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Demulsifier systems applied to breakdown petroleum sludge

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ABSTRACT

Three sets of demulsifier systems based on nonyl phenol ethoxylates ($n=9$, 11, 13) were prepared. These demulsifiers have been employed to breakdown petroleum sludge obtained from the main drainage basin of Al-Hamra Oil Company. These systems were composed of 4% inorganic acid solution, 10% of aqueous phase solution composed of NP-9, NP-11 and NP-13 as surfactants and isopropyl or butyl alcohol as co-surfactants and the balance of the system is an oil phase (benzene/toluene, 1:1mixture). The breakdown of petroleum sludges was evaluated by TPH analysis, determination of the amount of aqueous phase and sediments separated from the sludge. Furthermore, the oil phase recovered from the sludge was mixed with fresh crude oil obtained from Al-Hamra Oil Company in 1:1 ratio and the API of the mixture was calculated. Effect of demulsifier system composition and its concentration in parts per million were also studied. It was found that the best demulsifier composition for complete breakdown of the sludge was the one based on NP-13.

1. Introduction

Heavy fractions that separate from crude oil and precipitate on the bottoms of storage vessels are known as sludge or "tank bottoms." Sludge is a combination of hydrocarbons, sediments, paraffin and water. Typical composition of sludge is 10–12% solids, 30–50% water and 30–50% by weight oil (Einar (2002), Saikia et al. (2003) and Silva et al. (1998)). Sludge causes many problems; it can accelerate corrosion, reduce storage capacity and disrupt production and processing operations (Gray (1994) and Le Page (1992)). Formation of petroleum sludge is governed by two factors: presence of inorganic residues (such as sediments, sand, scales, and dust) and precipitation of paraffinic wax. Paraffinic waxes are sparingly soluble in crude oil and ready to precipitate under temperature changes. Furthermore, the oxidation of hydrocarbon fraction in crude oil due to climate changes or oxidizing fungi leads to loss of volatile components and increase the tendency of asphaltenes and resins to form sludge (Greg et al. (2004), Khan et al. (1998) and Leprince (2001)).

Lately, the landfill option as a disposal technique for crude oil sludge has been narrowed. So, to overcome this major environmental problem many technologies now are available to treat the tank bottoms sludges, these technologies are based on a combination of one or more of the following (Salameh and Kabrick (1992)):

(1) Physical methods such as centrifuging
(2) Addition of chemicals to demulsify the sludge
(3) Thermal treatment such as desorption
(4) Biological methods

The physical methods for sludge treatment are expensive and require certain equipments such as pumps, heaters and boilers so they cannot be applied in certain circumstances. These methods were previously studied by several authors (Shih et al. (2000), Stanislaus et al. (1994) and Storm et al. (1994)). Biological treatment is time consuming so that it is applied only under certain conditions (Hahn and Loehr (1992) and Salameh and Kabrick (1992)). Very little work studied the chemical treatment of the sludge. Usually, chemical treatment is combined by other processes such as heating (Nelson et al. (2009)). The aim of the present work is to treat the sludge chemically to separate its components by addition of certain chemical agents. This method has many advantages:

(1) It is cheaper than other methods.
(2) It does not require certain equipments.
(3) It is simple and applicable.
(4) It separates the sludge into its components, i.e. oil phase which consists of different hydrocarbons, water and sediments.
(5) The oil phase separated from the sludge is very valuable. It can be mixed with fresh crude to modify its API value or it can be used as fuel according to the ratio of its components.

2. Materials and methodology

The chemicals used in this work are supplied from El-Nasr Chemical Company; they are as following:

(1) Technical grade inorganic acids (HCl, H_2SO_4 and H_3PO_4)
(2) Nonyl phenol ethoxylates ($n=9$, 11 and 13 denoted as NP-9, NP-11 and NP-13 respectively)

Abbreviations: API, American Petroleum Institute; CMC, critical micelle concentration; EO, ethylene oxide; NP, nonyl phenol; TPH, total petroleum hydrocarbons.

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Table 1
Some physical and surface properties of NPs.

Property / NP	Moles EO	HLB[a]	Cloud point[b]	CMC[c]	Surface tension[d]
NP-9	9	12.9	54–57	60	32
NP-11	11	13.8	72–75	71	34
NP-13	13	13.9	82–84	66	35

[a] HLB range: <10 w/o emulsifier, >10 o/w emulsifier, 10–15 good wetting, 12–15 detergents.
[b] Cloud point: °C, 1 wt% aqueous solution.
[c] CMC: ppm at 25 °C.
[d] dynes/cm, 1% solution, at 25 °C.

(3) Technical grade organic solvents (benzene and toluene)
(4) Alcohols (isopropyl and butyl), purity 90%

Some physical and surface properties of NPs are listed in Table 1. The sludge sample was collected from the main drainage basin of Al-Hamra Company and also, the fresh crude oil was supplied from Al-Hamra Oil Company. The specifications of the crude oil are listed in Table 2.

2.1. Sludge characterization

After receiving the sludge sample, it was characterized as follows:

1. Water content was measured according to ASTM-D95.
2. Volatile hydrocarbon content: to determine the amount of light hydrocarbons inside the oily sludge. A sample of known weight was put in an oven (with ventilation) at 105 °C for 24 h. The reduction in its weight is equal to the moisture and light hydrocarbon content in the sludge. The light hydrocarbon content (in wt%) was calculated as follows:

$$\text{Light hydrocarbon} = \left[\frac{\text{Reduced mass in g}}{\text{Mass of tested sample in g}} \times 100\right] - \text{Water content in wt\%}$$

3. Solid content: The previously dried sample was placed in a furnace at 600 °C for 120 min. The residue showed the solid content of the sludge as weight percent:

$$\text{Solid content} = \frac{\text{Residue remaining after burning in g}}{\text{Mass of tested sample in g}} \times 100$$

4. Nonvolatile hydrocarbon content: after measuring the water content, light hydrocarbon content, and solids content, the nonvolatile hydrocarbon content can be calculated in weight percent as follows:

$$\text{Nonvolatile hydrocarbons} = \text{wt of tested sludge sample} - (\text{wt. of light hydrocarbons} + \text{wt of solid} + \text{wt of water content}) * 100/(\text{wt of tested sludge sample})$$

The data obtained are provided in Table 3.

Table 2
Characterization of Al-Hamra crude oil.

Test	Test method	Ref no.	Value
API gravity at 60 °F	ASTM D-1298	15	43.2
Specific gravity at 60 °F	ASTM D-1298	15	0.809
Water content (% vol.)	ASTM D-95	14	0.2
Pour point (°C)	ASTM D-97	16	−3
Kinematic viscosity at 40 °F (cSt.)	ASTM D-445	17	3.0
Sediments by extraction (wt%)	ASTM D-473	18	0.81
Asphaltene content (wt%)	IP 143/96	19	1.6

Table 3
Characterization of the studied sludge sample.

Physical properties	Water content, wt% (g)	Volatile hydrocarbons at 105 °C (g)	Non-volatile hydrocarbons wt% (g)	Solid content at 600 °C (g)	Carbon residue wt% (g)	Ash wt% (g)
Paraffinic soft sludge	5.6	1.1	68	22.9	1.4	1

2.2. Demulsifier preparation

Nonyl phenol ethoxylate was dissolved in the desired alcohol (0.1 g/10 ml) to which 4 ml of the inorganic acid is added then the mixture is completed to 100 ml by addition of benzene/toluene mixture (1:1 by volume). The constituents of the applied demulsifier systems are mentioned in Table 4. The prepared emulsions were homogenized by using a four-blade propeller stainless steel stirrer with LM II electrical mixer (Dioptra Turnov, Czech Republic) operated at a speed of 800 rpm for 15 min.

2.3. Application of the demulsifier systems to the sludge

About 50 g of the sludge sample was placed in 500 ml beaker and stirred by a mechanical stirrer at 800 rpm for 5 min then the desired concentration of the demulsifier system (100 up to 500 ppm) was added on continuous stirring until complete miscibility. The mixture was transferred to cone shape graduated tubes and centrifuged at 800 rpm for 5 min and then left to separate. The mixture was examined for phase separation after 6 h. A blank sample of a stirred sludge without demulsifier system was used for comparison. A screen test was carried to find out the optimum demulsifier system concentration which results in maximum % aqueous phase separation. It was found that the best performance was achieved at demulsifier system concentration 500 ppm. Thus the applied concentration was 500 ppm. After complete separation, the recovered oil layer was withdrawn for analysis, the quantity of separated aqueous phase was measured and the sediment was weighed.

2.4. Sample analysis

After sludge treatment, both liquid and solid products are separated. The analyses performed for the process evaluation include total petroleum hydrocarbons (TPH) test up to C19 and specific

Table 4
Codes and constitution of the applied demulsifier systems.

Group	Code	Aqueous phase (10%) NP	alcohol	Inorganic acid (4%)	Oil phase (86%)
A	NP-9-Iso1	NP-9	Isopropyl	HCl	Benzene: toluene
	NP-9-Iso2	NP-9	Isopropyl	H_2SO_4	Benzene: toluene
	NP-9-Iso3	NP-9	Isopropyl	H_3PO_4	Benzene: toluene
B	NP-11-Iso1	NP-11	Isopropyl	HCl	Benzene: toluene
	NP-11-Iso2	NP-11	Isopropyl	H_2SO_4	Benzene: toluene
	NP-11-Iso3	NP-11	Isopropyl	H_3PO_4	Benzene: toluene
C	NP-13-Iso1	NP-13	Isopropyl	HCl	Benzene: toluene
	NP-13-Iso2	NP-13	Isopropyl	H_2SO_4	Benzene: toluene
	NP-13-Iso3	NP-13	Isopropyl	H_3PO_4	Benzene: toluene
D	NP-9-Bu1	NP-9	Butyl	HCl	Benzene: toluene
	NP-9-Bu2	NP-9	Butyl	H_2SO_4	Benzene: toluene
	NP-9-Bu3	NP-9	Butyl	H_3PO_4	Benzene: toluene
E	NP-11-Bu1	NP-11	Butyl	HCl	Benzene: toluene
	NP-11-Bu2	NP-11	Butyl	H_2SO_4	Benzene: toluene
	NP-11-Bu3	NP-11	Butyl	H_3PO_4	Benzene: toluene
F	NP-13-Bu1	NP-13	Butyl	HCl	Benzene: toluene
	NP-13-Bu2	NP-13	Butyl	H_2SO_4	Benzene: toluene
	NP-13-Bu3	NP-13	Butyl	H_3PO_4	Benzene: toluene