# Evaluation of bio-surfactants enhancement on bioremediation process efficiency for crude oil contaminated soil at oilfield: Strategic study

Hashim R. ABDOLHAMID<sup>a</sup>, Maher A.R. SADIQ AL-BAGHDADI<sup>b</sup>\* and Abdulah K. EL HINSHIRI<sup>a</sup>

<sup>a</sup> Libyan Petroleum Institute, National Oil Cooperation, Tripoli, Libya <sup>b</sup> Higher Institute of Mechanical Engineering, Yefren, Libya

Abstract One of the most critical environmental impact of extraction and production of oil industry is the spillage of crude oil that causes severe soil contamination. A polluted soil by crude oil at the bank of produced water pit at a studied oilfield has been chosen as a case study area. A typical soil sample has been prepared from a mixing of twenty four contaminated soil samples that have been gathered from the top soil at the bank of produced water disposal pit. Total Petroleum Hydrocarbon (TPH) has been determined for the typical soil sample. Bioremediation study has been conducted, where the typical sample was divided into five controlled soil cells. Four cells have treated by biosurfactant in a certain concentration (0.05%, 0.5%), and volume (2.5, 10 cm<sup>3</sup>/Kg soil). One cell has been used as a reference.

An evaluation of the ability of aqueous biosurfactant solutions (rhamnolipid), for possible applications in crude oil contaminated soil bioremediation was carried out. The results showed that the biosurfactants were able to remove significant amount of crude oil from the contaminated soil at different solution concentrations and volumes comparing with untreated cell.

Computational fluid dynamics (CFD) model has been developed and employed to simulate the transport of TPH in the soil around the pit and then simulate the bioremediation process for completely studied area at the mentioned controlled parameters. CFD modeling provides insights into the environmental problems that would be too costly or simply prohibitive by experimental techniques alone. The added insight and understanding gained from environment modeling gives confidence in the design proposals, avoiding the added costs of oversizing and over-specification, while reducing risk. The model chosen to represent the transport and bioremediation process provided satisfactory results. The values calculated by the model were consistent with the experimental results. The model results were based to build up an effective plan of the bioremediation of contaminated soil by crude oil. This technique is applicable for many contaminated site cleanup programs.

Keywords: soil, bioremediation, biosurfactants, CFD models, Oil & Gas Industry.

### 1. Introduction

Produced water is water trapped in underground formations that is brought to the surface along with oil or gas. It is by far the largest volume byproduct or waste stream associated with oil and gas fields all over the world [1]. Water production quantities continue to increase as the oil and gas fields reach maturity. Produced water properties and volume can even vary throughout the lifetime of the reservoir.

Produced water is basically a mixture of formation water and injected water but also contains quantities of Dissolved organics (included hydrocarbons) and suspended oil (non-polar). Therefore produced water is the principal source for hydrocarbon discharges from the petroleum sector to the environment. Total Petroleum Hydrocarbon (TPH) is the constituent of produced water that receive the most attention in onshore, this compounds can lead to toxicity [2], see Figures 1 and 2.

The application of biotechnological processes involving microorganisms, with the objective of solving environmental pollution problems, is gradually growing. The bioremediation process presents countless advantages in relation to other processes employed to remove pollution (extraction with solvents, addition of chemical oxidizers, etc.). One of the best approaches to restoring contaminated soil is to make use of microorganisms able to degrade the toxic compounds in a bioremediation process.



Fig. 1. Surface pit of produced water disposal at oilfield



Fig. 2. Contaminated soil by crude oil at the bank of produced water disposing pit at oilfield.

Many factors affecting the bioremediation process, application of nutrients, microorganisms population count, and treatment by surfactant. Surfactants are amphiphilic molecules that consist of a hydrophilic head and a hydrophobic tail. They are the active ingredients found in soaps and detergents with ability to concentrate at the air–water interface and are commonly used to separate oily materials from a particular media [3].

Surfactants increase the aqueous solubility of non-aqueous phase liquids (NAPLs) by reducing their surface/interfacial tension at air-water and water-oil interfaces. As the interfacial tension is reduced and the aqueous surfactant concentration increased, the monomers aggregate to form micelles. The concentration at which micelles first begin to form is known as the critical micelle concentration (CMC) [3].

Surfactants produced from chemically based materials are known as synthetic surfactants like Sodium Dodecyl Sulphate, SDS as shown in Figure 3, and those from biologically based materials are biosurfactants like rhamnolipids, Rn as shown in Figure 4. Biosurfactants can be synthesized by many different micro-organisms [3].



Fig 3. Chemical structure of sodium dodecyl sulphate, SDS

Biosurfactants display excellent surface activities despite their bulky molecular structure in comparison to synthetic ones. As they originate from living organisms, biosurfactants have advantages of biodegradability, easily produced using renewable resources, possible regeneration, high specificity and less toxicity [4]. The use of biosurfactants eliminates the need for surfactant removal from effluents, due to their innocuous nature. They show high activity at extreme temperatures, pH, and salinity conditions. Thus they are expected to be more effective than synthetic surfactants Due [3]. to their physiochemical characteristics, biosurfactants are thus better suited to environmental applications than synthetic ones [5, 6]. Their productions, commercial application, biodegradation potential of hydrocarbon and metal removal from soil have been studied [4, 7].

Therefore, at this case the biosurfactant of microbial origin (rhamnolipid - Rn) has been elected to investigate its enhancement on the performance of biodegradation process.



RLL or R1 (- $\alpha$ -L-Rhamnopyranosyl- $\beta$ -hydroxydecanolyl- $\beta$ -hydroxydecanoate



RRLL or R2 (2-O- $\alpha$ -L-Rhamnopyranosyl- $\alpha$ -Lrhamnopyranosyl- $\beta$ -hydroxydecanolyl- $\beta$ -hydroxy decanoate.

Fig 4. Chemical structure of rhamnolipids, Rn.

# 2. Experimental

A typical soil sample has been prepared from a mixing of twenty four crude oil contaminated soil samples that have been gathered from the top soil at the bank of produced water disposal pit.

The basic properties of the typical soil samples have been identified according to standard analyses methods (Table 1).

Biosurfactant (Rhamnolipid) that has been used was a blend of  $C_{26}H_{48}O_9$  and  $C_{32}H_{58}O_{13}$ . It was composed of 15% active ingredient, supplied by Jeneil Biosurfactants Co., USA. The surfactant was used as supplied without further purification.

Five plastic cells  $(20 \times 20 \text{ cm})$  with depth 15 cm with capacity of 2000 gm, have been prepared in order to investigate the effectiveness of

concentrations and volume of surfactant solution on the biodegradation rate of crude oil contaminants. Table 2 shows the conducted experiments. The cells have been incubated for 12 months at ambient temperature.

Table 1: Basic properties of typical soil samp	les
--	-----

Properties	Value
Soil size fractions (%):	
Texture	Sandy loam
Clay (≤0.002 mm)	1.5
Silt (0.002-0.005 mm)	57
Sand (0.005 – 2 mm)	40
Gravel ( $\geq 2$ mm)	1
Soil moisture content (%)	14±2
pH	7.3
EC (µ mhos/cm)	34000
TPH (mg of oil/Kg soil)	21750
Available Potassium, K (mg/Kg	653
soll)	0.05
Available Phosphorus, N (mg/Kg soil)	0.25
Available Nitrogen, P (mg/Kg soil)	3355
Heavy Metals (ppm):	
Pb	9.25
Zn	20.57
Cd	< 0.01

Table 2:	Scope of	experiments	of	bioremediation
		atudre		

study					
Cell	Investigated factor	Controlled conditions			
No.					
1	Natural	Incubated 12 months at			
	biodegradation	ambient temperature.			
2	Surfactant	Incubated 12 months at			
	Concentration	ambient temperature			
	0.05%	and treated with 30 ml			
3	Surfactant	volume of Rn.			
	Concentration 0.5%	surfactant.			
4	Surfactant Volume	Incubated 12 months at			
	50 mL	ambient temperature			
5	Surfactant Volume	and treated with 0.3 $\%$			
	100 mL	(by mass) concentration			
		of Rn. surfactant.			

The treatment by surfactant for cell 2, 3, 4 and 5, has been repeated five times along the interval of the experiment, 12 months. At every treatment time, tilling and homogenizing of contaminated soil has

been conducted. THP has been determined for each cell, every one month according to EPA 413.

The previously developed computational fluid dynamics (CFD) model [8-10] has been applied to the present case study. The calculations presented in the paper have all been obtained on a Pentium IV PC (3 GHz, 2GB RAM) using Windows XP operating system.

# 3. Results and Discussions

The overall reduction in TPH values that has been observed, after 12 months for each cell were; (cell 1: 10%), (cell 2: 82%), (cell 3: 84.2%), (cell 4: was 78.3%) and (cell 5: 85.3%). Through the implementation of CFD modeling, step graphs have been accomplished showing the stages of THP reduction over whole interval of the experiment at the studied area, see Figures 5, 6, 7, 8, 9.



Fig.5: Cell 1, natural biodegradation



Fig. 6: Cell 2, treatment by surfactant concentration 0.05%



Fig. 9: Cell 5, treatment by surfactant volume 100 mL



Fig. 10: Overall reductions in each studied case after 12 months

## 4. Conclusions

It is very clear that the treatment of contaminated soil by surfactant solution has a substantial advantage on the oil contaminants removal in comparing with the untreated cell (natural biodegradation). Therefore it is believed that the treatment of contaminated soil by surfactant raised the efficiency of bioremediation process and increased TPH reduction by about eight times the reduction that has been observed at untreated cell. The effective surfactant solution reduces the hydrophobicity of the oil phase by lowering the interfacial tension and detach oil from the soil surfaces, has less sorption to soil, and stable foaming abilities [7].

This study showed that the concentration of surfactant solution has an influence on the rate of TPH reduction i.e. the efficiency of the bioremediation process. As the concentration of Rn increased the rate of TPH reduction was increased.

From the obtained results, the increase in volume of surfactant solutions shows a corresponding increase in the biodegradation of crude oil contaminants using Rn. Therefore, increase in volume enhances the interaction between crude oil and the surfactant solution.

#### 5. References

\*E-mail address: maher\_albaghdadi@yahoo.com

- H.Abdolhamid, W.Kassim, A. ElHinshiri and S. ElJawashi, Environmental Monitoring and Assessment Journal 145(1-3), 95-102 (2008).
- [2]. R. Lee, R. Seright, M. Hightower, A. Sattler, M. Cather, B. McPherson, L. Wrotenbery, D. Martin and M Whitworth, Strategies for Produced Water Handling in New Mexico. *Proceeding of the Ground Water Protection Council Produced Water Conference, Colorado Springs*, 2002, pp.16-17.
- [3]. K. Urum and T. Pekdemir, Chemosphere, **57**, 1139-1150 (2004)
- [4]. K. Urum T. Pekdemir and M. Copur, Journal of Colloid and Interface Science, 276, 456-464 (2004).
- [5]. Harvey, S., Elashvilli, I., Valdes, J.J., Kamley, D., Chakarbarty, A.M., 1990. Enhanced removal of Exxon Valdez spilled oil from Alaskan gravel by a microbial surfactant. BIO/Technol. 8, 228–230.
- [6]. Muller, H., Blaszczyk, R.R., Wagner, F., Kosaric, N., 1993. *Biosurfactants for environmental control.* In: Kosaric, N. (Ed.), Surfactant Science Series, 48: Biosurfactants. Marcel Dekker, New York, pp. 447–469.
- [7]. K. Urum, T. Pekdemir, D. Ross and S. Grigson, Chemosphere, 60, 334-343 (2005)
- [8]. Al-Baghdadi, M.; Abdolhamid, H.; ElHinshiri, A.; ElJawashi, S. Computational Fluid Dynamics Simulations for Environmental Applications in Oil and Gas industry. Proceedings of the 10th Mediterranean Petroleum Conference and Exhibition, Tripoli, Libya, 26-28 February 2008. pp. 40-52.
- [9]. Al-Baghdadi, M.; Abdolhamid, H.; ElHinshiri, A.; ElJawashi, S. Environmental Applications of Computational Fluid Dynamics: Some Case Studies. Proceedings of the first International Petroleum Environmental Conference and Exhibition, Tripoli, Libya, 12-14 May 2008.
- [10]. Abdolhamid, H.; Al-Baghdadi, M.; ElHinshiri, A.; ElJawashi, S. Simulation of Bioremediation Process and Strategic Study for Contaminated Soil by Crude Oil at Oilfield Using CFD Model. Proceedings of the first International Petroleum Environmental Conference and Exhibition, Tripoli, Libya, 12-14 May 2008.