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Treatment of Crude Oil Spills in Water Resources by Using Biological Method

Abstract- *Biological treatment has definite to be an effective and excellent method for the removal of aquatic oil spills. It is competent of being used as the best treatment method for cleanup of oil spills. Being a potential technology, significant work needs to be done to improve the capabilities of bioremediation for oil contaminated-aquatic environment. Novel application of combined solvent extraction and two-phase biodegradation processes using Two-Liquid Phase Partitioning Bioreactor (TLPPB) technique was proposed and developed to enhance the cleanup of high concentration of crude oil from aqueous phase using acclimated mixed consortiums in an anaerobic environment. Silicone oil was used as the organic extractive phase for being a water-immiscible, biocompatible and non-biodegradable. An application of one phase bioreactor was used, then "TLPPB" two-liquid phase partitioning bioreactor was sophisticated to decay hydrocarbons "crude oil" in this study) at concentration reach to 6000 mg/L. As the organic phase, Silicon oil was selected in TLPPB technique to hold the delivery of hydrocarbons in a liquid layer by absorbing method and after that transforming the pollution to the biological microorganisms. Based on TLPPB technique, the effectiveness of the organic layer "silicon oil" has been contrasted to the one-phase biological reactor. Then the result is completely treated of hydrocarbons pollutant to 100% was accomplished in the two-liquid phase partitioning bioreactor "TLPPB" contrasted to 69-78% treated efficiency of crude oil in the one-phase traditional biological reactor. Thus, the interpretation of "TLPPB" technique for crude oil treatment was estimated in terms of the salinity influence by using Tigris river water, and sea water samples. The rising rate of salinity in liquid layer causing reduction the microorganisms-activity and prohibit the amount of crude oil decay. Thus, this research mentions the possibility of TLPPB technique for consolidate transmission and the biodegradation of immiscible crude oil.*

Keywords- *Crude oil, Biological degradation, Two-phase bioreactor, Salinity, Silicon Oil.*

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1. Introduction

Crude oil is include of many various toxic compositions which imperil the environment due to the crude oil spill. Thus there are numerous naturalistic, regional microorganisms which can decay these toxic compositions. This operation of using microorganisms for removal of pollution from the aqueous media is known as biological treatment and this method has confirmed to be an effective method for treatment the aquatic areas which influenced by oil spills [1],[2]. Biological treatment is known as the use of biological microorganisms, in the rectification a polluted environment. Biological treatment for the employ of hydrocarbon pollution spill removal is each afford by bio augmentation or bio stimulation. Bio augmentation is using an extra amount of microorganisms which can decay the toxic hydrocarbons, to reduce the oil pollutants. Bio stimulation is using extra nutrient materials used by native hydrocarbon decaying biological microorganisms to obtain greater decay of harmful compositions existing in the crude oil [3]. The decay of hydrocarbons starts by the transmutation of "alkane chain" or "polycyclic aromatic hydrocarbon (PAH)" into alcohol compounds. Then oxidation mutates the generated alcohol to "aldehyde," and then into "acid" and ultimately into "water, carbon dioxide, and biomass" [4,5].

The status of the polluted region plays a great role in whether biological treatment is a suitable method to treat the specific oil spill. The success of biological treatment depends on natural factors and chemical factors. Natural factors such as surface area, the temperature of the crude oil spill, and the speed of the wind which move the water. Also to the chemical factors, such as oxygen and the containing of nutritious, pH, and the chemical component of the crude oi [6].

Biological treatment has many advantages than the conventional treatment techniques of liquid

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oil effuse. The main usefulness of biological treatment is the provision of expense and decreasing the time for treating a polluted position. The monetary provision of Biological treatment, when used rightly, have enormous advantages compared to conventional treatment procedures, and the biological procedure has no environmental impacts. The disadvantage of biological treatment for liquid oil sheds is that it is a little slow procedure [3,4]. Biological degradation of crude oil is a serious variation process with large economic effects for oil and gas production. Evidence is emerging to corroborate the assumption that in-container oil biological degradation is occasion by anaerobic bacteria to degradation hydrocarbon. The chemical directory also proposes that in many conditions the end-result of hydrocarbon biological degradation in crude oil containers is methane. From thermodynamic observances, hydrocarbons are convenient substrates for anaerobic biological degradation to methane. Thus, until latterly these compositions were thought to be hugely microorganism inefficient in the absence of oxygen, nitrate and sulfate. Due to the potential significance of methanogenic petroleum biological degradation, the limited knowledge of the microorganisms involved and of the techniques by which compositions of petroleum are degraded, it is significant that we know what rules the microorganism transformation of crude oil to methane [7],[8].

In this paper, results of investigating the comparison removal efficiency of crude oil from Tigris river water (TW) and sea water (SW) samples in one phase bioreactor and two-liquid phase partitioning bioreactor (TLPPB).

2. Materials and methods

I. Water Samples

To study the effect of water quality and the corresponding constituents in the aqueous phase on the efficiency of the anaerobic biodegradation process in TLPPB.

The interpretation of TLPPB technique for crude oil, two types of liquid samples were tested in this research,

1-Sample of Tigris river water (TW): Possessed from Tigris River, across Baghdad city.

2-Sample of Sea water (SW): Possessed from the Arabian Gulf, in Basrah city. The characteristics of water samples are shown in Table 1.

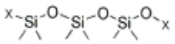
Table 1: Characteristics of water samples

Constituent	Average concentration, mg/L	
	Tigris River water (TW)	Sea water (SW)
TSS	31	130
TDS	567	48200
BOD_5	2.6	17
COD	Nil	33
Oil content	Nil	Nil
pH	8.0	7.3

II. Silicone oil

As the organic second aqueous phase, silicone oil (polydimethylsiloxane) was chosen in this research, supplied from "Gainland Chemical Company (GCC), UK." The characteristics of silicone oil are shown in Table 2.

Table 2: The characteristics of silicone oil [3]

Name	Silicone oil
Chemical formula	$[R_2Si\text{-}O]_n$
Structure	
Purity	100%
Biodegradability	None
Compatibility	compatible
Toxicity	None

III. Crude oil

Al-Basrah crude oil samples were taken from middle refineries corporation/from "Al-Dora Refinery Station." The characteristics of "crude oil" are shown in Table 3.

Table 3: Characteristics of Basrah crude oil [3]

Constituent	Value	Unit
Density	0.8745	gm/ml
Viscosity	55.0	cp
API gravity	30.3	-
Pour point	-30	°C
Water content	nil	%wt
Salt content	10	Ptb*
Sulphur	3.1	%wt
CCR	5.9	%wt
Wax	1.2	%wt
Asphaltene,	2.6	%wt
ASTM distillation cracking point	339	°C

*pound per thousand barrels

IV. Enriched Mixed Culture

Mixed culture was freshly collected from the aeration tanks in Al-Rustamia Sewage Treatment Plant, Baghdad. The stock culture was stored at 4°C. The nutrient media (NM) contained 15000 mg/L meat of papain peptone, and 15000 mg/L of Tryptone. The combination of "mineral salt media" in (mg/L) were, $(NH_4)_2SO_4$ (100), KH_2PO_4 (350), K_2HPO_4 (775), $MgSO_4$.$7H_2O$ (100), $CaCl_2$ (40), $FeSO_4.7H_2O$ (1), $MnSO_4.H_2O$ (1), $NaMoO_4$ (0.21), and Sodium Chloride (5000). The mineral salt media "MSM" was intended at pH 6.8, which was accurately controlled by daily measurement. Sulfuric acid (0.1M) and potassium hydroxide (0.1M) were used for pH adjustment. The prepared mineral salt media, then use an autoclave for sterilization for 30 min at 121°C. [8], [9].

3. Instruments and Measuring Devices

1-Fermenter (Model: BIOSTAT®U50, B.Broun Company, Germany).
2-Oil content analyzer (Model: HORIBA OCMA-350).

I. Removal of crude oil in Fermenter

A glass vessel of TLPPB (12-liter in volume) was used with a thermostatically jacket to maintain the temperature about 30±2oC for the present research (Fig.1). The reactor was agitated with two sets of the six-barb turbine. The microorganism cells were vaccinated in the aqueous medium, then through the ports existing on the stainless cover of the biological reactor, nitrogen gas flushing use in order to perform anaerobic condition, pH meter to control the acidity of the aqueous media, and biogas out flux due to the biological reaction, it was placed in one phase and two-phase biological reactor; in the meanwhile liquid solutions inclosing the hydrocarbon pollutions was teemed into the biological reactor (in one phase condition), and the contaminated water followed by the supplementation of organic solvent "silicon oil in two liquid phase technique", the biological reactor was emptied from air by using nitrogen gas to preserve anaerobic medium. Liquid samples in the reactor were tested every day to analyze the oil content.value.
The results of the analysis were carried out according to the type of liquid solution as follows:
- Tests performed with Tigris river water, which taken from Tigris River in Baghdad and synthetically contaminated with 2000, 4000, and 6000 mg/L of crude oil (for both one phase and two-phase conditions).
- Experiments performed with sea water, freshly obtained from Arabian Gulf in Basra, and synthetically contaminated with 2000, 4000, and 6000 mg/L of crude oil (for both one phase and two-phase conditions).

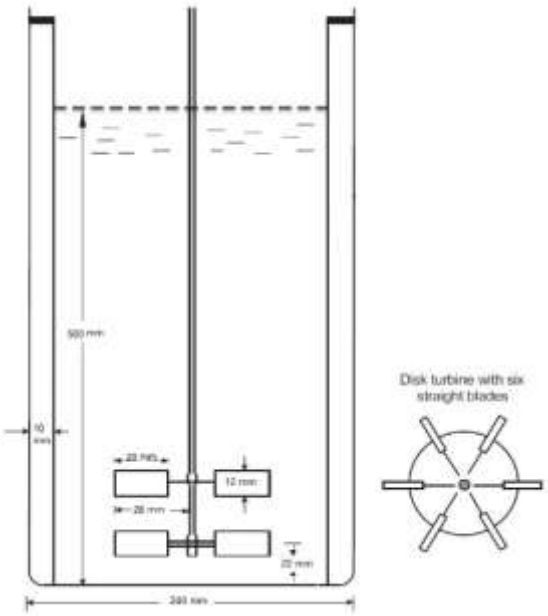


Figure 1: Bioreactor used for Crude oil removal from water sample

II. Oil Content Testing

Oil content analysis was carried out using the oil content analyzer based on the infrared analysis. It includes a single-beam, fixed wavelength, non-dispersive infrared filter-based spectrophotometer. Infrared radiation from a tungsten lamp is transmitted through a cylindrical, quartz cuvette containing a sample

extract. The radiation which passed through the extract enters a detector containing a filter that isolates analytical wavelengths in the 3400- to 3500-nanometer range.

4. Results and Discussion

I. Treatment of crude oil from Tigris river water and sea water

The TLPPB technique outcomes detected that, when the initial concentration of crude oil was about 2000 mg/L, high decreasing of "oil content value" were spotted after 5 and 9 days in Tigris river water, and sea water samples, consequently (Fig. 2), while they were needed 27 and 36 days for complete removal of crude oil from initial concentration of crude oil was 4000 mg/L (Fig. 3). At more concentration of hydrocarbons about 6000 mg/L, prolonged time was requested for complete treatment of crude oil which spotted after 24 and 32 days in Tigris river water, and sea water samples, consequently (Fig. 4). The difference of the time duration desired for complete treatment of crude oil could be assigned mainly to the effect of liquid phase salinity as high salt concentration constitutes in sea water a stressful factor for most of the living microorganisms causing decayed their activity and then the subordinate amount of hydrocarbons biological degradation procedure.

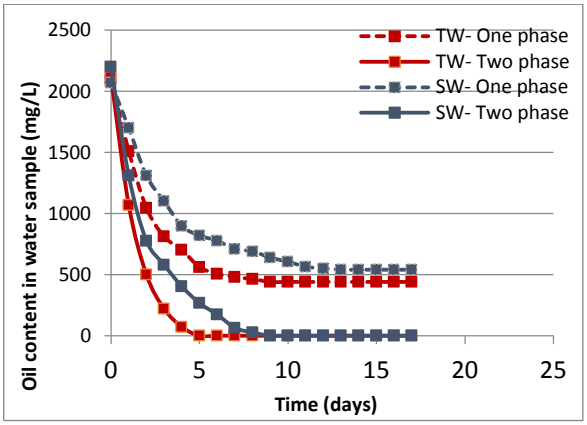


Figure 2: Oil content in Tigris river water and sea water samples in one phase and two-phase at 2000 mg/L initial concentration of crude oil Bioreactor

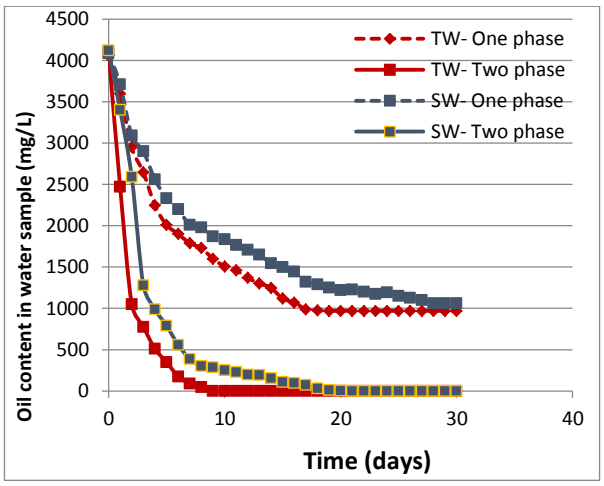


Figure 3: Oil content in Tigris river water and sea water samples in one phase and two-phase at 4000 mg/L initial concentration of crude oil Bioreactor

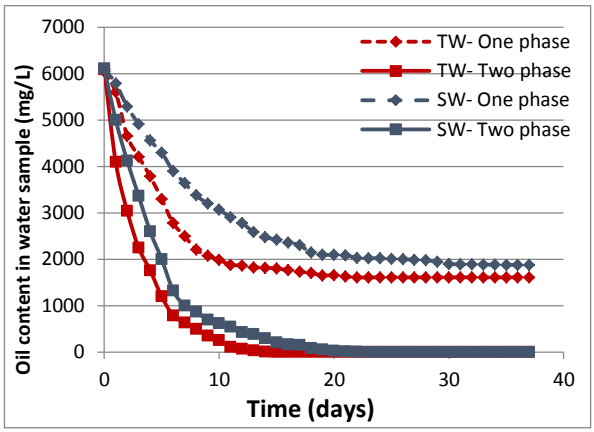


Figure 4: Oil content in Tigris river water and sea water samples in one phase and two-phase at 6000 mg/L initial concentration of crude oil Bioreactor

The research results are in a suitable covenant with the prior previous studies. Minai-Tehrani et al. [10] found that forty-one percent of crude oil decay in soil samples without NaCl added, while not more than twelve percent was acquired in samples matter to 50 g/L of sodium chloride after four months. The unfavorable effect of increasing salinity on hydrocarbons decay is also spotted in mediums wherever "halotolerant" and a little "halophilic" microorganisms resort to be prevalent, as the case of mangroves [11], [12]. Even in normal hyper saline environments a negative effect on hydrocarbon decay induced when increasing saline has been announce. Mielle et al. [13] found that when increasing the saline concentrations, the rate of biological degraded of oil decreased.

Thus, the periods for fully biological degradation of crude oil differed. This differences could be assigned mainly to the presence of (TDS) total dissolved solids, as the extremist's concentration of dissolve salt types may harm the

microorganism cultures and reduce their activity causing to a lower rate biological degradation technique due to the exclusive availability of active biomass. It is observed and in fact well expected that the concentration of TDS was very high in the sea water samples as given in Table 1. The overall efficiencies of crude oil removal for the 2 types of water samples were not affected and remained high up to 100% at the end of the incubation period in TLPPB.

II. Treatment of "crude oil" in one phase, and two-phase biological reactor

Experiments were carried out to discuss the accomplishment of the one phase bioreactor and TLPPB technique using alternatively Tigris river water (TW) and sea water (SW) synthetically contaminated with crude oil at initial concentrations of 2000, 4000, and 6000 mg/L. Results revealed that crude oil removals up to 100% in the TW-TLPPB and SW-TLPPB were obtained in three different concentrations, while removal efficiencies 74-78% in TW-one phase and 69-73% for SW-one phase (Table 4), as observed in Figs. 1, 2 and 3. The research results are in a suitable covenant with the previous studies. Yeom et al., (2001)7 found the treatment qualification of benzene was reach greater than ninety nine percent during one day in a "TPPB" technique, MacLeod & Daugulis (2003) [14] found that Polycyclic aromatic hydrocarbons such as "phenanthrene and pyrene" were wholly decayed during 96 hours in a "TPPB" technique.

Table 4: Percentage removal of crude oil by using one phase bioreactor

Reactor type	Crude oil concentrations (mg/L)	% Max. Removal	Duration of biodegradation (days)
TW- One phase	2000	78%	17
SW- One phase	2000	73%	21
TW- One phase	4000	77%	27
SW- One phase	4000	71%	36
TW- One phase	6000	74%	31
SW- One phase	6000	69%	44

The effect of using second phase (silicone oil) existence as the immiscible organic phase in the bioreactor was well observed in controlling the dispersion and transfer of crude oil into the aqueous phase to feed the biomass. Silicone oil exhibited as a sponge adsorbed the high initial concentration of crude oil and then gradually desorbs batch doses of oil as a substrate for the starving microorganisms to prevent the substrate shock loading which may cause consortiums toxicity and death.

5. Conclusion

This research proved the possibility of the two phases biological reactor to the remediation of high concentration of crude oil up to 2000, 4000, and 6000 mg/L in liquid phase one phase technique and two-phase technique (by using organic solvent "silicon oil" as the extractive phase in two-phase technique). The bioreactor safely enhanced the biological decay value of hydrocarbons "crude oil" and minimized the restrained and poisoning impact of pollutant on microorganisms. In the circumstances studied, crude oil was fully treated and biological decayed in "TLPPB" technique in about 5, 17 and 24 days at 2000, 4000, and 6000 mg/L crude oil in Tigris river water, while it was completely removed and biodegraded in TLPPB within 9, 29 and 32 days at 2000, 4000, and 6000 mg/L crude oil in sea water samples. The salinity of the liquid phase influenced the biomass activity proceeding more time interval for full elimination of crude oil. In one phase bioreactor the efficiency of removal of crude oil is 78%,77%, and 74% at 2000, 4000, and 6000 mg/L in Tigris river water and the efficiency of removal of crude oil is 73%,71%, and 69% at 2000, 4000, and 6000 mg/L in sea water.

While completely treatment of crude oil in the (TLPPB) technique was achieved compared to 69-78% removal efficiency in the one phase bioreactor.

Therefor the effectiveness of microorganisms for declination of hydrocarbons "crude oil" was extremely improved in the two-phase technique. In the condition of one phase biological reactor technique, microorganisms were in immediate touch with a very high ratio of "crude oil," and the microorganism outgrowth seemed to be limited. The organic phase seems to rule like a toweling that absorbs the "crude oil" from the liquid layer, and then the "silicon oil" will progressively release the pollutant to the mixed biological culture in the liquid layer.

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