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Plant Extracts as an Effective Solution to Mitigate Marine Pollution

Kaniklides Stavros [α] & Costas N. Costa [σ]

Abstract- Pollution in the marine environment has become a serious problem and the removal of pollutants from the sea has become a topic of great interest to researchers. In this regard, this paper attempts to examine the potential of plant extracts to act as anti-polluting agents of marine environment without degrading its flora and fauna. The present paper focuses on the use of the MSL formula and investigates its efficiency as a natural herder for the reduction of organic matter (including hydrocarbons) in marine waters.Tests for toxicity, Total Petroleum Hydrocarbon (TPH) removal, degradation and dispersant efficiency, as well as microbiological tests, were performed using the MSL product as the plant extract based formula (made up of 89 per cent plant extract solution, 3 percent hydrogen peroxide and 8 per cent of Isopropyl alcohol). Furthermore, four different parameters such as COD, BOD, TPH and FOG were analyzed in order to determine the effectiveness of the MSL formula. The present study has determined that the safe administration of the product will not affect aquatic life and hence this plant extract based formula will not function/behave as a polluting agent. The effectiveness of the MSL product was studied on site against different organic compounds by monitoring its activity and effects in the context of the Ayia Napa Port Project. Consequently, biodegradation test indicated that the maximum degradation rate of the mixture of the MSL and Arabian crude oil was 90.48 % after 96 hours of activity. The results demonstrate that plant extract formulas such as the MSL formula have the potential to act as eco-friendly, biodegradable, non-toxic, and cost-effective alternatives to be utilized in restoration strategies and clean up operations in marine environments.

I. Introduction

Industrialization as a mainstream basis for human development into new environments and habitats has resulted in an increasing rate of pollution wherein the marine ecosystem is being continuously subjected to the harmful effects of human activity. Both sea-based and off-shore based industrial operations have been contributing to marine pollution (Todd, Ong, & Chou, 2010). Among the various activities that contribute to marine pollution include oil and fuel spills from ship engines, run offs containing organic materials, disposal of construction materials containing solvents and paints, and accidents such as boat sinkings or sewage disposals (Fartoosi, 2013). The effects of these pollutants include the accumulation of organic and inorganic materials in the ocean, oil sedimentation, reduction of UV disinfection, increasing levels of water toxicity, algae and bacterial blooms, and foulodors (Tornero & Hanke, 2016). The main impact of pollution in marine environments is the disruption of the entire marine life and marine biodiversity (Derraik, 2002). Crude oil spills are one of the most hazardous pollutants for the marine ecosystem, thus considerable resources have been expended in efforts to try and limit their impact. One way to clean such spills is through the use of a special type of amphiphile known as chemical herder which is sprayed to the surface of the water where oil is spilled (Athas et al., 2014).Over the years, amphiphiles from plant extracts have been gathering more attention. The mechanism through which plant extracts work as anti-pollutant agents in water column is a topic that warrants further investigation. The pollution of water bodies such as lakes, rivers, ports etc. can be addressed through various ways such as reducing the surface tension of water to allow the spills to extend over a region for easy evaporation or increasing the forces of adhesion of the pollutants to make them come together either for the ease of burning or collecting of the waste material (Gunde, Dawes, Hartland, & Koch, 1992; Sridhar & Rami Reddy, 1984). As a result, reverse engineering is needed to understand how plant extracts work as antipollution solutions in water bodies. This paper provides an extensive discussion of plant extracts as an antipollution solution in water column by presenting the mechanism through which these extracts achieve their antipollution effects; furthermore, acceptance of their use as a dispersant is examined under the EPA Regulatory Protocol guidelines (Environmental Protection Agency, 2017).This paper focuses specifically on MSL, a plant extract based formula, and discusses its efficiency in the dispersion of oil spills in water column and the oil biodegradation rate upon treatment with the formula. Several advantages of the use of the MSL product as a plant extract alternative to the commercially available chemical dispersants have also been identified and are discussed in the paper.

II. Review Of Literature

The use of dispersants is increasing worldwide and guidelines are readily available for their substantial use in industrial settings (ExxonMobil Research and Engineering Company, 2008). However, their use in natural environments such as the aquatic ecosystem is

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controversial as these dispersants also have potential drawbacks. Most dispersants used in the sea do not exhibit significant levels of toxicity. Measured levels are on par with the toxicity observed in shampoos and household liquid dish wash solutions (Word, Clark, & Word, 2015). However, these dispersants are chemicals and when added to an area that has been negatively impacted due to oil spills only serves to further increase the levels of pollution in the affected area. Furthermore, when an oil slick is dispersed, it further mixes toxic substances into the water thereby becoming hazardous to living organisms (Prince, 2015). Hence, the need persists to develop natural dispersants that could potentially be used as dispersants without harming marine environments.

Plant extracts have been used over the years in water purification applications and schemes. Some studies have claimed that the coagulation properties of plant extracts such as M. oleifera make them suitable for the treatment of wastewater (Ghebremichael, 2004). Studies have also focused on the use of plant extracts for treating surface water (Jahn, 1986; Sanghi, Bhattacharya, Dixit, & Singh, 2006). Das and Chandran (2011) presented an updated overview of the petroleum hydrocarbon degradation by microorganisms under different ecosystems. Chachere (2012) reported on a team of USF researchers who demonstrated that the mucilage from prickly pear cactus also works as a natural, non-toxic dispersant for oil spills. The USF group, led by chemical engineering professor Norma Alcantar, carried out research to identify effective alternatives to chemical dispersants. According to the study, unlike chemical dispersants, cactus mucilage is non-toxic and is harmless to the marine environment.

Guo et al. (2014) aimed at utilizing a natural dispersant that was extracted from a cactus plant native to Mexico to form oil-in-water emulsions. In this process, the natural biomaterials extracted from the cactus plant are responsible for causing the dispersion of the oil phase into the water. The use of plant extracts as anti-pollutant solution in the water column was elaborated in detail by Gupta et al. (2015).The plant extract, phytol, is also biodegradable in the marine environment (Ramlagan, 2017). According to Gupta et al. (2015), phytol has an allylic bond next to the ester functional group which facilitates the hydrolysis of the amphiphile and as a result releases a highly water-soluble cationic group into the water column where it is readily diluted.

Zeiger et al. (2016) further recognized that the common cleanup methods for oil spills still have challenges due to the chemicals used, as these chemicals absorb large amounts of water in addition to the oil itself, thus rendering the entire process less effective. They further identified two aquatic plants, Salviniamolesta and Pistiastratiotes, which possess special characteristics due to their trichome-covered surface that repels water. This characteristic of the plants is a result of their hydrophobic surface chemistry and hierarchical micro and nano scale surface structure. Hydrophobic surface chemicals such as wax protect the plant from excessive evaporation of water, mechanical damage and degradation by water (Zeiger et al., 2016). An experiment was conducted by O'Brien and Tobin (2016) at the National Science Foundation to determine the effect of sunlight on oil spillage in a marine environment. According to the study, when the oil is exposed to excessive sunlight, light energy initiates or catalyzes certain chemical reactions that convert the spilled liquid oil into sludge. This sludge then inhibits the process of oil degradation. Consequently, as a result of this experiment, the researchers were able to come up with models that could assist with the design of optimum cleanup strategies for the marine environment (O'Brien & Tobin, 2016).

Choi & Cloud (1992) investigated the use of natural sorbents for the cleanup of oil spills and more specifically, tested the efficiency of milkweed (Asclepias) to remove spilled oil. However, treatment by alkali scouring agents reduces the oil sorption capacity of milk weed and cotton fiber significantly. It was further shown that with appropriate mechanical equipment, the recovery of absorbed crude oil from milkweed and cotton can be facilitated wherein the fiber can be reused several times during the cleanup. The results of the research demonstrate that partial or total commercial synthetic oil sorbent substitution using natural sorbent materials is advantageous for oil spill cleanup operations.

Some of the more commonly used chemical herders are silicone polyethers (identified as SilsurfA108 and Silsurf A004-D)(Ottawa, 2012). However, these chemical herders are not biodegradable and will persist in the marine environment even long after the oil has been burnt in situ. These chemical herders have high levels of water toxicity contributing to increased secondary adverse impacts to the marine life (Lassen, Hansen, Mikkelsen, & Maag, 2005). Green herding is an alternative to chemical herding as green herders are degradable and exhibit reduced levels of water toxicity compared to chemical herders (Wanger sky, 1982).

The role of dispersants is not only to mix small droplets with water and allow the natural degradation and microbial action to take place more efficiently, but to also disperse the oil in an extended area so as to facilitate faster evaporation of the oil. When the oil-water tensile force is reduced, the polluting oil is allowed to spread within a broad area, which exposes more of the oil to direct sunlight as well as increases the surface-volume ratio to evaporate the oil naturally. The spreading of oil over a large section of a marine environment also means that the harmful effects of the oil spill are felt not just in a single region but are spread across an expansive region, thereby minimizing their effectiveness (Allen, 1984).

Another identified method for cleaning up marine environments is phytoremediation, or phytoextraction (Zalewsk & Nogalska, 2014). These methods involve a number of processes that utilize plants for the uptake, storage and degrading of contaminants within the plant tissues. Yet another process uses disphytostimulation or rhizodegradation, which utilizes hizospheric associations between the plants and symbiotic microbes to degrade the oil spills (Oh, Cao, Li, & Cheng, 2014). Phytovolatilization, based on the ability of plants to uptake pollutants from the growth matrix, which subsequently transforms and volatilizes the pollutants to the atmosphere, has also been used in marine environments (Limmer & Burken, 2016).

When the oil is spilled in seawater, one way to clean it up is through absorption of the oil, leaving the seawater intact. In such cases, plant extracts have been used to absorb oil pollutants from the marine environment. The most common materials used include sawdust and other aquatic plants. A major shortcoming of these traditional materials is that they absorb both oil and water and thus are less effective in selectively removing the oil from a water environment. With this in mind, researchers have investigated plants that can potentially repel water (super hydrophobic) and at the same time attract oil (super oleophilic). These materials could theoretically achieve selective absorption of oil. Two plant materials that have been identified and isolated for such a purpose are Salviniamolesta and Pistiastratiotes. These plants have certain structural characteristics that allow them to repel water and attract oil (Zeiger et al., 2016). The advantage of these materials is that they do not have any negative impact on the aquatic life. They are biodegradable and can be processed by microbes if traces of their residues remain in the marine environment. The selective absorption properties of these materials imply that they do not interfere with seawater either, however, they cannot be effective in cases of large spills especially when oil spills occur in the deep seas. Research studies have also attempted to investigate whether plant extracts could act as anti-pollutants in marine environments through chemical action, in cases where plant materials have been utilized to achieve the cleanup, usually in small-scale oil spillage incidents. And although plant extract based amphiphiles are biodegradable, they might prove hazardous to marine life, hence, there is a need to carefully examine levels of toxicity when using such extracts. In this regard, the MSL solution, which is a plant extract formulation and is the focus of the present study, is investigated in terms of its cleanup efficiency, toxicity and bio-degradability.

III. Methods

Having thoroughly examined and extensively explained the advantages of natural herders, the present paper has focused on exploring the use of the MSL formula and investigating its efficiency as a natural herder for the reduction of organic matter (including hydrocarbons) in marine waters. Absorbance measurements have been used to assess concentrations of crude oil using the UV/V spectrophotometer and demonstrate the efficiency of MSL as a dispersant. MSL is used as the plant extract formula, which is made up of 89 per cent plant extract solution, 3 per cent hydrogen peroxide and 8 per cent Isopropyl alcohol. Several tests have been conducted to understand the efficiency, mechanism of action and degradation capabilities of the MSL product. The research study was designed to determine the efficiency of the natural herders wherein degradation tests for the known oil dispersant were also conducted. Furthermore, toxicity studies were undertaken to examine the optimum concentration of the formula in seawater.

a) Efficiency and degradation tests

For the determination of the efficiency index of the MSL formula, Appendix A to WSL Report LR 448 (OP) was used to guide the experiment. This is a guideline specification that relates to procedures for applying oil spill dispersants at sea or on beaches and is prepared in compliance with UK recommendations before any dispersant can be recommended for use.

Effectiveness assessment is important for a dispersant to attain the global standards and for the marketability of the product. Firstly, the efficiency test of the sample of MSL as a dispersant was performed. In the preparation of dispersed oil, the stock of dispersed oil was prepared by adding 5 ml of crude oil to natural seawater. The mixture was prepared in the ratio of 1:10 for MSL and crude oil respectively. The mixture was shaken vigorously for 10 minutes. The absorbance reading was taken for different concentrations of crude oil using a UV spectrometer at 580 nm. The calibration curve for absorbance versus different concentrations of crude oil was plotted. In order to determine the effectiveness as a dispersant, the following formula was used:

Efficacy %= (Final weight (g) of crude oil × 100)/ (initial weight (g) of crude oil)

In addition, bio-degradation tests were conducted with the sample solution of the MSL formula.The degradation test was conducted for 96 hours. After the data was tabulated (Table 1), the curve of the residual concentration mix against the time taken for observation of the rate of biodegradation was plotted (Fig. 1).

b) Toxicity tests

The toxicity tests were conducted under three different test conditions where natural phytoplankton, shrimp and fish where mixed with the MSL product. The formula was first tested in natural zooplankton population (Table 2), then in shrimp population (Table 3) and then in fish (Table 4) wherein the test conditions included salinity of 39 per cent, temperature of 23 – 24 °C and pH of 7.5- 8.The concentration of the MSL solution was increased from 25 to 400 ppm wherein a Chi2 test was used to examine whether a best fit was acquired.

c) Total Petroleum Hydrocarbon (TPH) removal tests

Tests were performed to examine the efficiency of the MSL plant extract formulation in reducing hydrocarbons in the coastal waters of the city of Limassol wherein the MSL product was sprayed to the surface of the seawater using a specially equipped boat. It was observed that the entire dispersion process of the MSL formula, from the addition to the water column of the marine environment to the end of the biodegradation phase, occurs in five stages. In stage one, the oil spill is black in color at the surface of water column with some oil stuck to the sediments in the marine environment. In stage two, the solution turns brown when the MSL formula has acted on the oil and the evaporation is at its initial stage. In stage 3, the solution is light brown in color and there is moderate evaporation and biodegradation. In stage 4, a sheen solution is formed and the pollutant has started to clear at the end of the evaporation process. Finally, the marine environment is clean and there is adequate ventilation of the water and the aquatic life can thrive without being affected by any toxicity in the marine environment. Samples of seawater were taken 2 hours after spraying the formulation. The treatment with the MSL product was carried out by spraying the formula in a specific route twice in a 2-week span at a distance of about 200 meters from the coastline. The points for analysis were taken from the Old Port to the Crown Plaza Hotel in Limassol.

d) Microbiological tests

Microbiological tests were performed in the same region specified in the previous section (Limassol coast line). Enterobacter, E. coli, and Enterococcus colonies were examined in 100 ml seawater samples taken during the same 2-week span. The values of colonies per 100 ml were checked both before and after treatment

e) Test of other contaminant parameters

Several tests were carried out in marine locations to determine the effectiveness of the MSL formula on different contaminant parameters: biological oxygen demand (BOD), chemical oxygen demand (COD), total petroleum hydrocarbons (TPH), and Fats oils and Grease (FOG).TP (Total Phosphorous) and TKN (Total Kjeldahl Nitrogen) were also tested as additional parameters.

IV. Results and Discussion

In the process of cleanup and dispersion of oil spills in the marine environment, the MSL formula works through a mechanism of action, the effectiveness of which is based on the high surface tension process. MSL acts to change the surface tension of the water column relative to that of the oil spills and consequently affects the interaction of the two liquid molecules. Marine environment pollutants such as oil spills and other organic compounds are composed of hydrocarbon compounds. When these organic compounds come into contact with the MSL formula, a significant surface tension reaction is initiated. This results in organic components taking the maximum surface area on the surface of water. The larger surface area of the oil implies that the rate of evaporation of these pollutants will increase and thus the degradation rate will also increase. When the MSL formula comes into contact with the organic compounds, the cohesive forces within the molecules are significantly reduced. As a result, the surface tension of the water in relation to oil, or the oil-water interface force is greatly reduced, resulting in the oil molecules spreading on the surface of water column. The oil is also broken down into tiny droplets of oil that spread over a large surface area, and through the action of solar rays, the oil evaporates at a faster than normal rate. Another way through which the MSL process facilitates the marine environment cleanup process is through the breaking down, by microbes, of the small droplets of oil created after the dispersion action, resulting in an accelerated rate of natural degradation. The evaporation and the natural degradation of the oil spill result in an immediate reduction in the concentration of the oil- MSL mix, as is the case with organic oil solutions such as Arabian crude oil. In the case of organic sediments such as TPH (Total Petroleum Hydrocarbons), the actions of the MSL formula at the early stage should convert the organic sediments to liquid form, and then facilitate their dispersion and evaporation.

Thus, it is imperative to examine the efficiency, bio-degradation capability and the toxicity properties of the MSL formula, which is important for examining its safety and efficiency in real world scenarios.

In order to calculate the efficiency of the sample that was used in the laboratory, the formula for efficiency was used:

$$\text{Effectiveness (\%)} = \text{Total oil dispersed x } 100/(\ell_{oil}V_{oil})$$

$$\text{Effectiveness (\%)} = \text{Final weight (g) of crude oil x } 100/\text{initial weight (g) of crude oil}$$

$$= 3.99 \text{ x } 100/4.62$$

$$= 86.36\%$$

The next procedure involved the biodegradation test of the sample solution of the MSL formula. The degradation test was conducted for 96 hours and the following table was prepared.

Table 1: Results of degradation test

Time (hr)	Abs*Dil	Residual Concentration (ppm)	Degradation (%/day)	Cumulative degradation (%)
0	0.420	4740.00	0.00	0.00
24	0.230	2595.71	45.24	45.24
48	0.090	1015.71	33.33	78.57
72	0.060	677.14	7.14	85.71
96	0.040	451.43	4.76	90.48

After the data was tabulated, the curve of the residual concentration mix against the time taken for observation of the rate of biodegradation was plotted in Figure 3.

When the experiment was conducted to determine the efficiency of the MSL as the plant extract formula using Arabian crude oil as the oil spill in a water column, the test indicated that the MSL is efficient when used as a crude oil anti-pollutant or used in any dispersant capacity. The efficiency of the MSL was found to be 86.36%. This was found to be far greater that the 60% efficiency for a dispersant which is recommended by EPA 1993. This means that when the MSL is used in the cleanup of marine environment after an oil spill has occurred, it will remove at least 86% of the crude oil that has spilled into the sea.

The biodegradation test indicated that the maximum degradation rate of the mixture of the MSL and the Arabian crude oil was 90.48 % after 96 hours. This corresponded to 72.38% of the initial concentration of 4740mg/L (ppm). The finding demonstrated that the rate of MSL biodegradation is high during the oil spill cleanup process. This rate of degradation means that when MSL is used in the case of an oil spill, after 96 hours over 90% of the oil and MSL mixture will be degraded.

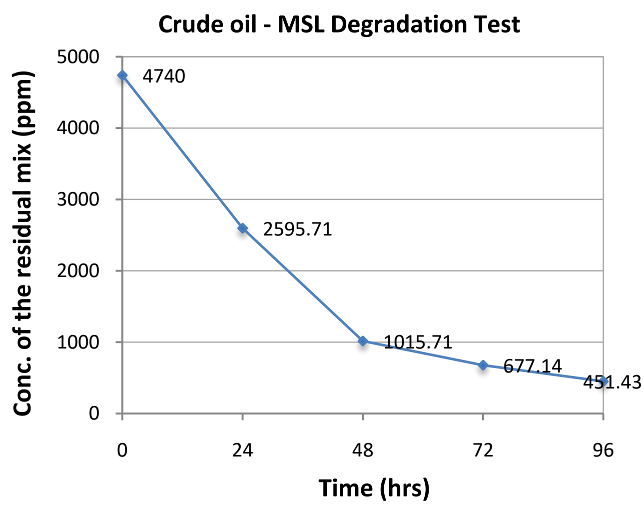


Figure 1: Biodegradation test for mix of crude oil and MSL after 96 hr.

For the toxicity tests, the MSL formula was first tested in the natural zooplankton population wherein the test conditions included salinity of 39 per cent, temperature of 23 – 24 °C, pH of 7.5- 8and with Chlorella salina as the predominant organism. The concentration of the MSL solution was increased from 25 to 400 ppm wherein a Chi2 test was used to examine whether a best fit was acquired. The results of the toxicity tests in natural phytoplankton population revealed that the average number of cells was reduced significantly wherein with (n-2) degrees of freedom (9-2=7), a critical Chi2 value of 2.167 was acquired (which is less than the total Chi2 of 35.08, see Table 3).

Table2: Toxicity tests with natural phytoplankton population

No.	Concentration (ppm)	Average of cells x 10^6 / ml after 96 h	% reduction compared to control	Chi2 test
1	Control	19.4	0	0.00
2	25	17.7	8.8	0.37
3	50	16.4	15.4	1.14
4	100	16.3	20.6	1.21
5	150	15.0	23	2.45
6	200	15.1	22	2.34
7	250	14.3	26	3.29
8	300	11.8	39	7.30
9	400	7.8	59	17.00
Total Chi2				35.08

The MSL is then tested in seawater containing shrimp population wherein the test conditions included salinity of 39 per cent, temperature of 23 – 24 °C, pH of 7.5- 8 and with Palaemonserratus as the predominant organism. The concentration of the MSL solution was increased from 50 to 600 ppm wherein a Chi2 test was used to examine whether a best fit was acquired. The results of the toxicity tests in the shrimp population demonstrated that the average number of cells was reduced significantly after 96 hours wherein with (n-2) degrees of freedom (12-2=10), a critical Chi2 value of 3.94 was acquired, which was less than the total Chi2 at 48.00 (Table 4).

Table 3: Toxicity tests with Shrimp

No.	Concentration (ppm)	%observed mortality	Chi2 test
1	Control	0	2.00
2	50	0	2.00
3	100	0	2.00
4	150	0	2.00
5	200	0	2.00
6	250	0	2.00
7	300	0	2.00
8	350	10	10
9	400	10	10
10	500	30	30
11	550	60	60
12	600	90	90
Total Chi2			48.00

The MSL formula was then tested in seawater with fish population wherein the test conditions included salinity of 39 per cent, temperature of 23 – 24 °C, pH of 7.5- 8 and with Mugilcephalus as the predominant organism. The concentration of the MSL solution was increased from 50 to 600 ppm wherein a Chi2 test was used to examine whether a best fit was acquired. The results of the toxicity tests on the fish population revealed that the average number of cells was reduced significantly after 96 hours wherein with (n-2) degrees of freedom (12-2=10), a critical Chi2 value of 3.94 was acquired, which was less than the total Chi2 at 48.55 (Table 5).

Table 4: Toxicity tests with fish

No.	Concentration (ppm)	%observed mortality	Chi2 test
1	Control	0	3.80
2	50	0	3.80
3	100	0	3.80
4	150	0	3.80
5	200	0	3.80
6	250	10	2.06
7	300	10	2.06
8	350	30	0.17
9	400	50	0.38
10	500	80	4.64
11	550	100	10.12
12	600	100	10.12
Total Chi2			48.55

The entire dispersion process of the MSL formula from the addition to the water column in the marine environment to the end of the biodegradation stage occurs in five states. In stage one, the oil spill is black in color at the surface of water column with some stuck at the sediments in the marine environment. In stage two, the solution turns brown when the MSL product has acted on it and the evaporation is at its initial stage. In stage 3, the solution is light brown in color and there is moderate evaporation and biodegradation. In stage 4,a sheen solution is formed and the pollutant has started to clear at the end of the evaporation process. Finally, the marine environment is clean and there is adequate aeration of the water and the aquatic life and thrive again without being affected by the possible toxicity of the environment. This process is shown in Figure 2.

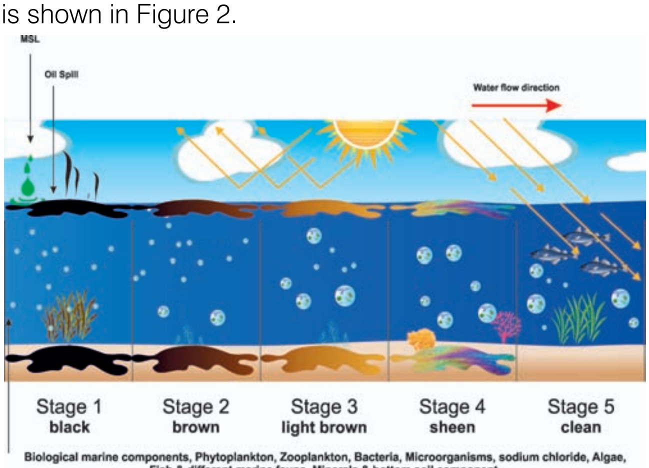


Figure 2: Mechanism of action of MSL on oil spills in the marine environment

An EPA supervised test to assess reduction of the Total Petroleum Hydrocarbons (TPH) on the marine sediments in the Larnaca Marina showed similar results to the reduction rate observed in this experiment. The initial concentration of the TPH given in mg/kg was tested at various dates between June and December of 2016. The initial concentration of the TPH was at 1191.00 mg/kg, and at the end of the test period (6 months) the TPH concentration was at 54.10 mg/kg. This represented a remarkable 95% reduction in the concentration of TPH. The curve drawn for the concentration (mg/kg) against time in sampling dates, showed a similar negative slope as the one shown for the MSL action on the Arabian crude oil. However, the difference in the time taken for the reduction in the TPH concentration in the two cases could be attributed to the different levels of starting concentrations used for the Arabian crude oil and the TPH. The higher percentage decrease in the concentration of the TPH can be attributed to the longer time of test compared to only 96 hours that was used for the MSL action on the Arabian crude oil. The curve that was obtained for the Larnaca test is shown in Figure 3.

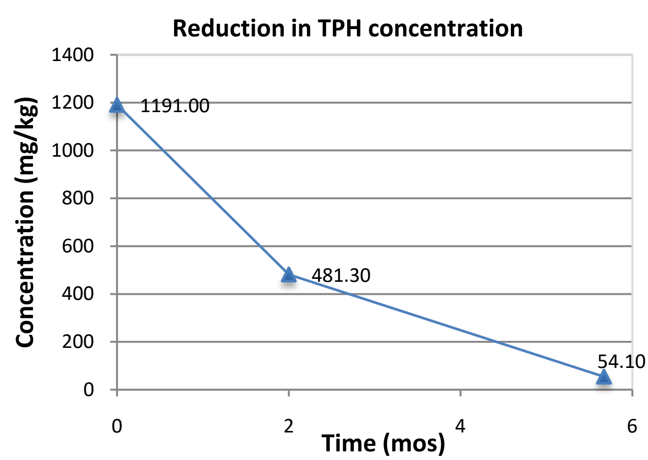


Figure 3: Reduction of TPH concentration using the MSL formula at the Larnaca Marina

The MSL formula has further advantages such as efficiency for cleaning up both the organic compounds deposited on the surface of water column and those that are deposited on sediments in the marine environment. This ensures that all traces of organic compounds that have adverse impacts on the marine environment degrade completely. This is especially important in the case of pollution that occurs when organic compounds are washed down from higher grounds through surface run-off and rest on sediments on the beaches of water bodies. The action of the MSL formula ensures that all the pollutant traces and the dispersant traces are cleaned up thoroughly after the application. This is possible because MSL is biodegradable unlike chemical dispersants, traces of which can be found in the marine environment after they have carried out their dispersion function. This can be attributed to the fact that chemical dispersants are not biodegradable while their efficiency is below that of MSL meaning traces of the organic compounds they are meant to clean up will still be present in measurable quantities in the marine environment. After the application of the MSL formula, oil molecules are broken down into tiny droplets most of which evaporate easily while the remaining are degraded by the microbes in the marine environment. The use of MSL leaves the marine environment in the state prior to the use of the formula and it may even clean other pollutants that are present even before the oil spillage incident occurs. In order to illustrate the clean up capabilities of the MSL formula, images of the Nissi Beach in Ayia Napa, Cyprus, before and after the use of the product are shown in Figures 4 (a) and (b). This effect was achieved within a 7-day treatment period in July 2016.

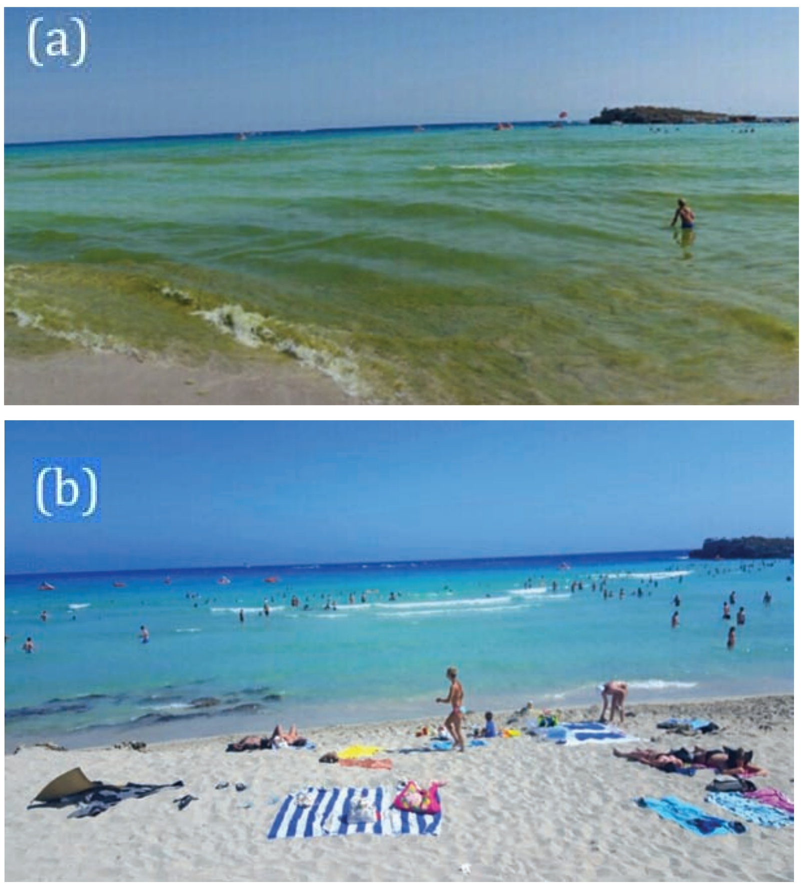


Figure 4: Nissi Beach (a) before and (b) after treatment with the MSL formula

Furthermore, the present study examined the application of the MSL formula on the coastline of Limassol, which revealed a significant reduction in the concentration of TPH in the seawater samples tested (Figure 5). In addition, significant reduction in the Enterobacter, E.coli, and Enterococcus colonies was observed in the samples of water taken twice during the 2-week span of the treatment (Figures 6-8).The MSL formula can be applied in an open marine environment where it is exposed to sunlight and the action of microbes that can facilitate the process of degradation. The product can also be applied to different concentrations of oil spills depending on the type of crude oil and, in this case, there are other factors that affect the process of dispersion. Seawater salinity, waves and water currents, exposure to sunlight, concentration of microbes, and concentration of pollutants are highly likely to affect the process. Sunlight is the first factor that affects the rate of dispersion. After organic compounds are spread on the surface of water, the intensity of sunlight then determines the rate of biodegradation through evaporation. In the case where there is intense solar radiation, the evaporation process takes place rapidly, which implies that the degradation will take place faster. Thus, the MSL formula is more efficient in intense sunlight.

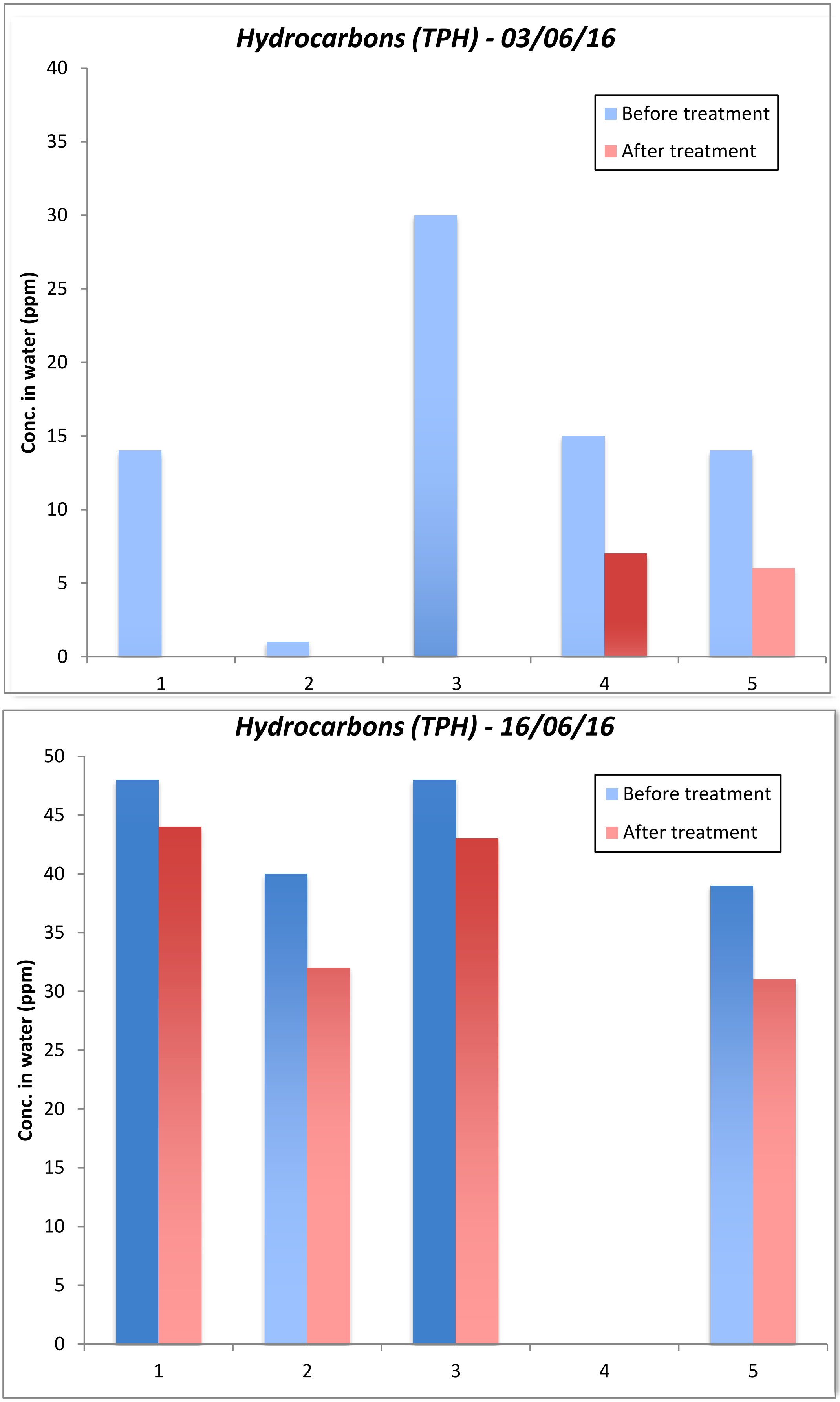
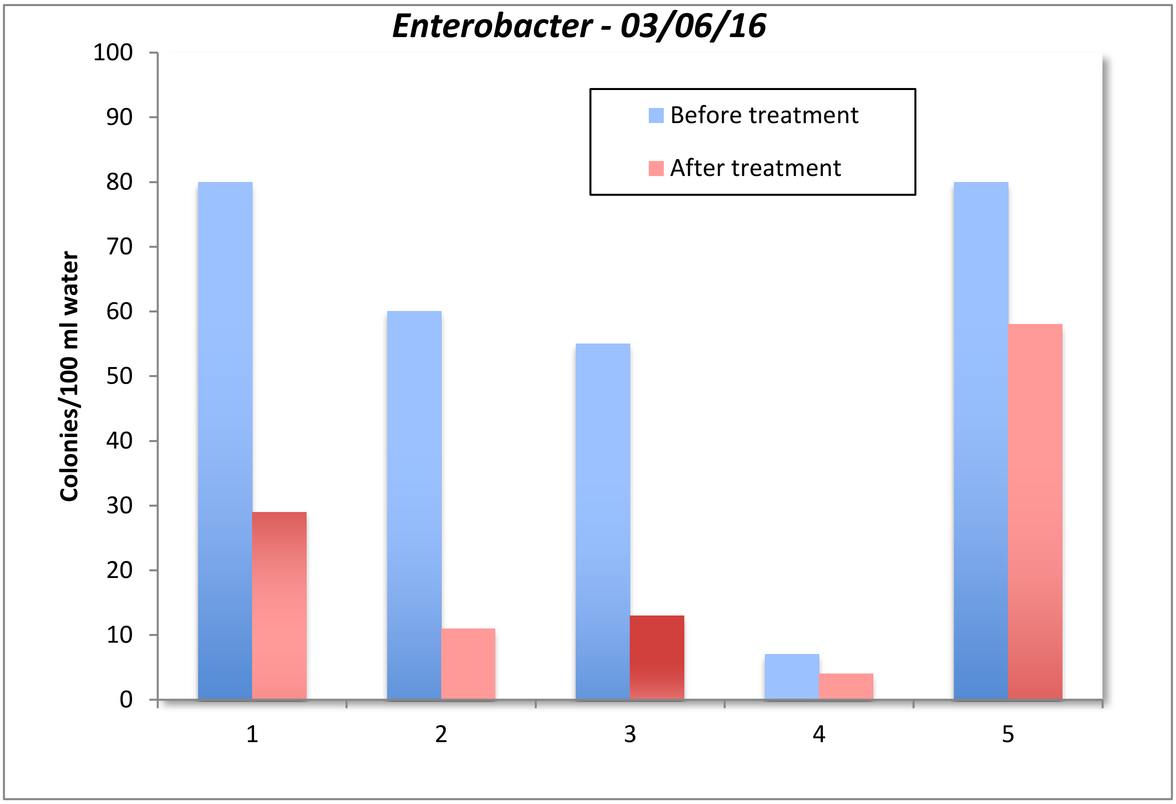


Figure 5: Analysis Results (TPH)



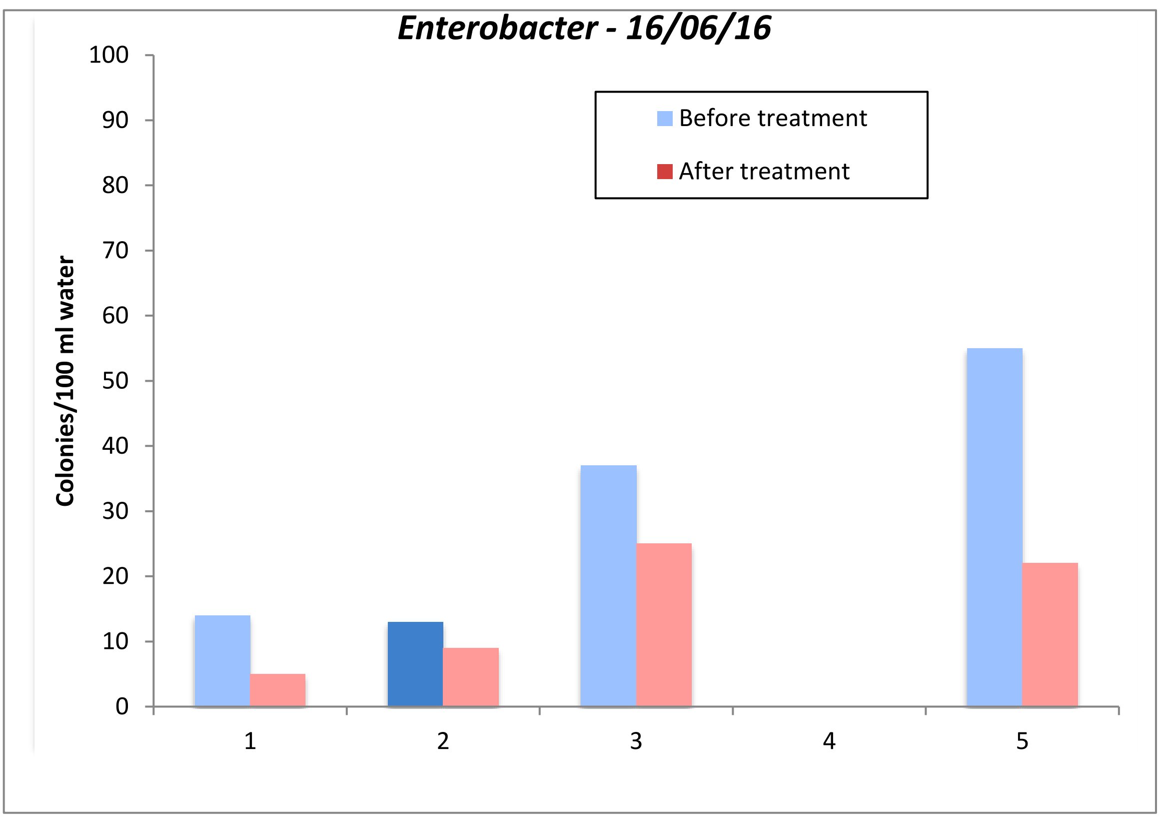


Figure 6: Microbiological tests (Enterobacter)

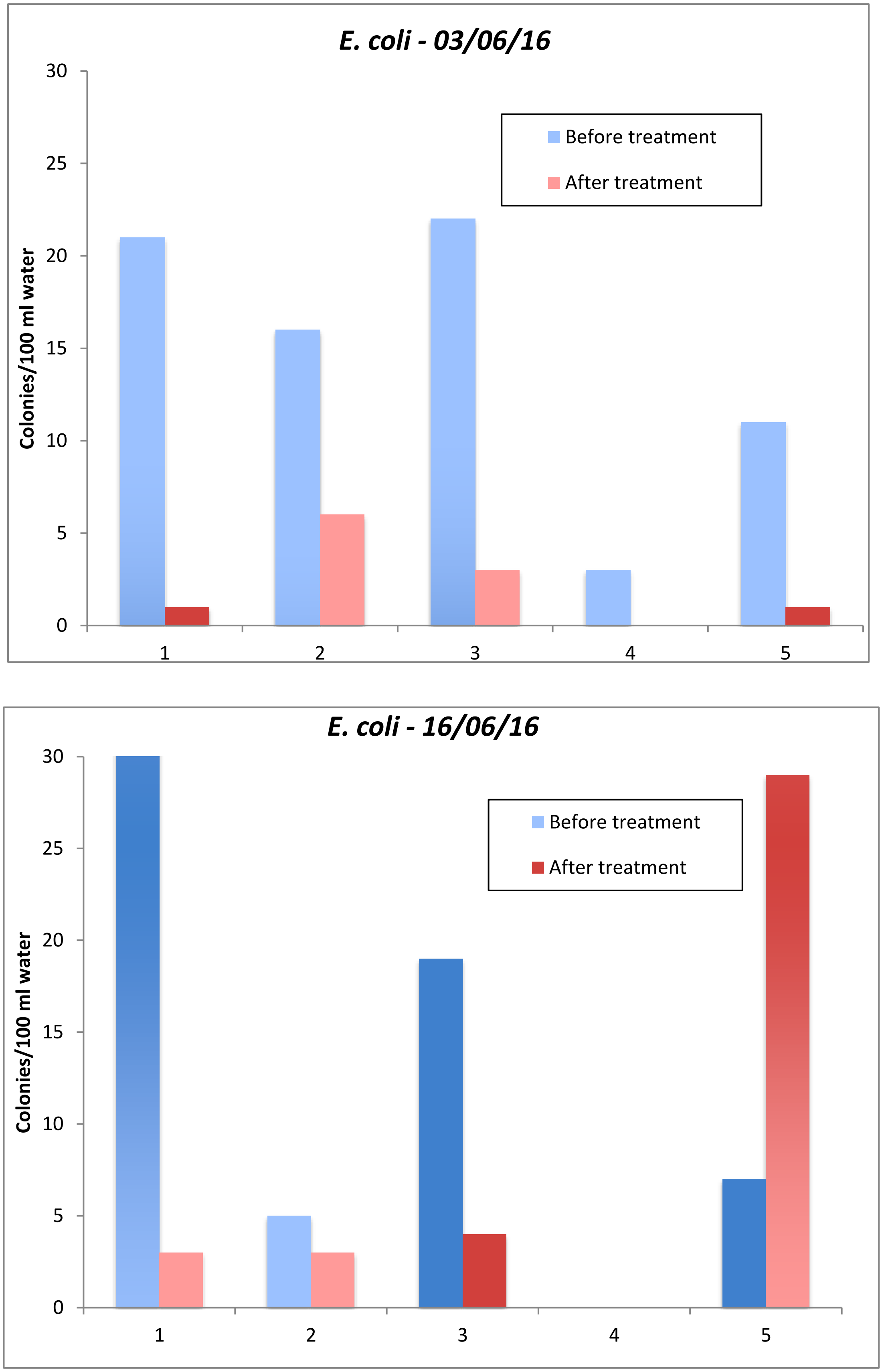


Figure 7: Microbiological tests (E. coli)

Global Journal of Science Frontier Research (E) Volume XVII Issue I Version I Year 2017

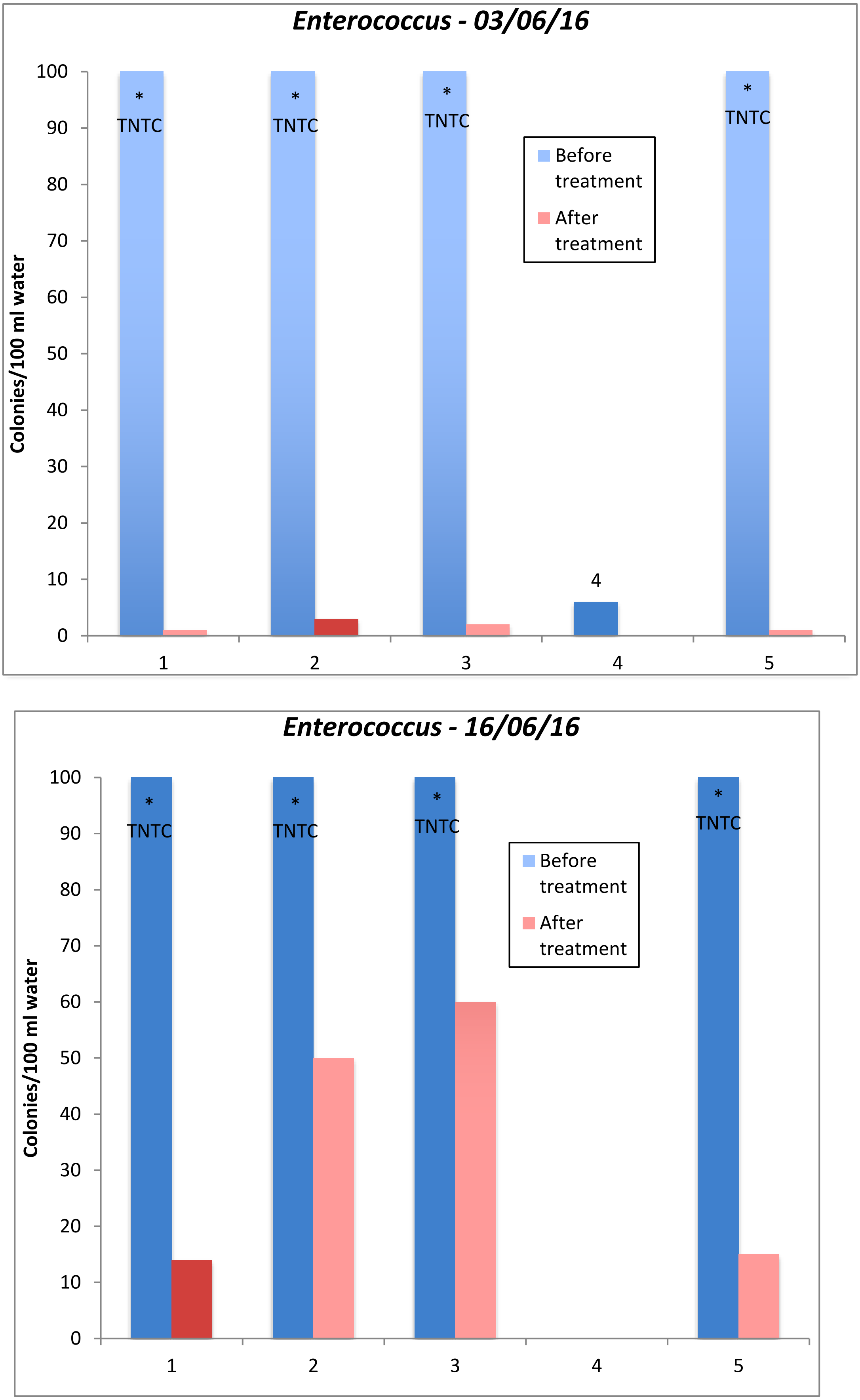


Figure 8: Microbiological tests (Enterococcus)

Water salinity is another factor that affects the rate of action of the dispersant on organic compounds. Nevertheless, in the EPA-based investigations of the MSL formula, there was no study done to determine the impact of the level of salinity on the functionality of the dispersant. However, in the different marine environments that the dispersant was applied to, such as coastal waters, beaches, ports and marinas, the MSL formula achieved the desired levels of reduction based on the resulting concentrations of the organic compounds. This means that salinity should not block the anti-pollution activity, however there is still a possibility that it could slow it down since different times of action were reported in each test. The waves and water currents are other important parameters that may affect the process of the MSL driven dispersion of organic compounds in marine environment. When there are waves and currents, it is easier for the dispersant to interact with the oil-water interface and reduce the surface tension. The waves and water currents also contribute to the dispersion by carrying and dispersing the tiny oil droplets to the maximum possible distance and allowing for an increased surface area for solar radiation to facilitate the process of evaporation. Microbes also play a major role in the breaking down of organic compounds through the natural biodegradation process. In marine environments that are rich in microbes, the process of degradation takes place more rapidly compared to environments where microbes have been destroyed by the chemical action of the pollutants. The MSL formula does not have any toxicity effects on the microbe population and thus their action and effectiveness should not be impacted. Finally, the concentration of organic compounds in the oil spill is the last factor that affects the rate of degradation following the treatment of the marine environment with the MSL. The higher the concentration of the organic pollutants, the longer it will take for the dispersant to carry out the optimum concentration reduction process. This explains why the rate of degradation is different for different types of hydrocarbon compounds such as the Arabian crude oil and the Total Petroleum Hydrocarbons (TPH).

Tests were carried out in several locations to determine the effectiveness of the MSL formula using different contaminant parameters: biological oxygen demand (BOD), chemical oxygen demand (COD), total petroleum hydrocarbons (TPH), and Fats oils and Grease (FOG). The results of these tests indicate that the MSL action was most effective on the TPH and FOG. The greatest changes after the treatment were observed in the COD and the BOD values, depending on the initial measurements. In conclusion, the use of MSL formula on all locations demonstrated its significant effectiveness on the parameters tested and confirmed the suitability of this environmentally friendly option as an antipollution agent in marine environments. The application of MSL in different scenarios achieved comparable result, indicating that effectiveness is not dependent on location. This is an advantage to chemical dispersants that cannot be applied in places such as marinas, harbors and floating cage farming operations because of their toxic properties and non-biodegradability, which may cause secondary pollution to these environments.

An example of such a study was done at the Ayia Napa Port,where tests were carried out to assess the rate of reduction of different organic compounds under the MSL action. Among the organic compounds that were observed after varying durations of treatment included BOD, COD, FOG, and TPH as described above, and with TP and TKN as additional parameters. The concentration of these parameters was measured and recorded before the treatment was initiated. The concentration was then measured for all the parameters after treatment, with the duration of the treatment ranging from one to two weeks. It was noted that for all the parameters tested, there were significant reductions throughout the observation period. The remaining amounts were directly proportional to the initial amount for each parameter at the beginning of the treatment. The parameters that had comparatively higher concentrations at the beginning of the treatment also ended up with higher remaining concentrations at the end of the treatment period. This study was undertaken to assess the effectiveness of the MSL formula under different parameters and the results of the test confirmed its effectiveness under all parameters tested. Nevertheless, there are some instances where the weight of the parameters was observed to increase after a number of applications/treatments. This remains to be explained and further research needs to be conducted to find out the underlying cause/mechanism. For FOG and TPH, reduced levels were achieved after the second test and there was no further reduction. This could mean that the maximum possible reduction had already been achieved after the first two applications. The data that was obtained for the Ayia Napa Port Project is shown in Table 5.

Table 5: Results of Ayia Napa Port Project using the MSL formula (all dates 2015, all concentration values in mg/L)

	Before applicat (Aug 06)	After 1st applicat (Aug 10)	After2nd applicat (Aug 27)	After 3rd applicat (Sep 14)	After 4th applicat (Oct 02)
BOD	80,00	<3,00	4,00	<3,00	<1,00
COD	483,00	14,00	7,00	<7,00	8,00
FOG	38,00	5,00	<1,60	<1,60	<1,60
TP	0,02	0,05	0,01	<0,04	<0,04
TKN	1,20	0,96	2,67	1,02	4,80
TPH	33,14	4,84	<0,17	<0,17	<0,17

The MSL formula is manufactured from plant extracts and has been known to exhibit several advantages over the more commonly used chemical dispersants. MSL is known to be rapidly and readily biodegradable and furthermore the product is non-toxic to marine environment. Unlike other chemical treatment methods, which are used for the cleaning up of marine environments from other pollutants of oil spillages, the MSL product is based on herbal formulas designed to enhance the effects that the clean up has on the environment and to promote the use of green technologies in addressing the environmental concern. It is an efficient solution that does not cause secondary pollution nor does it have any effect on the aquatic ecosystem. The application of the MSL formula is also cost-effective compared with conventional chemical dispersants. The use of green technologies to curb environment pollution and to perform cleanup of the polluted environment is of growing interest and many researchers and scientists are continually discovering and patenting solutions that are claimed to be environmentally friendly. However, for any green oil dispersant or any other cleanup solution to be recommended for commercial use, it needs to meet the EPA set conditions for the dispersion efficiency and biodegradation rate (Theodorou, 2017).

The MSL formula is the green herder technology that was the focus of this study. This is an efficient, eco-friendly, innovative product that is based on natural ingredients (plant extracts). MSL does not pollute or disturb the marine environment, is non-toxic and has the ability to restore the delicate balance of marine ecosystems. The efficiency of the MSL formula, assessed on Arabian crude oil according to the EPA recommendations for dispersants, was found to be at 86.36%. Maximum degradation rate was found to be 90.48% after 96 hours when tested, again on Arabian crude oil. The MSL formula has been investigated and found to be suitable for different marine environments, such as coastlines and beaches, harbors and marinas, and floating cage-farming operations.

Most dispersants used in sea waters do not exhibit significant levels of toxicity and are similar to those of common household items such as shampoos and liquid dish wash solutions (Word et al., 2015). However, these dispersants are chemicals and when added to an area that is already negatively impacted byan oil spill, the result is an increase in the levels of pollution in the affected area. Furthermore, when an oil slick is dispersed, it further mixes toxic substances into the water thereby proving hazardous to living organisms (Prince, 2015). The MSL product indicated considerably lower levels of toxicity in similar situations.

Phytoremediation is a promising technology since it is cost-effective, has aesthetic advantages, is biodegradable, and has long-term applicability (Das & Chandran, 2011). Nevertheless, this technology also has some challenges wherein there is little data regarding the removal rates and efficiencies of the contaminants that are directly attributable to the plants under field conditions. Nevertheless, phytoremediation does not involve the use of plant extracts as an anti-pollution solution since this methodrelies on the use of living plants. In this regard the MSL formula has also proven to be an effective and eco-friendly anti-polluting agent.

V. Conclusions

A comprehensive discussion of plant extracts as an antipollution solution in water column is discussed in this paper. The mechanism through which these extracts achieve their antipollution effects and whether they meet the EPA Regulatory Protocol guidelines for an acceptable dispersant has also been investigated. Different methods used for the cleaning up of the marine environment were identified wherein the use of herding process is identified to facilitate the in-situ burning. The second method that was discussed is dispersion with the use of dispersive agents. The third method, although not practical in all situations, is the selective absorption of the polluting organic compounds through the use of materials that can selectively attract the organic compounds while at the same time repeling the water.

Global Journal of Science Frontier Research (E) Volume XVII Issue I Version I Year 2017

Traditionally, chemical approaches have been employed for these latter two processes. However, it has been shown that chemical approaches result in secondary pollution of the marine environment. In order to address this issue, green alternatives have been identified that have distinct advantages over chemical herders. One such green herder is the MSL formula, which is an eco-friendly solution based on natural ingredients (plant extracts). It has no adverse impact such as toxicity and secondary pollutant effects. Tests were carried in on different locations such as the Ayia Napa Port, Nissi Beach, and Larnaca Marina to assess the effectiveness and economic viability of treating with the MSL product. These tests demonstrated that the MSL formula is effective and suitable for different areas such as coastlines, beaches, and marinas. The present study investigated the action of MSL on Arabian crude oil. Through the experiments that were performed, it was assessed that the efficiency was 86.36% and a degradation rate of 90.48% after 96 hours for the same specimen. This was above the EPA recommended standards for a viable oil dispersant. The results showed that plant extracts have the potential to act as eco-friendly, biodegradable, non-toxic, and cost-effective alternatives for anti-polluting agents in marine environments.

In the study undertaken to assess the effectiveness of the MSL formula, the results confirmed the superior characteristics of the product under all parameters tested. Further studies are required to explain the abnormal behavior where an increase in concentration of some parameters was observed when the MSL formula is used to cleanup a polluted marine environment. Further research is also needed to explain the possible minimum concentration that some organic substances attain after treatment with the MSL formula and below which no further reduction can be achieved.

Following the conclusion of this research study, it is clear that further studies are recommended regarding the use of MSL as a plant extract formulation suitable for mitigating the harmful effects of organic pollutants in marine environments. For example, the effect of seawater salinity on the effectiveness of the MSL formula has not yet been identified. According to the literature, it has been shown that salinity has an impact on the action of chemical dispersants when used on hydrocarbons. The effects of salinity on the MSL action needs to be investigated so that the optimum conditions for the use of the MSL formula can be determined in order to minimize the environmental and financial damages from oil spill incidents.

Sunlight plays both a negative and positive role in the process of degradation. Continued exposure of the organic compound and dispersant mixture to direct sunlight results in the formation of sludge. Sludge cannot degrade easily and slows down the natural degradation since microbes cannot act on the sludge as efficiently as they can on the tiny droplets of dispersed oil spills. The positive role that sunlight plays on the degradation process is the consequent dispersal after the oil has been broken down through the process of dispersion. Therefore, further tests need to be conducted to determine whether sunlight could potentially have the same negative role on the oil spills following treatment with MSL. This will help set the optimum conditions in order to achieve the maximum possible efficiency of the MSL formula.

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