review. Trends Food Sci. Technol. 106, 78-90. https://doi.org/10.1016/j.tifs.2020.10.009

Wang, R., Yang, C., Hu, H., Yang, Q., and Du, B., 2021. The impact of the varying nutrient concentrations on the enhanced biological phosphorus removal performance and functional phosphorus-accumulating and denitrifying genes in an anaerobic–aerobic–anoxic sequencing batch reactor. Environmental Technology and Innovation, 21, 101256. https://doi.org/10.1016/j.eti.2020.101256

Wang, S., Ma, M., Zhang, Q., Sun, G., Jiao, T., Okazaki, R.K., 2015. Efficient phosphate sequestration in waters by the unique hierarchical 3D artemia egg shell supported nano-Mg(OH)$_2$ composite and sequenced potential application in slow release fertilizer. ACS Sustain. Chem. Eng. 3, 2496-2503. https://doi.org/10.1021/acssuschemeng.5b00594

Waqas, M., Rehan, M., Daud Khan, M., Nizami, A.-S., 2018. Conversion of Food Waste to Fermentation Products. https://doi.org/10.1016/B978-0-12-812687-5.22294-6

Wazir, A., Gul, Z., Hussain, M., 2018. Comparative Study of Various Organic Fertilizers Effect on Growth and Yield of Two Economically Important Crops, Potato and Pea. Agric. Sci. 09, 703-717. https://doi.org/10.4236/as.2018.96049

Weber, W. J.; Jones, B. E. (1986), Toxic Substance Removal in Activated Sludge and PAC Treatment Systems, U. S. EPA-600/S2-86-045, Cincinati, OH

Wei, J., Meng, X., Wen, X., Song, Y., 2020. Adsorption and recovery of phosphate from water by amine fiber, effects of co-existing ions and column filtration. J. Environ. Sci. (China) 87, 123-132. https://doi.org/10.1016/j.jes.2019.05.009

Widiana, D. R., Wang, Y.-F., You, S.-J., Yang, H.-H., Wang, L.-C., Tsai, J.-H., and Chen, H.-M. (2019). Air Pollution Profiles and Health Risk Assessment of Ambient Volatile Organic Compounds above a Municipal Wastewater Treatment Plant, Taiwan. Aerosol and Air Quality Research, 19(2), 375-382. https://doi.org/10.4209/aaqr.2018.11.0408

Wijekoon, K.C., Visvanathan, C., Abeynayaka, A., 2011. Effect of organic loading rate on VFA production, organic matter removal and microbial activity of a two-stage thermophilic anaerobic membrane bioreactor. Bioresour Technol 102, 5353-5360. https://doi.org/10.1016/j.biortech.2010.12.081

Witek-Krowiak, A., Gorazda, K., Szopa, D., Trzaska, K., Moustakas, K., and Chojnacka, K., 2022. Phosphorus recovery from wastewater and bio-based waste: an overview. Bioengineered, 13(5), 13474-13506.

https://doi.org/10.1080/21655979.2022.2077894

Wright, M.M., Daugaard, D.E., Satrio, J.A. and Brown, R.C., 2010. Techno-economic analysis of biomass fast pyrolysis to transportation fuels. Fuel, 89, pp. S2-S10. https://doi.org/10.1016/j.fuel.2010.07.029

Wu, B., Dai, X., Chai, X., 2020. Critical review on dewatering of sewage sludge: Influential mechanism, conditioning technologies and implications to sludge re-utilizations. Water Res. 180, 115912. https://doi.org/10.1016/j.watres.2020.115912

Xia, W. J., Guo, L. X., Yu, L. Q., Zhang, Q., Xiong, J. R., Zhu, X. Y., and Jin, R. C., 2021. Phosphorus removal from diluted wastewaters using a La/C nanocomposite-doped membrane with adsorption-filtration dual functions. Chemical Engineering Journal, 405, 126924. https://doi.org/10.1016/j.cej.2020.126924

Xiang, Z., Chen, X., Bai, J., Rong, H., Li, H., Zhao, Y., and Huang, X., 2023. A novel anaerobic/aerobic-moving bed-dynamic membrane combined biofilm reactor (A/O-MB-DMBR) treating mariculture wastewater with chitosan (CTS): Performance, control and microbial community. Environmental Technology and Innovation, 29, 103009. https://doi.org/10.1016/j.eti.2023.103009

Xie, Q., Li, Y., Lv, Z., Zhou, H., Yang, X., Chen, J., and Guo, H., 2017. Effective adsorption and removal of phosphate from aqueous solutions and eutrophic water by Fe-based MOFs of MIL-101. Scientific reports, 7(1), 3316. https://doi.org/10.1038/s41598-017-03526-x

Yang, L., Huang, Y., Zhao, M., Huang, Z., Miao, H., Xu, Z., Ruan, W., 2015. Enhancing biogas generation performance from food wastes by high-solids thermophilic anaerobic digestion: Effect of pH adjustment. Int. Biodeterior. Biodegrad. 105, 153-159. https://doi.org/10.1016/j.ibiod.2015.09.005

Yang, X., López-Grimau, V., Vilaseca, M., Crespi, M., 2020. Treatment of textilewaste water by CAS, MBR, and MBBR: A comparative study from technical, economic, and environmental perspectives. Water (Switzerland) 12. https://doi.org/10.3390/W12051306

Yang, Y., Zhao, Y.Q., Babatunde, A.O., Wang, L., Ren, Y.X., Han, Y., 2006. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge

51, 193-200. https://doi.org/10.1016/j.seppur.2006.01.013

Yao, Y., Gao, B., Chen, J., Yang, L., 2013. Engineered biochar reclaiming phosphate from aqueous solutions: Mechanisms and potential application as a slow-release fertilizer. Environ. Sci. Technol. 47, 8700-8708. https://doi.org/10.1021/es4012977

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L., 2011. Bioresource Technology Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential. Bioresour. Technol. 102, 6273-6278. https://doi.org/10.1016/j.biortech.2011.03.006

Ye, M., Liu, J., Ma, C., Li, Y.Y., Zou, L., Qian, G., Xu, Z.P., 2018. Improving the stability and efficiency of anaerobic digestion of food waste using additives: A critical review. J. Clean. Prod. 192, 316-326. https://doi.org/10.1016/j.jclepro.2018.04.244

Yeoman, S., Stephenson, T., Lester, J. N., and Perry, R., 1988. The removal of phosphorus during wastewater treatment: a review. Environmental Pollution, 49(3), 183-233. https://doi.org/10.1016/0269-7491(88)90209-6

Zhao, B., Shang, Y., Xiao, W., Dou, C., Han, R., 2014. Journal of Environmental Chemical Engineering Adsorption of Congo red from solution using cationic surfactant modified wheat straw in column model. Biochem. Pharmacol. 2, 40-45. https://doi.org/10.1016/j.jece.2013.11.025

Zhao, J., Li, Y., Euverink, G.J.W., 2022. Effect of bioaugmentation combined with activated charcoal on the mitigation of volatile fatty acids inhibition during anaerobic digestion. Chemical Engineering Journal 428. https://doi.org/10.1016/j.cej.2021.131015

Zhang, N., Liu, W., Peng, Y., and Song, X., 2021. Anaerobic membrane bioreactors for livestock wastewater treatment and resource recovery: opportunities and challenges. Current Pollution Reports, 7, 277-285. https://doi.org/10.1007/s40726-021-00192-6

Zimmermann, J., Dott, W., 2009. Sequenced bioleaching and bioaccumulation of phosphorus from sludge combustion - A new way of resource reclaiming. Adv. Mater. Res. 71-73, 625-628. https://doi.org/10.4028/www.scientific.net/AMR.71-73.625

APPENDIX I

Title: Thermally treated eggshells in anaerobic digestion: buffering acidification in AD and evaluating end products from phosphate adsorption as soil conditioners.

Table S5-1. Concentration in mg L^{-1} of phosphates and other components in real wastewater solutions.

	Other components in Anaerobic effluent						**Nitric leachate**		**Sulfuric leachate**		**Anaerobic effluent**	
Elements	NO_3^-		NH_4^+		COD		PO_4^{3-}					
Time (h)	0	24	0	24	0	24	0	2	0	2	0	2
Concentration (mg L^{-1})	0.3	0.1	16.1	8.9	1058	999	104	16	124	3.4	70.8	15.2
Removal (%)	62.2		44.3		5.5		85		97.2		78.4	

APPENDIX II

Title: Phosphate recovery from the effluent of a submerged anaerobic membrane bioreactor using columns of eggshell and seagrass residues.

Table S6-1. Reject wastewater characterisation.

Values	AVG	STD
pH	7.91	-
Conductivity (mS cm^{-1})	4.97	-
TS (% w/w)	0.16	0.01
VS (% w/w)	26.79	3.21
Nitrates (mg L^{-1})	0.47	0.14
Phosphates (mg L^{-1})	29.68	1.74
Ammonium (mg L^{-1})	7.51	1.11
COD (mg L^{-1})	195.19	15.59

Table S6-2. Concentration of NH_4^+ and PO_4^{3-} during the SAnMBR and Column adsorption process.

Sample	**Time (d)**	**Ammonium (mg L^{-1})**	**Phosphate (mg L^{-1})**
SAnMBR Inlet*	**0**	10.40±0.76	25.74±3.33
	8	7.26±0.43	24.25±0.00
	16	6.82±0.23	22.34±4.15
	32	8.57±0.45	16.12±1.04
	50	8.26±0.47	24.45±1.96
SAnMBR Outlet*	**0**	8.68±0.00	23.65±3.20
	8	8.54±2.55	22.90±0.68
	16	10.36±4.92	20.10±2.99
	32	8.94±1.05	15.33±0.44
	50	7.54±0.26	19.26±0.28
EGSL Out*	**0**	- -	- -
	10	1.46±0.09	1.63±0.30
	21	5.62±0.47	1.93±1.03
	39	7.74±1.28	0.00±0.00
	60	4.92±0.96	2.26±0.46
SG Out*	**0**	1.75±0.68	1.13±0.68
	10	5.98±1.30	5.35±0.38
	21	7.17±3.72	6.78±0.42
	39	7.21±0.28	4.38±0.82
	60	6.15±0.87	6.73±0.69

*Values comprise sum of the concentration measured in the liquid phases and are given as average (mean) and standard deviation contents calculated over triplicates.

APPENDIX III

Title: SAnMBR followed by thermally treated biowaste and PAC adsorption processes for domestic wastewater treatment and resource recovery.

Table S7-1. Synthetic wastewater composition.

Constituent salt Concentration	**(mg L^{-1})**
Glucose	710.0
Sodium acetate	200.0
Sodium hydrogen carbonate	750.0
Ammonium chloride	90.0
Potassium dihydrogen phosphate	90.0
Magnesium sulphate	50.0
Calcium chloride	30.0
Sodium chloride	30.0
Yeast extract	15.0
Cysteine	500.0

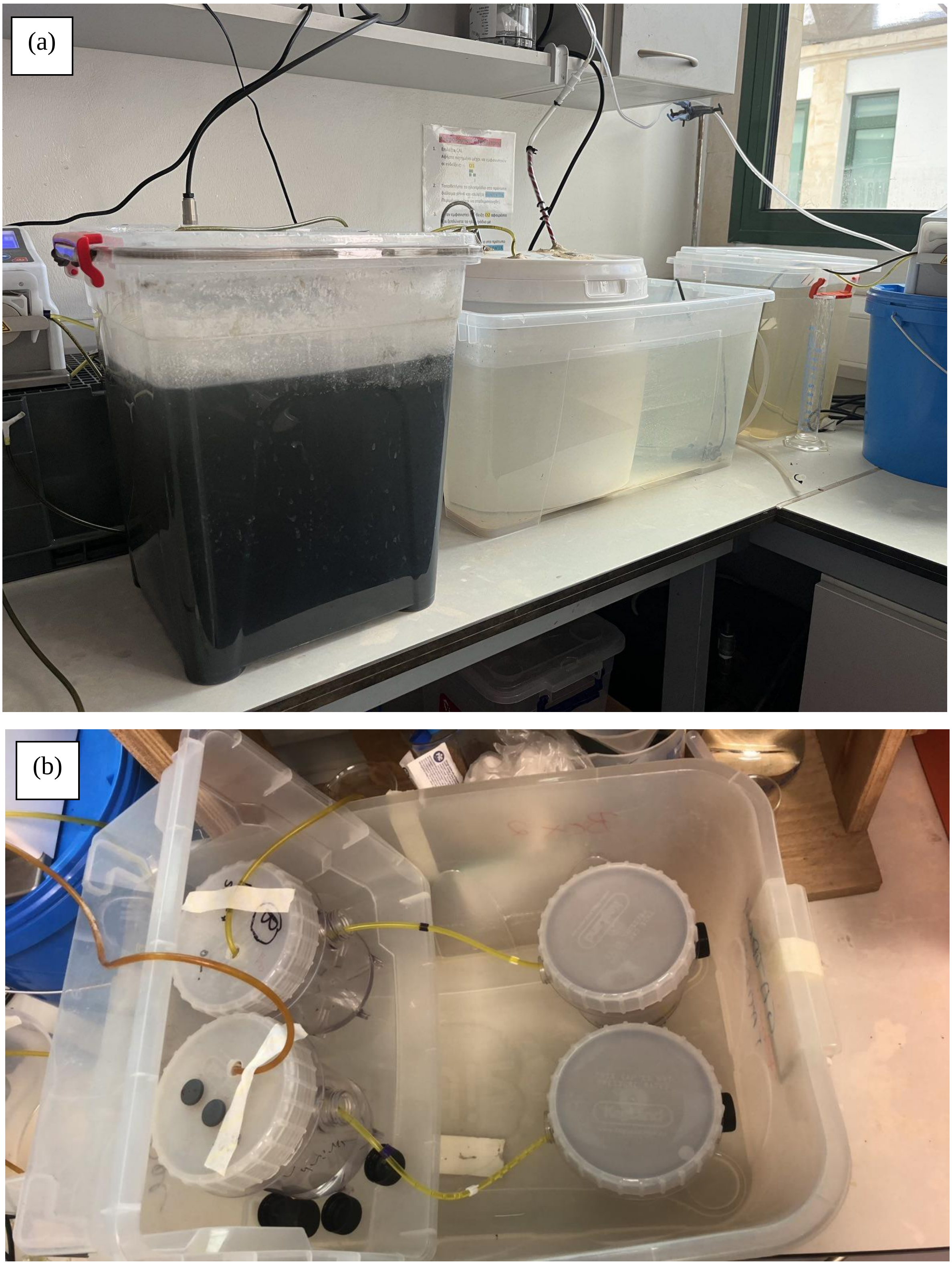


Fig. S7-1 (a-b). Pictures from the experimental configuration in the lab (a) SAnMBR (b) adsorption reactors with SG-TT, EGSL-TT and PAC.

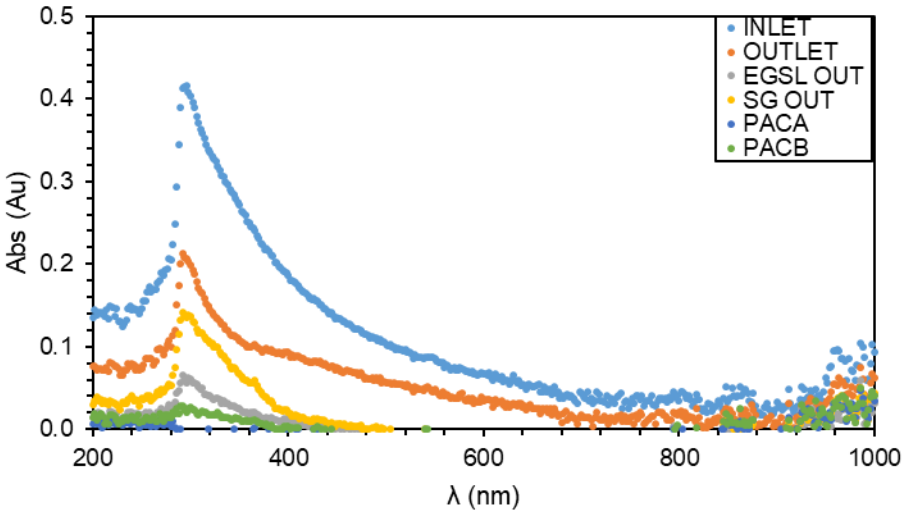


Fig. S7-2. UV/Vis spectra of (1) domestic effluent (2) SAnMBR effluent (3) eggshell effluent, (4) seagrass effluent and (5) effluent after PAC_A, and (6) effluent after PAC_B.

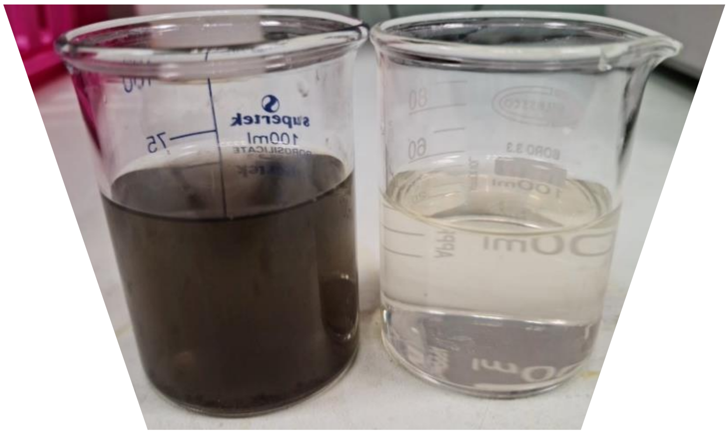


Fig. S7-3. Turbidity removal before and after the treatment process.

Table S7-2. PAC composition.

Property	**Value**
Loss on drying (105°C)	Max. 7 %
Granulation <= 40 µm Min.75 %	Complying
Iron (Fe)	Max. 0.3 %
Vapor Pressure	<0.1 mmHg (20 °C)

Autoignition Temperature	842 °F
Resistivity	1375 μΩ-cm, 20 °C (graphite)
Form	Powder

Table S7-3: VOCs detected in the wastewater inlet.

VOCs	**MW**	**Ref.**
Acids		
Acetic acid	60.03	
Butanoic acid	88.11	
Benzoic acid	122.12	
Nonanoic acid	158.23	
Hexanoic acid, 3,5,5-trimethyl-	158.24	
Alcohols		
2-propanol, 2-methyl-	74.12	
1-butanol, 2,2-dimethyl-	102.17	
2-butanol, 1-methoxy-	104.15	
1-Hexanol, 2-ethyl-	130.23	1
3-heptanol, 3,6-dimethyl-	144.25	
Cyclohexanemethanol, .alpha,. Alpha,4-trimethyl-	156.27	
Cyclohexanol, 4-(1,1-dimethylethyl)-, trans-	156.27	
7-Octen-2-ol, 2,6-dimethyl-	156.27	
3-octanol, 3,7-dimethyl-	158.28	
Aldehydes		
Butanal	72.11	3,5
Pentanal	86.13	5
Hexanal	100.16	3,5
Benzaldehyde	106.12	2,4
Heptanal	114.19	2,3,5
Octanal	128.21	3,5
Nonanal	142.24	3,5
Decanal	156.27	5
Amide		
Butamide, 3-methyl-	101.15	

Methyldiethanolamine	119.16	
Benzenethamine, 4-methoxy-. Alpha, -methyl-(+/-)	165.23	
Esters		
Acetic acid, methyl ester	74.08	
Butanoic acid, methyl ester	102.13	
Sulfurus acid, dimethyl ester	110.09	
Cyclopropanecarboxylic acid, isopropyl ester	128.17	
Propanoic acid, 2,2-dimethyl-, propyl ester	144.21	
Diethyl Phtalate	222.24	1
Hydrocarbons		
1-propene, 2-methyl-	56.11	
Benzene	78.11	2,2,3
n-Hexane	86.18	6
Toluene	92.14	2,2,3,4,5,6
Cyclopentyl acetylene	94.15	
Heptane	100.21	
p-xylene	106.16	1,2,3,4,6
7-methylbicyclo[4.2.0]octane	124.22	
1-Decene	140.27	
Decane	142.29	2
7-oxabicyclo[2.2.1]heptane, 1-methyl-4-(1-methylethyl)-	154.25	
Undecane	156.31	2
Cyclododecane	168.32	
1-Dodecene	168.32	
Ketones		
Acetone	58.08	6
2-Butanone	72.11	
2-pentanone	86.13	
3-pentanone	86.13	
Cyclohexanone	98.15	
3-heptanone	114.19	
Acetophenone	120.15	
2-heptanone, 4-methyl-	128.21	
Phorone	138.21	

Terpenes		
Fenchone	152.23	
Eucalyptol	154.25	
I-Menthone	154.25	
.alpha.-terpineol	154.25	
Linalool	154.25	
Camphor	152.23	
Levomenthol	156.27	
D-Limonene	136.23	2,6,7
Phenols		
Phenol	94.11	2,4
p-cresol	108.14	
3,5-difluorophenol	130.09	
Phenol, 2,3,5,6-tetramethyl-	150.22	
o-hydroxybiphenyl	170.21	
Phenol, 2-cyclohexyl-	176.26	
2,4-Di-tert-butylphenol	206.32	
Sulfides		
Disulfide, dimethyl	94.20	2,3,6,7
Dimethyl, trisulfide	126.26	4,6,8,9
Others		
Pyridine	79.10	
2-chloroprop-2-enamide	139.96	
4,7-methano-1H-indenol, hexahydro-	192.25	

References of Table S7-3

1. Dargnat, C., Teil, M.-J., Chevreuil, M., and Blanchard, M. (2009). Phthalate removal throughout wastewater treatment plant. *Science of The Total Environment*, *407*(4), 1235–1244. https://doi.org/10.1016/j.scitotenv.2008.10.027
2. Gomez-Rico, M. F., Fullana, A., and Font, R. (2008). Volatile organic compounds released from thermal drying of sewage sludge. *Water Pollution IX*, 425–433. https://doi.org/10.2495/WP080411

3. Almatouq, A., Ahmed, M. E., Khajah, M., and Al-Yaseen, R. (2022). Assessment of Volatile Organic Compounds Removal in Kuwait Wastewater Treatment Plants. *International Journal of Environmental Science and Development*, *13*(6), 287–291. https://doi.org/10.18178/ijesd.2022.13.6.1406
4. Liang, Z., Wang, J., Zhang, Y., Han, C., Ma, S., Chen, J., Li, G., and An, T. (2020). Removal of volatile organic compounds (VOCs) emitted from a textile dyeing wastewater treatment plant and the attenuation of respiratory health risks using a pilot-scale biofilter. *Journal of Cleaner Production*, *253*, 120019. https://doi.org/10.1016/j.jclepro.2020.120019
5. Dincer, F., and Muezzinoglu, A. (2008). Odor-causing volatile organic compounds in wastewater treatment plant units and sludge management areas. *Journal of Environmental Science and Health, Part A*, *43*(13), 1569–1574. https://doi.org/10.1080/10934520802293776
6. Widiana, D. R., Wang, Y.-F., You, S.-J., Yang, H.-H., Wang, L.-C., Tsai, J.-H., and Chen, H.-M. (2019). Air Pollution Profiles and Health Risk Assessment of Ambient Volatile Organic Compounds above a Municipal Wastewater Treatment Plant, Taiwan. *Aerosol and Air Quality Research*, *19*(2), 375–382. https://doi.org/10.4209/aaqr.2018.11.0408