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Comparative Study of Ternary and Binary Solvent Blend Performance in Hydrocarbon Recovery from Nigerian Tank Bottom Sludge

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Abstract

Ternary mixtures (B1, B2 and B3) of solvents from previously tested binary blends were examined for hydrocarbons recovery from Tank Bottom Sludge (TBS). The resulted oil recovery were compared with binary mixture with the view to determine possible improvement in oil recovery from TBS. Two samples, untreated (S1) and treated (S2) were contacted with the various blends for dissolution of oil, and the resulting solution separated into solid residue, aqueous and oil phases. Average oil recovery of 85.26667±0.901850 % from S1 was obtained compare to 63.46667±2.726872 % reported for binary blends recovery from same sample S1. The average recovery from S2 with ternary blends was 65.73333±1.474223 % as against 56.575±1.818653 %, using binary blends. Recoveries from S1 and S2 using by ternary blends were both higher than values obtained with binary blends. In both cases of ternary and binary blends, average oil recovery from S1 was higher than from S2. B1, recovered optimally (86.20 %) at xylene-mole fraction of 0.316793 from S1 and 64.6 % at the same xylene-mole fration from S2. A ternary combination of solvents improved oil recovery from the wastesream (TBS). More oil is recoverable from S1 than from S2.

***Keywords**: Solvent; Binary solvent blend; Ternary solvent blend; Oil recovery; Oil sludge and tank bottom sludge.*

1. Introduction

Oil sludge is a solid or gel in crude oil caused by the oil gelling or solidifying, usually at temperatures lower than 100ºC [1]; it is an unusable by-product of crude oil; a sediment settling to the bottom wherever oil is produced, transported, stored in tanks, vessels, containers, pipelines and in the processes of drilling, extracting and refining the mass. The bottom sediments obtained from storage tanks, vessels and containers are referred to as Tank Bottom Sludge (TBS). TBS is the heavy ends that separate from the crude oil and deposited on the bottoms of storage vessels [2]. Storage tanks and other vessels at production terminals (tank farm) and refinery contain TBS, which accumulate over time and by its nature becomes unpumpable waste that is difficult to remove from the tank or pit. They contain solids that settled together with the hydrocarbons oil and water.

TBS is undesirable by-product of oil production and refining operations, it is especially common and troublesome in oilfield operations where the produced crude oil is being handled. It has technical, economic, environmental, health and regulatory effects on companies and human lives. A large quantity of TBS are produced during oil production and processing activities. They are sometimes costly to store or destroy, and contaminated areas in the past, have required expensive remediation processes to minimize contaminant dispersion. Sludge that usually accumulates in refineries may often result in pump failure and desalter failure [3]. Environmental degradation due to the discharge of polluting TBS from industrial sources is a real problem in several countries including Nigeria. TBS may result in corrosion acceleration corrosion, storage capacity reduction and operations disruption in production and refinery.

There are valuable hydrocarbons in the sludge, chiefly comprising of paraffin, aromatic and asphaltene [4]. The composition of the substance varies but, as a common characteristic, it is compounded from various oils, tars and sorbents, held together by sand to form a paste-like consistence that tends to become friable [4]. TBS contains a reasonable and recoverable quantity of hydrocarbon oil [5, 7-11].

In cleaning operations, in some cases, wastes removed are dump in nearby pit. A typical composition of the sludge is 10 -12% solids, 30 - 50% water and 30 - 50% by weight oil [5]. In another analysis as reported in literature [6], crude oil sludge is composed of valuable paraffin, asphaltene and hydrocarbon [6]. As reported in literature, oil sludge (TBS) from a Nigerian oilfield consists of 62 - 67% valuable and recoverable hydrocarbon oil, while the water and solid contents of the sludge are in the ranges of 27.08-29.03% and 5.44-10.64% respectively [7]. Another report shown that sludge composition is in the range of 50-65% crude oil, 20-35% water and 5-20% solids [8]. Other literature have reported that about 25% of the tank sediment is water, 5% inorganic sediments such as sand, 70% hydrocarbons, which accounted for 7.8% of asphaltenes, paraffin 6% and ash content of 4.8% [9-10].

The use of hexane confirmed the oil content (hydrocarbon) of 42.08 % (± 1.1%) for oil refinery tanks bottom sludge [11]. A hydrocarbon recovery of 30.41 and 37.24% using methyl ethyl ketone (MEK) and toluene respectively was also reported [12]. The use of MEK and Liquefied Petroleum Gas condensate (LPGC) recovered 39 % and 32 % of oil, respectively from oily waste sludge [13]. Supercritical ethane and dichloromethane extractions of hydrocarbons from petroleum sludge recovered oil in the range of 16% to 55% of the original sludge mass for supercritical ethane and approximately 50% for dichloromethane [14]. Several other solvents, including naphtha cut, kerosene cut, n-heptane, toluene, methylene dichloride, ethylene dichloride, and diethyl ether have also been reported to recover oil from dry and semi dry petroleum sludge. Extraction with toluene resulted in the highest poly-hydrocarbons (PHCs) recovery [15]. PHCs recovery rate of 75.94% was also reported [16] using petroleum solvent oil with extract of a high percentage of ring compounds (especially, naphthenics and aromatics). Catalytic cracking of heating oil has high potential for dissolving asphaltenic components in oily sludge, and solvent oil, which are paraffinic in character are also effective in recovering oil from sludge with more paraffinic (waxy) components. The use of turpentine for oil recovery was reported to recover 13–53% of the original sludge mass [17]. The use of solvent blends could recovered higher percentage oil than the single solvent [18].

Conventional methods for removal, recovery and disposal are expensive taken all costs into consideration. The use of solvent, single or blend has potential for the dissolution of sludge to recover valuable hydrocarbon.

This study aims at developing solvent blends for the treatment of petroleum sludge and optimizing the recovery of valuable hydrocarbon oil from the sludge samples, thereby, reducing the waste stream risk to the environment. Specifically, recovery of hydrocarbon from sludge samples using ternary solvent mixtures [hexane (HE), cyclohexane (CH) and xylene (XY)] were examined and their performances compared with the binary mixtures performance previously studied. The oil recoverable with ternary mixture of solvents and their effects on oil recovery from sludge sample are expected to be determined. It will propose a process for recovering optimally the remaining crude hydrocarbon in the sludge before it is disposed into the environment, in order to reduce the pollution effect of the sludge on the environment. This study uses ternary combinations of the reported solvents in literature [18] to determine any improvement in oil recovery from TBS.

2. Materials and methods

2.1. Materials

The crude oil sludge S1 is a dark brown liquid from ESCRAVO Oilfield (Tank number 5) while S2 is a black semi-solid suspended in liquid (which has undergone treatment) from the same field. The ternary solvent blends are various combinations of hexane (HE), cyclohexane (CH) and xylene (XY). The blends were prepared by keeping one component of the blend fixed at a time and either increased or decreased the volumes of the other components.

The apparatus used include conical flask, round bottom flask, Buckner funnel, measuring cylinder, separating funnel, retort stand and clamp, spatula, filter paper. The main equipment used are vacuum pump and weighing balance.

2.2. Methods

Several technologies for treating tank bottoms sludge (or crude oil sludge) are available. The method employed was dissolution of the sludge hydrocarbons captured in the matrices of the TBS by addition of chemicals, that is, solvent extraction. The same methods reported in literature [15] for extraction, separation of residue-filtrate mixture and separation of aqueous-oily phase were employed in this study.

2.3. Extraction process procedure

The mass of a 250 mL conical flask was weighed and recorded as m_1 and 5 g of the sample was weighed into the weighed conical flask. The prepared 50 mL solvent blend containing n-hexane, cyclohexane and xylene at various proportion were added to the conical flask containing the samples. The mixture was then shaken till the sample completely dissolved. The mixture in the conical flask was then covered with aluminum foil to prevent the more volatile components of both the solvent and hydrocarbon from evaporating. The extraction experiment was carried out at room temperature of 29^{o}C.

2.4. Separation of residue-filtrate mixture

A Buckner funnel was fitted into a filtration flask connected to a vacuum pump. The mass of filter paper was initially weighed and recorded as m_{f1}. The pre-weighed filter paper was placed in the Buckner funnel. The sludge-solvent mixture was poured onto the filter paper in the Buckner funnel. The mass of conical flask after pouring was weighed and recorded as m_2. The vacuum pump was switched on to commence the filtration under low pressure (vacuum pressure). The filter paper containing the residue was dried in an oven at 105^{o}C and the mass of the dried filter paper was weighed and recorded as m_{f2}.

2.5. Separation of aqueous-oily phase

The filtrate obtained was poured into a separating funnel and shaken for water and oily phases to separate. Water formed the lower layer while the upper layer comprises of crude oil and solvent blend. The mass of a 10 mL dried measuring cylinder was initially weighed when empty and recorded as m_{c1}. The tap of the separating funnel was open to separate the lower layer into the pre-weighed measuring cylinder and the new mass of the measuring cylinder with the separated water was weighed and recorded as m_{c2}.

The mass of oil extracted was determined by using the expression:

$Mass\ of\ oil\ =\ mass\ of\ sample$ – $(mass\ of\ solid\ +\ solid\ in\ flask\ +\ mass\ of\ water)$.

where, $Mass\ of\ water = m_{c2} - m_{c1}$; $Mass\ of\ solid = m_{f2} - m_{f1}$

thus, $m_{oil} = 5 - \{(m_{f2} - m_{f1}) + (m_{c2} - m_{c1}) + m_{solid-in-flask}\}$

These procedures were repeated in triplicates for various proportion of solvent ratios in the blends.

3. Results and discussions

The extraction was carried out using a ternary solvent blend of hexane, cyclohexane and xylene. The use of solvent blend was to increase the recovery of oil from the sludge.

Correlation of xylene-mole fraction (X1) and solubility parameter (SP) of the solvent blend shows a linear relationship with root square mean (RSM) values ranging from 0.9977-0.9992 (Table 1), implying that the xylene-mole fraction in the blend correlate well with the solubility parameter of the solvent blend. Thus, the xylene-mole fraction effect on oil recovery is related to that of the solubility parameter.

Table 1 RMS values for correlation of xylene-mole fraction and solubility parameter of the solvent blend

X1	X1 (Run-1)	X2 (Run-2)	X3 (Run-3)
RSM value	0.9992	0.9977	0.9988

3.1. Ternary solvent blends performance

As can be observed Table 2, 3, the ternary blends, recovered more oil from the S1 (untreated sample) than from S2 (treated sample). This indicates that more oil can be recovered from S1 than from S2. B1 recovered optimally (86.20%) at xylene-mole fraction of 0.316793 (SP = 16.488) from S1 and 64.6 % at the same xylene-mole fraction from S2. At fixed hexane, the recovery increases till optimum value was reached. As the xylene mole fraction increases, more hydrocarbon compounds of the TBS (crude sludge) disperse in the solvent mixture, which causes the solvent to dissolve the hydrocarbon molecules; a continuous increase in mole fraction of xylene X1 content of blend does not necessarily have a continuous increase effect on oil recovery; an optimum X1 value conditions exist. The dissolution effect of hydrocarbon oil in the sludge is a non-linear dependency on xylene mole fraction of the blend. For other ternary blends B3 and Blend B2, the optimum recovery were respectively 85.20 % (at X1=0.393951) and 84.40 % (at X1=0.194994) for S1, while for S2 the optimum recoveries for the two ternary blends were 65.20 % (at X1=0.393951) with B3 and 67.40 at X1=0.38508 with B2. An optimal condition of the blend is thus required for determination of optimum recovery.

Table 2. Summary of percent oil recovery by the ternary solvent blends

Run 1			Run 2			Run 3		
X_1, xylene-mole fraction	% oil recovery from S1	% oil recovery from S2	X_1, xylene-mole fraction	% oil recovery from S1	% oil recovery from S2	X_1, xylene-mole fraction	% oil recovery from S1	% oil recovery from S2
0.52834	83.4	41.2	0.496851	80.0	44.0	0.409681	79.0	40.2
0.400096	82.6	52.6	0.38508	82.4	67.4	0.400096	82.3	63.0
0.316793	86.2	64.6	0.271607	82.4	52.2	0.393951	85.2	65.2
0.194994	77.7	49.4	0.194994	84.4	53.4	0.385080	84.0	57.4
0.076833	74.0	48.6	0.078599	76.4	50.6	0.376599	84.95	47.2

Table 3. Summary of optimum oil recovery by the ternary solvent blends

Blend	SP	X1-optimum	% Oil recovery from S1
B1	16.488	0.316793	86.2
B2	16.32	0.194994	84.4
B3	16.752	0.393951	85.2
Blend	SP	X1-optimum	% Oil recovery from S2
B1	16.488	0.316793	64.6
B2	16.98	0.38508	67.4
B3	16.752	0.393951	65.2

3.2. Binary blends performance

The binary blends performance as earlier reported [18] have shown that recoveries from S1 were greater than from S2; increase in oil recovery as SP increases to an optimum value was also established. The binary blends with highest performance were observed to be 66.25% at SP condition of 16.22 MPa$^{1/2}$ (XY-HE) from S1 and 61.10% at SP condition of 17.50 MPa$^{1/2}$ (XY-CH) from S2.

3.3. Comparison of binary and ternary solvent blends performance

Table 4 as well as Figure A4 (in the supplementary document) present the oil recoveries and the average oil recoveries, respectively from samples S1 and S2, using binary and ternary blends. The average recoveries (Table 4) by ternary blend from the two samples are higher than the average binary recoveries: S1-Ternary average oil recovery (85.26667±0.901850 %) is higher than S1-binary average (63.46667±2.726872). In addition, from S2, ternary average oil recovery (65.73333±1.474223 %) is greater than S2-binary (56.575±1.818653). Thus, the ternary combination of the selected solvents have higher performance than binary combinations. Also, it is better to recover oil directly from the TBS by solvent extraction for optimum value recovery from the waste stream and to reduce the cost of management.

Table 4. Average Oil Recoveries by Binary and Ternary Combinations of Selected Solvents from UT and TD Samples

	Recovery (%) B1	Recovery (%) B3	Recovery (%) B2	Average oil recovery (%)
Ave. Ternary UT	86.200	85.200	84.400	85.2667 ±0.901850
Ave. Binary UT	66.250	63.350	60.800	63.4667 ±2.726872
Ave. Ternary TD	64.600	65.200	67.400	65.7333 ±1.474223
Ave. Binary TD	54.475	57.625	57.625	56.5750 ±1.818653

4. Conclusion and recommendation

The method of solvent extraction could be an economical management option for recovery of oil from production sludge. The use of the ternary solvent blend recovers more oil from the crude oil sludge when compared with the binary solvent blend. Recovery of oil directly from the TBS by solvent extraction gives optimum value from the waste stream without requirement for treatment, thereby, reduce the cost of management. An optimum condition of solvent combination or blend is required for optimum value recovery from TBS, which can be determined by experimenting with selected solvent combinations.

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