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Use of resin technology for removal of oil from industrial wastewater

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ABSTRACT

Water plays a major role in the entire process from oil and gas extraction and production to its transformation into fuel in refineries. Thus, it is not surprising that refinery waste water represent by far the largest waste product by volume in the Oil & Gas industry. The composition of the refinery waste waters is complex and typically contains high level of hydrocarbons, BTEX (benzene, toluene, ethylbenzene and xylenes), dissolved solids, suspended solids, heavy metals, high content of biological oxygen demand (BOD) and chemical oxygen demand (COD). Several technologies are already in place to treat the refinery waste water. However, the technologies currently available in the market have an efficiency gap when dealing with dissolved oil. Real oily water samples from the Dow ethylene cracker were tested. The oily water samples were treated using two resins, AMBERLITE™ ROC110 and DOWEX™ OPTIPORE™ L493, characterized by having a high efficiency in removing the concentration of organics from water. Total Petroleum Hydrocarbons (TPH) were analyzed in the feed and after passing through the resins. Further to this study, it is concluded that both resins tested, AMBERLITE™ ROC110 and DOWEX™ OPTIPORE™ L493, are efficient in treating water containing hydrocarbons. From the two resins tested, DOWEX™ OPTIPORE™ L493 achieve a complete removal of TPH while AMBERLITE™ ROC110 does not. If full removal is required, it can be considered using only DOWEX™ OPTIPORE™ L493. However, this might represent high cost due to the need of regeneration. The use of AMBERLITE™ ROC110 as a pre-treatment of DOWEX™ OPTIPORE™ L493 seems the optimal solution, since the first one is self-regenerated.

Keywords: Hydrocarbons; Oil; Refinery; Wastewater; C-H; AMBERLITE™ ROC110; DOWEX™ OPTIPORE™ L493; Adsorbent resin; Total petroleum hydrocarbons (TPH)

1. Introduction

In the refining processes, large amount of water are used especially for cooling systems, distillation, hydro-treating and desalting, equipment flushing or surface water runoff [1]. Typically, these waste waters are collected in at least two different effluents and treated separately. One of the effluents may collect storm water and surface runoff meanwhile another may handle all process and utilities unit water. The waste water generated may contain high levels of biological oxygen demand (BOD), chemical oxygen demand (COD), desalter water, suspended solids, hydrocarbons, heavy metals and other pollutants. Among them, separation of oil from water is becoming essential due to different market drivers. These include the relatively high oil price, the increasing water to oil ratio (WOR) in oil and gas extraction, the increasingly stringent environmental regulations for water discharge and disposal and the water scarcity which force the optimization and reuse of water used in industrial processes [2].

Oil/water separation technologies are used to remove oil droplets from oily waste water in order to get the target water quality to be reused or discharged and at the same time, to also recover the oil from the waste water. Within this context, dispersed oil and dissolved oil can be distinguished.

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Dispersed oil is the oil in the form of small droplet's ranging in size from sub-microns to hundreds of microns, which are stable due to electrical charges (and other forces). The dispersed oil can contain both, aliphatic and larger forms of aromatic hydrocarbons being mainly non-polar compounds with tendency to float. Dissolved oil includes organic acids, natural organics, polycyclic aromatic hydrocarbons, phenols and volatile hydrocarbons being normally polar. The treatment of this oil is difficult, especially when the oil droplets are smaller than 30 microns, being affected by the oil density and the interfacial tension between the oil and water phases [3].

The industry typically uses different parameters in order to quantify the amount of organics in water such as Total Organic Concentration (TOC), Total Oil & Grease (TOG) oil and grease concentration or total petroleum hydrocarbons (TPH). Oil and grease includes different organic fractions and compounds but does not measure the high soluble organic components. The most widely accepted method to measure TPH is the EPA. TPH is defined as the measurable amount of petroleum-based hydrocarbon in an environmental media. TPH is considered as the mixture of aliphatic and aromatic compounds.

With the increasing stringent limits for water discharging, standard refinery waste water treatment such as dissolved air flotation (DAF) or biological treatments are not effective enough. In order to remove further the dissolved oil from water, activated carbon was traditionally used as a polishing. However, it needs to be frequently regenerated or disposed after being consumed and may cause plugging of the membrane filtration such as Reverse Osmosis (RO) systems if those are placed downstream.

Other emerging technologies for oil/water separation applications are being developed to cover the existing gap in the removal of dissolved oil from water. Most of these technologies are based on adsorbent resin bed columns. These technologies are claimed to reduce the dispersed and dissolved oil in water by more than 99.8%. Among these technologies, resins and in particular, DOWEX™ OPTIPORE™ L493,regenerable Polymeric Adsorbant may be a choice for organic removal because of its high capacity for organics and good desorption characteristics.

2. Objectives

The main objectives of the present study are:

- Provide a solution to deal with real waters containing disperse and dissolved oil.
- Understand the efficiency of two DOW resins AMBERLITE™ ROC110 and DOWEX™ OPTIPORE™ L493 in removing dissolved and dispersed oil from water.
- Test different resin set-up in order to understand the most efficient configuration when dealing with oily-waters.

3. Material and methods

3.1. Ion exchange resins used

Two different DOW resins were tested during the experiment, AMBERLITE™ ROC110 and DOWEX™ OPTIPORE™ L493.

3.1.1. AMBERLITE TM ROC110

The AMBERLITE™ ROC110 [4] is an ion exchange resin used as a pre-treatment of downstream water applications for oil removal thanks to its oleophilic properties allowing oil molecules attraction. Due to its properties, AMBERLITE™ ROC110 is typically used in coalescence processes. The resin beads absorb oil on their surface, forming a film around the beads and progressively grow to make droplets. When droplets meet their critical size, they float to the top of the resin bed. Thus, the separated oil is collected in the top of the vessel and can be recovered. The coalescence process when big droplets rise to the top follows Strokes' law (Eq. (1)). Since the oil is removed from the top of the bed vessel the resin does not require regeneration. However, when the differential pressure between the feed and the treated water arrives to the trigger, water backwash should be performed.

$$v = \frac{p_{water} - p_{oil}}{18n} \cdot g \cdot d^2 \qquad (1)$$

where v = velocity; p = density; n = viscosity; g = gravity constant; d = diameter of the oil droplets.

3.1.2. DOWEX™ OPTIPORE™ L493

DOWEX™ OPTIPORE™ L493 [5] is a highly cross-linked polymer adsorbent with a high surface area and unique pore size distribution. It is designed for removing aromatic and relatively non-polar organic molecules from water. Typical properties of the two forms are shown below in Table 1.

The resin will require regeneration as the adsorption forces are generally weak and heavily influenced by the nature of the compound desorbed and the process. When dealing with oily water, regeneration is typically done with steam but other chemicals may be used as acids, bases or organic solvents.

3.2. Experiment set up

The set up consisted of two columns connected to run in series or in parallel. The first column was loaded with AMBERLITE™ ROC110 meanwhile DOWEX™ OPTIPORE™ L493 was used in the second column. A volume of 200 ml of resin was loaded in each of the columns. The columns were fixed on a metal stand with a clamp and a collection flask was placed underneath at the bottom of the column. The feed flow direction was from top to bottom maintaining at a constant bed volume per hour of 5BV/h.

Three different set up configurations were tested:

(a) *Parallel set up:* The oily water passes through the two resins mounted in parallel in order to evaluate the individual resin rejection. Fig. 1 shows the parallel lab column set up.

(b) *Series set up:* The oily water is firstly treated with AMBERLITE™ ROC110 resin. The effluent is then treated by DOWEX™ OPTIPORE™ L493 resin. Fig. 2 shows the series lab column set up.

Table 1
Typical physical and chemical properties of DOWEX™ OPTIPORE L493

	DOWEX™ OPTIPORE L493
Matrix structure	Macroporous styrenic polymer
Physical form	Orange to brown spheres
Particle size	20–50 mesh
Moisture content	50–65%
BET surface area (m^2/g)	1,100
Total porosity (cc/g)	1.16
Average pore diameter	46
Apparent density (g/cc)	0.62
(lbc/cf)	42
Ash content (%)	<0.01
Crush strength (g/bead)	>500
Heat capacity (cal/g°C)	0.75
Thermal conductivity (cal/s cm°C)	0.00033

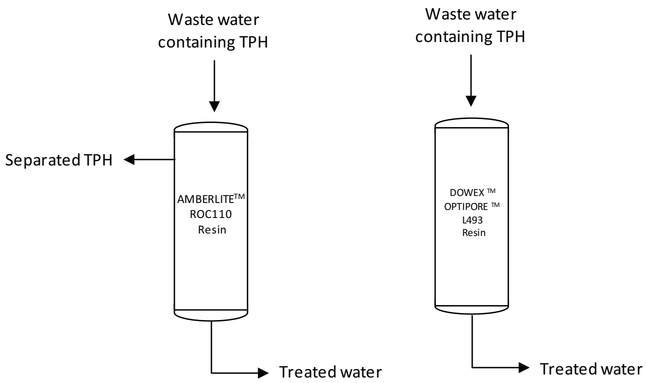

Fig. 1. Lab parallel set up configuration.

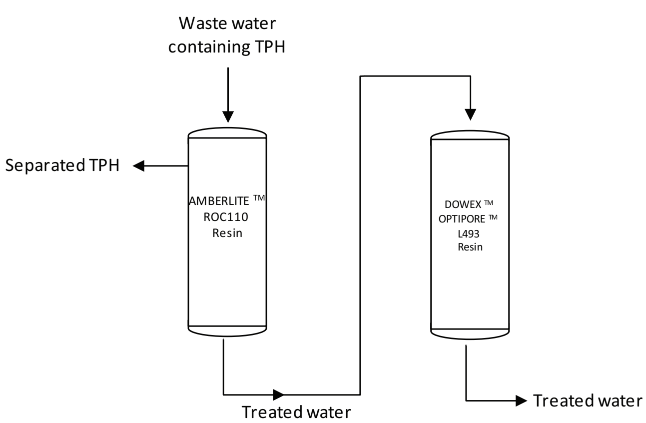

Fig. 2. Lab series set up configuration.

(c) *Double pass set up:* The oily water is passed twice through the AMBERLITE™ ROC110 and then treated by DOWEX™ OPTIPORE™ L493. Fig. 3 shows the second pas lab column set up.

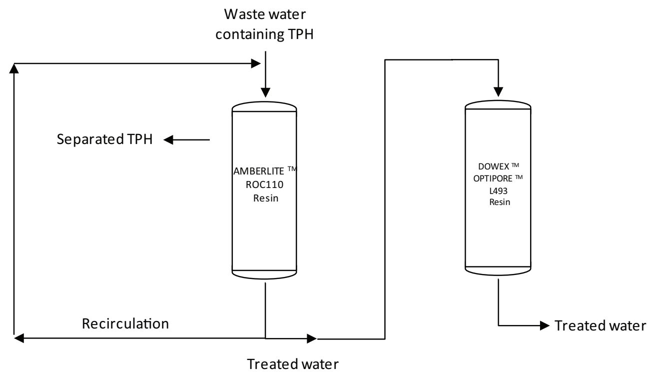

Fig. 3. Lab second pass set up configuration.

3.3. Sample

The oily samples treated during the experiment were real samples from the DOW Tarragona Ethylene Cracker in Spain. Two different samples were analyzed:

(i) *Process waste water:* residual water coming from process units.
(ii) *Maintenance waste water:* water used to clean different cracker equipments when those are in maintenance.

The samples were extracted from the same sample point but during different days. Thus, the oily concentration may vary depending on different operational factors. Nevertheless, the two waters may contain hydrocarbons, BTEX, dissolved solids, suspended solids, heavy metals, high content of BOD and COD in different proportions.

3.4. TPH method

The method used to quantify the Total Petroleum Hydrocarbons (TPH) follows two official methods, the ASTM D-7066-4 [6] and the EPA 5520-C [7]. These are based on the absorbance emitted by the energy bonding between C-H present within the most important organic molecules.

The different feed and treated water samples are measured using Fourier Transformed Infrared Spectroscopy (FTIR). The spectrum generated covers the range between 3060 and 2900 cm^{-1}, considering the aliphatic species (2930 cm^{-1} for $–CH_2$ and 2960–2965 cm^{-1} for $–CH_3$) and also the aromatic species (3030 cm^{-1}) to have a complete characterization of the organic components present in the samples. The area below the spectrum is linearly related to the TPH concentration, expressed as the sum of the individual areas.

4. Results and discussion

4.1. Parallel set up configuration

Table 2 below shows the TPH concentration of the two types of samples tested (process waste water and maintenance waste water). The table also shows the TPH values in the treated water after passing through the resins. If the results are compared, it is observed that the two resins have similar percentage of removal when dealing with the pro-

Table 2
Oily water removal by AMBERLITE™ ROC110 resin and DOWEX™ OPTIPORE™ L493 resin

	AMBERLITE™ ROC110		DOWEX™ OPTIPORE™ L493	
	Feed water (mg/L TPH)	Treated water (mg/L TPH)	Feed water (mg/L TPH)	Treated water (mg/L TPH)
Process waste water	62	<1 (< LOQ)	51.5 ± 1.37	<1 (< LOQ)
Maintenance waste water	600	8.9	1220 ± 11.6	<1 (< LOQ)

cess waste water, reducing TPH from around 50 mg/L in the feed to below the limit of quantification of the method (<1 mg/L). The high efficiency of both resins, AMBERLITE™ ROC110 and DOWEX™ OPTIPORE™ L493 is explained because of the low dissolved oil content in the process waste water. The FTIR-ATR spectra (Fig. 4) indicates that feed process waste water contains mainly dispersed oil (–CH2 and –CH3 bands) but practically no dissolved oil (aromatic band). When dealing with maintenance waste water, AMBERLITE™ ROC110 is only partially removing the TPH from water. Thus, the TPH content is decreased from 600 mg/L to 8.9 mg/L. As observed in Fig. 5, the remaining TPH are associated with dissolved oil (–CH2 band and aromatic band). The second resin tested, DOWEX™ OPTIPORE™, is

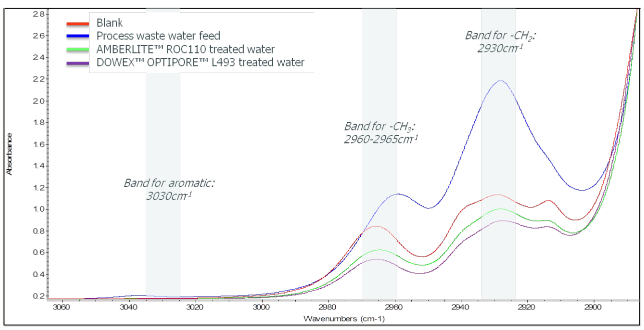

Fig. 4. FTIR-ATR spectra for the process waste water feed and treated sample.

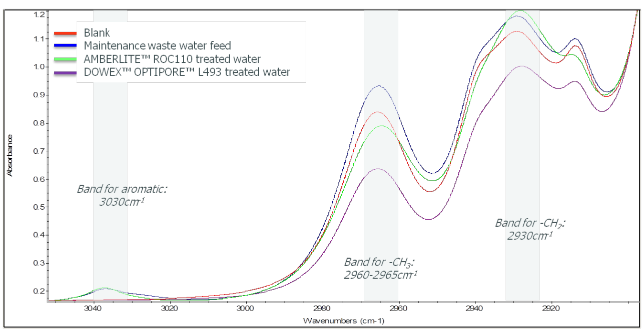

Fig. 5. FTIR-ATR spectra for the maintenance waste water feed and treated sample.

more efficient in reducing the TPH from 1220 mg/L in the feed to lower than the limit of quantification (<1 mg/L).The standard deviation for the samples with DOWEX™ OPTIPORE™ L493 resin was obtained doing two repetitions per sample. The feed samples showed in Table 2 were taken from two different sources on two different days.

Figs. 4 and 5 show the FTIR-ATR spectrum of the parallel set up experiment. Fig. 5 shows the results for the process waste water. Four different spectra are shown: process waste water feed (in blue), AMBERLITE™ ROC110 treated water (in green), DOWEX™ OPTIPORE™ L493 treated water (in purple) and the blank. The blank is referred to the tetrachloroethylene signal used in the liquid–liquid sample extraction in order to eliminate the presence of water and to preconcentrate the sample to be analyzed. As it can be observed, when dealing with process waste water, the two resins are removing the TPH from feed water, being the spectrum signal lower than the blank (in red).

Fig. 5 shows the results for the maintenance waste water. As it is observed, AMBERLITE™ ROC110 resin is removing the oil corresponding to the band for –CH3 but it is not removing the band of aromatics and –CH2. Nevertheless, the DOWEX™ OPTIPORE™ L493 resin is efficient when removing the dissolved oil, being always below the blank.

4.2. Series set up configuration

Table 3 below represents the results of the second trial. In this trial, AMBERLITE™ ROC110 was used as a pre-treatment of DOWEX™ OPTIPORE™ L493. The trial only considers the treatment of maintenance waste water due to test in previous section showed that no dissolved oil was present in this sample.

Results show that the combination of the two resins can reduce the TPH concentration of the maintenance waste water sample until below the limit of quantification (<1 mg/L TPH).

4.3. Second pass set up configuration

The last trial includes two passes by AMBERLITE™ ROC110. The treated water after being passed twice by the first resin is then passed through the second resin, DOWEX™ OPTIPORE™ L493. Trial results are shown in Table 4 below. The results show that a second pass through AMBERLITE™ ROC110 does not help to reduce further the oil content in this type of sample. Thus, it is required the second resin, DOWEX™ OPTIPORE™ L493, in order to reduce the oil until below the limit of quantification. Then, it can be concluded that the maintenance waste water sam-

Table 3
Maintenance waste water removal by AMBERLITE™ ROC110 resin and DOWEX™ OPTIPORE™ L493 resin series set up configuration

AMBERLITE™ ROC110		DOWEX™ OPTIPORE™ L493	
Feed water (mg/L TPH)	Treated water (mg/L TPH)	Feed water (mg/L TPH)	Treated water (mg/L TPH)
400	13.75	13.75	<1 (< LOQ)

Table 4
Maintenance waste water removal by AMBERLITE™ ROC110 resin and DOWEX™ OPTIPORE™ L493 resin second pass set up configuration

	Feed water (mg/L TPH)	Treated water (mg/L TPH)
First pass AMBERLITE™ ROC110 resin	400	13.75
Second pass AMBERLITE™ ROC110 resin	13.75	13.33
DOWEX™ OPTIPORE™ L493 resin	13.33	< 1

ple used during the experiment may contain approximately 13 mg/L TPH of dissolved oil, being the rest dispersed oil.

4. Conclusions

From this study, the following conclusions are:

- AMBERLITE™ ROC110 is an ion exchange resin with oleophilic properties specially developed for the continuous treatment of oily waters. DOWEX™ OPTIPORE™ L493 is a polymeric adsorbent resin developed for the removal of organics from water. It has been demonstrated that the combination of the two resins are a solution for refinery waste water and produce water treatment in order to remove the disperse and dissolved oil from water.
- AMBERLITE™ ROC110 resin is an efficient resin for the partial removal of TPH concentration. FTIR shows that this resin is removing basically the disperse hydrocarbons (normally aliphatic compounds).
- DOWEX™ OPTIPORE™ L493 resin shows high efficiency in removing total TPH from feed water, including both dispersed and dissolved oil.
- A second pass through AMBERLITE™ ROC110 does not improve the removal efficiency. Thus, DOWEX™ OPTIPORE™ L493 resin is needed if dissolved oil is present in the sample to achieve further TPH removal.
- The most efficient configuration tested is the series configuration with AMBERLITE™ ROC110 as a pre-treatment and DOWEX™ OPTIPORE™ L493 downstream. AMBERLITE™ ROC110 is a self-regenerated resin. Thus, when used as a pre-treatment it may help to reduce cost increasing the regeneration cycles of DOWEX™ OPTIPORE™ L493 downstream.

Acknowledgments

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