Solvent Extraction-Gas Chromatography for Oil Recovery from Petroleum Sludge using Petroleum Cuts

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Abstract: Petroleum cuts were used as solvents to recover oil from dry and semi dry petroleum sludge. The effects of various parameters, namely shaking time, temperature and the solvent volume upon oil recovery were investigated. Within the range of the studied operating conditions herein, the maximum oil recovery obtained varied from 80% to 97% depending upon the amount of oil within the sludge and the solvent efficiency used for extraction. A detailed study of the kinetics of solvent extraction based on oil recovery was carried out. This technology reuses of separated components and minimizing greatly the waste disposal problems created by land ban. The overall cost as well as time involved for recovery and the disposal of hydrocarbon residue has been decreased. Capillary gas chromatography was used to estimate the economic value and reuse of recovered oil.


Keywords: Petroleum cuts, solvent extraction, petroleum sludge, shaking time, oil recovery and Capillary gas chromatography

1. Introduction

The heavy ends that separate from the crude oil are deposited on the bottoms of storage vessels are known as sludge or "tank bottoms". Sludge is a combination of hydrocarbons, sediment, paraffin and water. Sludge can accelerate corrosion, reduce storage capacity and disrupt operations. Paraffin-based crude oil sludge forms when the molecular orbital of individual straight-chain hydrocarbons are blended by proximity, producing an induced dipole force that resists separation. These dipole forces are called London Dispersion Forces, or Van der Waal bonds, and are responsible for like molecular aggregation (1).

A huge amount of oily sludge is generated from petroleum refineries during their storage operations and through on-going operations. This sludge contains a reasonable amount of oil (hydrocarbons). Most of the storage tanks and other vessels in a refinery contain bottom sediments which accumulate over time. These sediments contain solids settled along with the hydrocarbons and water. The industrial sludge could contain not only organic and inorganic matter, but also bacteria and viruses, oil and grease, nutrients such as nitrogen and phosphorus, heavy metals and organochlorine compounds (2-4). Sludge usually accumulates in refineries because of pump failures, desalter failure, oil draining from tanks and operation units, periodic cleaning of storage tanks and pipeline ruptures (5).

Saikia et al. (6) discussed that during cleaning operations, all these wastes are removed and dumped in a nearby pit. The typical composition of sludge is 10–12% solids, 30–50% water and 30–50% by weight oil (6). Because of its hazardous nature, storage and management oily sludge is a crucial issue in almost all refineries. Apart from this, seepage during storage and from the pit also poses a problem as it leads to contamination of ground water. In Incineration processes oil sludge or oil waste is incinerated to give ash, flue gases, and energy, the energy is usually used for the production of steam for steam turbines, or heating, and it is used as a heating source for the waste oil-reclaiming unit (7). Several process technology options for treating petroleum sludge have emerged during the past several years in response to the enhancement of environmental regulation governing these wastes. Current technologies for treating refinery wastes are very expensive and are mostly inadequate to meet current and future regulations (8). Most of these technologies do not satisfy a new sustainable development approach and the elimination of the greenhouse effect leading to climate change. There is a demand for a universally applicable technology for the treatment of petroleum sludge. The technology should be capable of recovering petroleum in a form that can be redirected to a refinery for further processing to produce higher quality petroleum products (9). Over the next few decades, oil will remain the single largest source of primary energy (10).

Solvent extraction can be both an effective and cost efficient process for separating hazardous contaminants from non-hazardous materials and concentrating the hazardous materials for further treatment. Because the contaminants are separated, the
II-Material and Methods:

II-1. Chemical Materials

a) n-Heptane (pure) 99% from sds.
b) Ethylene dichloride 99% from Egyptian petrochemical company.
c) Toluene 99% from Elameria Petroleum Company.
d) Methylene dichloride and diethyl ether each 99% from ADWIC.
e) Naphtha cut (straight run naphtha), see table (1).
f) Kerosene cut (straight run naphtha), see table (1).

II-2 Sampling techniques:

Representative Samples from two different Crude oil tanks (TK-C2 & TK-C15) are collected during manual clean. Solid sample from TK-C2 and semi dry sample from TK-C15.

A- Solvent Extractions of Samples:

The solvents chosen in our study are methylene dichloride, diethyl ether, ethylene dichloride, toluene, n-heptane, naphtha cut and kerosene cut. Kinetic study was performed to estimate the ideal conditions of extraction.

B- Characterization of samples:

Oily sludge is a mixture of different kinds of hydrocarbons (light and heavy fractions), water, soil, and suspended materials (7). The following fractions of sludge were assessed (Table 1):

1- Water content: - was measured according to ASTM - D95(12) standard method
2- Volatile hydrocarbon content: to determine the amount of light hydrocarbons inside the oily sludge, a sample of known mass was put in an oven (with ventilation) at 105 °C for 24 hrs. The reduction in mass indicated the moisture and light hydrocarbon content in the sludge. As water content was measured previously, the light hydrocarbon content (in wt. %) was calculated as follows:

\[
\text{Light hydrocarbon} = \frac{[\text{reduced mass in g}]}{[\text{mass of tested sample in g}]} \times 100\% - \text{(water content in wt. %)}
\]

3- Solid content: - Dried samples (105°C) were placed in a furnace at 550 °C for 120 min. The residue showed the solid content of the sludge as weight percent:

\[
\text{Solid} = \frac{[\text{residue remaining after burning in g}]}{[\text{mass of tested sample in g}]} \times 100\%
\]

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:-

Nonvolatile hydrocarbon = 100% - (light hydrocarbon in wt. % + solid in wt. % + water content in wt. %).

C- Preparation of samples:

Solid samples (TK-C2) are grinded, and then sieved with ASTM sieve 60/80 and then collected from receiver.

Weighting 5 grams of Sample in each bottle with cap and adding threefold of solvent, at 70 °C and shaking for 30 min., allowing to settling and decant of liquid into vials and kept in the refrigerator to be injected later in gas chromatography.

II-3 Gas Chromatography:

Recovered hydrocarbon samples were analyzed using Hewlett Packard gas chromatograph of model 5890 series II equipped with flame ionization detector (FID), using HP-1 fused silica capillary column Packed with 100 % dimethyl polysiloxane as stationary phase, 100 meter in length, 0.53 mm int. diameter, and thickness film 0.5 µm. Nitrogen (Oxygen-free) was used as mobile phase, all gas flow rates were set to manufacturer specifications, performing conditioning and standardization of the system. The flow rate was measured from the end of the column with a soap bubble flow rate. Methane as an unretained marker was used to correct the dead volume in the column. Injections were made in split mode with a split ratio of 1:15. Glass linear is packed with deactivated glass wool which changed after six injections. The column oven was programmed from 50 °C (hold 1 min) to 350 °C at a rate 5 °C / minute with 190 minute hold at 350 °C. The injector temperature is set at 300 °C and the detector temperature is 320 °C. The data was estimated by integration of the area under the resolved chromatographic profile, using TotalChrom, Ver. 6.2.1 Software, via Interface NCI 900, Manual Injection of 1 µL of samples after washing syringe with sample’s solvent and injected 1 µL of solvent.

III-Results and Discussion

III-1- Characterization of sludge samples and Petroleum cuts

The characterization of the two studied sludge samples from two different crude oil tanks TK-C2 and TK-C15 are given in Table 1. The sludge TK-C2 is dried solid and the second sludge TK-C15 is semi dry solid. From their physical properties which measured at the same conditions, it has been found that the two sludge samples under study have no water content. The solid content and carbon residue are higher in the dry solid sludge TK-C2 than in the semi dry solid sludge TK-C15.

In this study the solvents used for extracting hydrocarbons are methylene dichloride, diethyl ether, ethylene dichloride, toluene and n-heptane. Beside these solvents we have used naphtha cut and kerosene
cut as solvent for hydrocarbons recovery from the studied solid and semi solid sludge samples. The physicochemical properties of these two cuts are measured according to the standard methods ASTM and given in Table 2.

Table (1) Characterization of the studied sludge samples

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>Physical properties</th>
<th>Water content, wt %, ASTM D95(12)</th>
<th>Volatile matter @ 105 °C for 24 hrs, wt %</th>
<th>Solid content @ 550 °C, wt %</th>
<th>Nonvolatile Hydrocarbons, wt %</th>
<th>Carbon residue, wt %, ASTM D189(13)</th>
<th>Ash, wt %, ASTM D482(14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TK-C2</td>
<td>Dried Solid, oil content melted at 65 °C</td>
<td>Nil</td>
<td>0.73</td>
<td>16.73</td>
<td>82.54</td>
<td>29.60</td>
<td>15.63</td>
</tr>
<tr>
<td>TK-C15</td>
<td>Semi dry Solid, oil content melted at 50 °C</td>
<td>Nil</td>
<td>6.69</td>
<td>2.88</td>
<td>90.43</td>
<td>13.03</td>
<td>2.63</td>
</tr>
</tbody>
</table>

From their properties, the naphtha fraction started from pentane at boiling point 38 °C until reached decane at boiling point 168 °C and the kerosene fraction started from decane at boiling point 137 °C until reached pentadecane at boiling point 227 °C. The sulfur content in kerosene fraction exhibits higher value than naphtha fraction due to the high molecular weight and high specific gravity of kerosene fraction as shown in Table 2.

Table (2) Characterization of petroleum cuts as solvent extraction

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test</th>
<th>Specific gravity @15 °C/15 °C, ASTM D4052(15)</th>
<th>Flash point, °F, ASTM D93(16)</th>
<th>Distillation, ASTM D86(17)</th>
<th>Color Lovibond, IP 17(18)</th>
<th>Sulfur content, wt %, ASTM D1266(19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha Cut</td>
<td></td>
<td>0.711</td>
<td>-</td>
<td>38</td>
<td>168</td>
<td>0.5</td>
</tr>
<tr>
<td>Kerosene Cut</td>
<td></td>
<td>0.789</td>
<td>97</td>
<td>137</td>
<td>227</td>
<td>1</td>
</tr>
</tbody>
</table>

III-2- Factors affecting the recovery of hydrocarbons

A- Solvent - sludge ratio

In order to study the preferred and ideal solvent sludge ratio, we would measure the recovery of hydrocarbons from sludge using various volumes of the studied solvents (different sludge-solvent ratio) as given in Tables 3 and 4. Various volumes of the studied solvents were used at constant temperature of 70 °C and constant shaking time of 45 minute until the recovery was fixed. Each solvent was added as batches each 5 min with the minimum ratio 1:2 (sludge (gram): solvent (ml)).

It has been found that toluene is the best single solvent used for extracting hydrocarbons from sludge giving recovery of 75.94 % using a volume of 8 ml but it is difficult to remove it from the recovered oil. But the petroleum fractions naphtha and kerosene cuts are the preferred for the process of hydrocarbon recovery reaching 83.99 % using volume 7 ml only from these cuts.

Table (3) Hydrocarbons recovery from solid sludge TK-C2 at various volumes of the studied solvents.

<table>
<thead>
<tr>
<th>Sludge-Solvent ratio</th>
<th>solvent type</th>
<th>n-heptane</th>
<th>toluene</th>
<th>Methylene dichloride</th>
<th>Ethylenedichloride</th>
<th>Diethyl ether</th>
<th>Naphtha cut</th>
<th>kerosene cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td></td>
<td>45.50</td>
<td>50.20</td>
<td>50.30</td>
<td>51.45</td>
<td>49.60</td>
<td>65.56</td>
<td>63.16</td>
</tr>
<tr>
<td>1-7</td>
<td></td>
<td>60.70</td>
<td>68.14</td>
<td>65.54</td>
<td>67.10</td>
<td>65.45</td>
<td>80.54</td>
<td>83.99</td>
</tr>
<tr>
<td>1-8</td>
<td></td>
<td>66.89</td>
<td>75.94</td>
<td>72.30</td>
<td>70.05</td>
<td>70.19</td>
<td>80.54</td>
<td>83.99</td>
</tr>
<tr>
<td>1-9</td>
<td></td>
<td>72.48</td>
<td>75.94</td>
<td>72.30</td>
<td>70.05</td>
<td>70.19</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1-10</td>
<td></td>
<td>72.48</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
Table (4) Hydrocarbons recovery from semi solid sludge TK-C15 at various volumes of the studied solvents

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>Sludge-Solvent ratio</th>
<th>n-heptane</th>
<th>Toluene</th>
<th>Methylene dichloride</th>
<th>Ethylene dichloride</th>
<th>Diethyl ether</th>
<th>Naphtha cut</th>
<th>Kerosene cut</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-2</td>
<td>55.59</td>
<td>67.85</td>
<td>69.20</td>
<td>69.68</td>
<td>59.99</td>
<td>78.03</td>
<td>80.97</td>
</tr>
<tr>
<td></td>
<td>1-3</td>
<td>65.92</td>
<td>83.00</td>
<td>80.70</td>
<td>87.60</td>
<td>73.77</td>
<td>90.80</td>
<td>92.00</td>
</tr>
<tr>
<td></td>
<td>1-4</td>
<td>77.60</td>
<td>91.00</td>
<td>89.60</td>
<td>95.92</td>
<td>83.00</td>
<td>97.09</td>
<td>97.20</td>
</tr>
<tr>
<td></td>
<td>1-5</td>
<td>85.20</td>
<td>95.68</td>
<td>95.32</td>
<td>95.92</td>
<td>91.00</td>
<td>97.09</td>
<td>97.20</td>
</tr>
<tr>
<td></td>
<td>1-6</td>
<td>90.75</td>
<td>95.68</td>
<td>95.32</td>
<td>--</td>
<td>95.06</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>1-7</td>
<td>94.26</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>95.06</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>1-8</td>
<td>94.26</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

B- Temperature

The temperature was studied at the ideal sludge-solvent ratio and at shaking time 45 minute. This study carried out for both solid sludge TK-C2 and semi solid sludge TK-C15 at three different temperatures, room temperature 35°C, 70°C and 80°C the effect of temperature on the oil recovery from solid sludge was given in Table 5 and from semi solid sludge was given at Table 6. Generally, the oil recovery increases as a function of temperature till reached to the maximum value then there is no increase in recovery with any increase of temperature. The temperature 70 ºC is the preferred for all individual solvents and petroleum cuts using solid and semi solid sludge giving the maximum oil recovery for each solvent.

The petroleum cuts naphtha and kerosene are the more efficient solvents for the two studied sludge samples giving maximum oil recovery. Using petroleum cuts the oil recovery reached more than 80 % from solid sludge and more than 97 % from semi solid sludge.

Table (5) Hydrocarbons recovery from solid sludge TK-C2 at various temperatures

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>Temperature (ºC)</th>
<th>n-heptane</th>
<th>Toluene</th>
<th>Methylene dichloride</th>
<th>Ethylene dichloride</th>
<th>Diethyl ether</th>
<th>Naphtha cut</th>
<th>Kerosene cut</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35.00</td>
<td>48.70</td>
<td>44.14</td>
<td>40.16</td>
<td>45.97</td>
<td>49.54</td>
<td>47.73</td>
<td>48.21</td>
</tr>
<tr>
<td></td>
<td>70.00</td>
<td>72.48</td>
<td>75.94</td>
<td>72.30</td>
<td>70.05</td>
<td>70.19</td>
<td>80.54</td>
<td>83.99</td>
</tr>
<tr>
<td></td>
<td>80.00</td>
<td>72.48</td>
<td>75.94</td>
<td>72.30</td>
<td>70.05</td>
<td>70.19</td>
<td>80.54</td>
<td>83.99</td>
</tr>
</tbody>
</table>

C- Shaking time

The shaking time was affected by the physical properties of sludge samples, generally, the oil recovery increases as the shaking time increase. For solid sludge sample, the recovered oil was completed at shaking time 75 min. and for semi solid sludge sample; the recovered oil was completed at shaking time 45 min.

The shaking time was affected by the physical properties of sludge samples, generally, the oil recovery increases as the shaking time increase. For solid sludge sample, the recovered oil was completed at shaking time 75 min. and for semi solid sludge sample; the recovered oil was completed at shaking time 45 min. Using the petroleum fractions naphtha and kerosene cuts at the optimum conditions of extraction, sludge-solvent 1 - 7 ratio, temperature 70ºC and shaking time 75 min for solid sludge sample and 45 min for semi solid sludge, we can obtain maximum oil recovery. Tables 9, 10 and Figures 1, 2 indicate the recovery percentages of the paraffin and UCM using...
different solvents from solid sludge and semisolid sludge. It has been found that the total recovery from semi solid sludge was higher than that from solid sludge using the same solvents and the same conditions. This may be due to the nature of the sludge. Naphtha and kerosene cuts exhibit highest hydrocarbon recovery from solid and semi solid sludge than the other used solvents, reflecting their powerful extraction. The pristane and phytane are important isoprenoids used as fingerprinting the original crude oil. There presence and their ratios (pristane / phytane) are used as biomarkers and give information about the extracted crude oil from sludge. Also, the ratios nC17/pristane and nC18/phytane from both solid and semi solid sludge in Tables 11 and 12 reflect the recovery of the normal paraffin’s and their corresponding isoprenoids.

Table (7) Hydrocarbons recovery from solid sludge TK-C2 at various times

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>n-heptane</th>
<th>Toluene</th>
<th>Methylene dichloride</th>
<th>Ethylene dichloride</th>
<th>Diethyl ether</th>
<th>Naphtha cut</th>
<th>Kerosene cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.00 min.</td>
<td>47.50</td>
<td>49.20</td>
<td>48.30</td>
<td>49.45</td>
<td>47.60</td>
<td>62.56</td>
<td>60.16</td>
</tr>
<tr>
<td>60.00 min.</td>
<td>72.48</td>
<td>75.94</td>
<td>72.30</td>
<td>70.05</td>
<td>70.19</td>
<td>80.54</td>
<td>83.99</td>
</tr>
<tr>
<td>75.00 min.</td>
<td>72.48</td>
<td>75.94</td>
<td>72.30</td>
<td>70.05</td>
<td>70.19</td>
<td>80.54</td>
<td>83.99</td>
</tr>
</tbody>
</table>

Table (8) Hydrocarbons recovery from semi solid sludge TK-C15 at various times.

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>n-heptane</th>
<th>Toluene</th>
<th>Methylene dichloride</th>
<th>Ethylene dichloride</th>
<th>Diethyl ether</th>
<th>Naphtha cut</th>
<th>Kerosene cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.00 min.</td>
<td>65.92</td>
<td>67.85</td>
<td>69.20</td>
<td>69.68</td>
<td>59.99</td>
<td>78.03</td>
<td>80.97</td>
</tr>
<tr>
<td>30.00 min.</td>
<td>81.00</td>
<td>88.00</td>
<td>86.96</td>
<td>85.00</td>
<td>78.77</td>
<td>89.00</td>
<td>90.00</td>
</tr>
<tr>
<td>45.00 min.</td>
<td>94.26</td>
<td>95.68</td>
<td>95.32</td>
<td>95.92</td>
<td>95.06</td>
<td>97.09</td>
<td>97.20</td>
</tr>
<tr>
<td>60.00 min.</td>
<td>94.26</td>
<td>95.68</td>
<td>95.32</td>
<td>95.92</td>
<td>95.06</td>
<td>97.09</td>
<td>97.20</td>
</tr>
</tbody>
</table>

Using the petroleum fractions naphtha and kerosene cuts at the optimum conditions of extraction, sludge-solvent 1-7 ratio, temperature 70 ºC and shaking time 75 min for solid sludge sample and 45 min for semi solid sludge we can obtain maximum oil recovery.

III-3 the resulting benefits

Value-added products

A substantial amount of money each year can be saved by applying this method by two ways eliminated hydrocarbons from sediment being disposal and the recycled of the used solvent by refinery beside the amount of product that produced from recovered hydrocarbons Table (13).

2 -Greenhouse gases (GHGs) mitigation:

Gradual release of volatile hydrocarbons, which are trapped in the colloidal particles, causes a significant increase in the amount of greenhouse gases worldwide. Light hydrocarbons are important contributors to the GHG effect; for example, methane has a heat-trapping effect 21 times higher than that of carbon dioxide. Therefore, the capture of these gases could have a huge impact on global warming. In addition, the reuse of sludge results in preserving natural resources and would substantially decrease the emission of GHG. This estimation is based on simple life cycle analysis of a fuel product. If a refinery is assumed to produce 30 000 tons of oily sludge each year (11). The recovery of only 30% of these sludge components per refinery will lead to the generation of 10 000 tons of fuel products per year per refinery. Bearing in mind that there are significant numbers of refineries across the world, the reduction of GHG will be considerable (7).

Table (9) Recovery % of Paraffins and UCM with different solvents from solid sludge

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>Carbon Group type</th>
<th>n-heptane</th>
<th>Toluene</th>
<th>Methylene dichloride</th>
<th>Ethylene dichloride</th>
<th>Diethyl ether</th>
<th>Naphtha cut</th>
<th>Kerosene cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td></td>
<td>22.58</td>
<td>32.92</td>
<td>33.81</td>
<td>16.30</td>
<td>25.33</td>
<td>31.75</td>
<td>69.47</td>
</tr>
<tr>
<td>UCM</td>
<td></td>
<td>49.90</td>
<td>43.02</td>
<td>38.49</td>
<td>53.75</td>
<td>44.86</td>
<td>48.79</td>
<td>14.52</td>
</tr>
<tr>
<td>Total Recovery</td>
<td></td>
<td>72.48</td>
<td>75.94</td>
<td>72.30</td>
<td>70.05</td>
<td>70.19</td>
<td>80.54</td>
<td>83.99</td>
</tr>
</tbody>
</table>
### Table (10) Recovery % of Paraffins and UCM from semi solid sludge

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>n-heptane</th>
<th>Toluene</th>
<th>Methylene dichloride</th>
<th>Ethylene dichloride</th>
<th>Diethyl ether</th>
<th>Naphtha cut</th>
<th>kerosene cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>30.301</td>
<td>36.656</td>
<td>23.894</td>
<td>41.789</td>
<td>20.823</td>
<td>44.284</td>
<td>89.40</td>
</tr>
<tr>
<td>UCM</td>
<td>63.959</td>
<td>59.024</td>
<td>71.426</td>
<td>54.131</td>
<td>74.237</td>
<td>52.806</td>
<td>7.80</td>
</tr>
<tr>
<td>Total Recovery</td>
<td>94.26</td>
<td>95.68</td>
<td>95.32</td>
<td>95.92</td>
<td>95.06</td>
<td>97.09</td>
<td>97.20</td>
</tr>
</tbody>
</table>

**Figure 1. Distribution of paraffines and UCM with different solvents from solid sludge**

### Table (11) Recovery % of Pristane, Phytane, nC17/Pristane and nC18/Phytane with different solvents from solid sludge

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>n-heptane</th>
<th>Toluene</th>
<th>Methylene dichloride</th>
<th>Ethylene dichloride</th>
<th>Diethyl ether</th>
<th>Naphtha cut</th>
<th>kerosene cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristane</td>
<td>0.25</td>
<td>0.24</td>
<td>0.24</td>
<td>0.16</td>
<td>0.25</td>
<td>0.27</td>
<td>0.71</td>
</tr>
<tr>
<td>Phytane</td>
<td>0.35</td>
<td>0.31</td>
<td>0.32</td>
<td>0.22</td>
<td>0.32</td>
<td>0.38</td>
<td>0.87</td>
</tr>
<tr>
<td>Pristane/Phytane</td>
<td>0.71</td>
<td>0.77</td>
<td>0.76</td>
<td>0.74</td>
<td>0.76</td>
<td>0.71</td>
<td>0.82</td>
</tr>
<tr>
<td>nC17/Pristane</td>
<td>2.01</td>
<td>1.90</td>
<td>1.97</td>
<td>2.01</td>
<td>1.92</td>
<td>1.99</td>
<td>1.86</td>
</tr>
<tr>
<td>nC18/Phytane</td>
<td>1.51</td>
<td>1.41</td>
<td>1.51</td>
<td>1.51</td>
<td>1.47</td>
<td>1.50</td>
<td>1.52</td>
</tr>
</tbody>
</table>

### Table (12) Recovery % of Pristane, Phytane, nC17/Pristane and nC18/Phytane from semi solid sludge

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>n-heptane</th>
<th>Toluene</th>
<th>Methylene dichloride</th>
<th>Ethylene dichloride</th>
<th>Diethyl ether</th>
<th>Naphtha cut</th>
<th>kerosene cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristane</td>
<td>0.39</td>
<td>0.51</td>
<td>0.34</td>
<td>0.59</td>
<td>0.21</td>
<td>0.63</td>
<td>2.53</td>
</tr>
<tr>
<td>Phytane</td>
<td>0.57</td>
<td>0.66</td>
<td>0.52</td>
<td>0.72</td>
<td>0.34</td>
<td>0.87</td>
<td>3.03</td>
</tr>
<tr>
<td>Pristane/Phytane</td>
<td>0.69</td>
<td>0.77</td>
<td>0.66</td>
<td>0.81</td>
<td>0.61</td>
<td>0.73</td>
<td>0.83</td>
</tr>
<tr>
<td>nC17/Pristane</td>
<td>2.39</td>
<td>2.02</td>
<td>2.51</td>
<td>1.93</td>
<td>4.89</td>
<td>2.44</td>
<td>1.93</td>
</tr>
<tr>
<td>nC18/Phytane</td>
<td>1.47</td>
<td>1.41</td>
<td>1.51</td>
<td>1.42</td>
<td>2.68</td>
<td>1.68</td>
<td>1.50</td>
</tr>
</tbody>
</table>
Conclusion

- All studied solvents can extract hydrocarbons from sludge samples but with different degrees of efficiency depending on the solvent type.
- The petroleum fractions naphtha and kerosene are the efficient solvents increasing the total recovery of hydrocarbon residue from oily sludge. This method is a stable, simpler, higher performing and significantly more economical process than the other solvent extraction technologies and the rest of the sludge after extraction can be disposed friendly (free from hydrocarbon).
- Recycling of maximum hydrocarbon residue from a waste-stream product to a usable refinery product was achieved using these optimum conditions: sludge-naphtha or kerosene ratio 1-7, temperature 70 °C and shaking time 75 min for solid sludge sample and 45 min for semi solid sludge. The high benefit resulting is a substantial amount of money each year can be saved by applying this method by two ways eliminated hydrocarbons from sediment being disposed and the recycled of the used solvent by refinery beside the amount of product that produced from recovered hydrocarbons.
- The selected petroleum fractions as solvent extraction change the management of petroleum wastes and reuse of separated components and solve the waste disposal problems created by land ban. Also, they decrease the overall cost and time involved for recovery and disposal of hydrocarbon residue.
- These technologies may necessitate a high pressure system design, incur considerable loss of expensive solvents (especially the BTX) and carry operating concern of personnel hazard. In comparison, we use liquid solvent formulated of common, commercially available petroleum cuts which is inexpensive (as it’s recovered again and produced by the refinery plant) and benign to operation and environment.

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