Original Research

Treating Produced Water Using Induced Air Flotation: The Effect of Ethanol on Conditioning and Flotation of PAHs in the Presence of Tween 80

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Abstract

Induced air flotation (IAF) was used to recover the total polycyclic aromatic hydrocarbons (PAH_{tot}) from produced water (PW), a real oilfield effluent sampled from the hydrocarbon storage tanks at SONATRACH of Bejaia. Tween 80 was used as a collector at a test concentration of 0.5% (V/V%) and ethanol was used as a frother at a test dosage of 0.5 mL/1000 mL of PW. The natural presence of NaCl at greater concentrations may improve the removal efficiency of PAH_{tot} from PW by IAF. We found that the conditioning step before initiating the flotation process is important for PAH_{tot} recovery. A PAH_{tot} recovery of 93.67% was achieved at 30 min of conditioning and 20 min of flotation. We also found that in the presence of Tween 80 during the conditioning step, PAH_{tot} have a tendency to reach the water-air surface. It was disclosed that the addition of ethanol in PW during the conditioning has reduced both the conditioning time from 30 min to 10 min and the flotation time from 20 min to 12 min, which is beneficial from an economic standpoint. The effect of ethanol on the flotation kinetics of PAH_{tot} was explained well by the Higuchi model.

Keywords: produced water, polycyclic aromatic hydrocarbons, induced air flotation, Tween 80, ethanol, kinetics, environment

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Introduction

Produced water (PW), the largest waste stream generated in the petrochemical industry, is one of the major technical, environmental, and economic problems associated with oil and gas production [1, 2]. The properties of PW are dependent on the geographic location of the field, the geological host formation, and the type of hydrocarbon produced, as well as the reservoir lifetime [1]. This kind of water can limit the productive life of the oil and gas wells and can cause severe problems, including the corrosion of tubing and fines migratatic loading [2, 3]. A great deal of scientific research has been carried out to determine the consequences of long-term exposure of PW on the environment, and to develop an effective and inexpensive separation method [4-8]. Some of this research has given alarming results [1, 8]. Among those alarming compounds, polycyclic aromatic hydrocarbons (PAHs) are considered to be the largest contributor to offshore PW toxicity [4, 8].

The analysis of PW discharged into the Mediterranean Sea (at Bejaia, Algeria) reveals the presence of a considerable amount of total PAHs (PAH\textsubscript{tot}) at concentrations of about 3243 mg/L [8]. Algerian Decree No. 26 (23 April 2006), regulating the discharge of industrial effluents into the environment and issued by a joint decree of the Minister for the Environment, the Minister for Hydraulics, and the Minister for Health, set down the discharge limits of total hydrocarbons to 10 mg/L [9]. However, no regulatory limits are listed for PAHs, although PAH\textsubscript{tot} concentration was higher [8] than the regulatory concentration limits set for total hydrocarbon PAHs [9]. Produced water also contains various inorganic species [8] with significantly higher concentrations [9]. In particular, oils that have a density close to that of water are extremely difficult to treat because they tend to form stable emulsions in water due to the waxes and other impurities present [10].

Induced air flotation (IAF) is utilized in the petrochemical industry for oil-water separation [11]. This method is usually preceded by chemical treatment of the sample to break oil-in-water emulsions in order to allow effective removal of contaminants [8, 12]. The chemical reagents, called collectors such as Tween 80, are added to adsorb selectively on surfaces of contaminants and increase their hydrophobicity [13]. Tween 80 is widely used in different fields, e.g., for the removal of petroleum hydrocarbons from wastewater by coagulation pretreatment or increasing of growth effect on microorganisms, their lipid accumulation and fatty acid composition [14-15]. By applying micelles of Tween 80, the production of clean water and recovery of valuable PAHs from PW could be achieved with low or no undesirable effect on the environment and aquatic species. Frothers are reagents that impact the air-water interfacial properties at low concentration by adsorption at the interface [13]. It seems that frothers have a greater effect on bubble size by affecting the bubble break-up process [16]. The alcohol frothers tend to produce relatively shallow froths that carry little water [10, 17]. These factors play a significant role in the kinetic viability of the process and the recovery [18].

Flotation occurs from a true solution to a real problem encountered in industries; this is generally considered to be one of the main advantages of the flotation process, i.e., its ability to avoid consuming time. The duration of agitation or the conditioning time of the sample before the introduction of bubbles could have a positive influence on separation and it has been recognized for some time as an important methodology for improving the performance of the flotation process [10, 19]. Nevertheless, some researchers have advised not using an introduction period, but adding the surfactant at the beginning of the flotation or even stepwise during the flotation process [10].

This paper aims to investigate and evaluate the effects of conditioning step on the recovery of PAH\textsubscript{tot} from a real oilfield effluent, and the influence of both collector and frother on the conditioning step by constructing analytical methods for determining operating conditions. It should be noted that many important parameters such as the concentrations of both collector and frother were not considered in this work; only the effect of their presence on the recovery of PAH\textsubscript{tot} by flotation process was studied. The flotation tests were carried out on a real oilfield effluent at pH 2, already optimized in the presence of Tween 80 at a test concentration of 0.5% (V/V%) (non-ionic collector). The effect of ethanol at a test dosage of 0.5 mL/1000 mL of PW on the flotation kinetics of PAH\textsubscript{tot} was studied; the first-order kinetics and the Higuchi model for the flotation of PAH\textsubscript{tot} in the presence of ethanol at different conditions and times were proposed. Flotation tests were carried out in a conventional mechanically agitated cell (Denver D-12, Laboratory Flotation Machine, Metso Minerals Industries, Danville, USA).

Material and Methods

Experimental Design

Sites and Sampling

Produced water was obtained from the SONATRACH Company of Bejaia, Algeria. Samples were collected in situ, at the outlet of hydrocarbon storage tank, and stocked in amber glass bottles in order to prevent the photodegradation of organic matter. The basic physical properties and chemical composition of a sample of these real oilfield effluents is shown in Table 1, and the analytical methods were detailed in a previous work [8].
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Chemicals

Hydrochloric acid (HCl) 35-37%, sodium hydroxide (NaOH), and non-ionic collector (Tween 80) were obtained from BIOCHEM Chemopharma, (Montreal, Canada). Ethanol (C2H6O) 96% (V/V%) was obtained from SIGMA-ALDRICH. Naphthalene (C10H8) was obtained from PANREAC QUIMICA SA (Spain).

Flotation Tests

The flotation tests were carried out on a real oilfield PW, in a Denver laboratory cell of 2 L capacity under the following conditions:
- Room temperature.
- pH 2.
- Impeller speed of 750 revolutions per minute (rpm).
- Tween 80 at a test concentration of 0.5% in ultra pure water (V/V%).
- Ethanol at a test dosage of 0.5 mL/1000 mL of PW.

First, a set of the flotation tests was performed to investigate the effect of the conditioning step on the flotation of PAH\textsubscript{tot}. Tween 80 was used as the collector, at a test concentration of 0.5% (V/V%), and was added in order to destabilize the oil-water emulsion. In this study, no frother (ethanol) was used. The tests were carried out at different conditioning times of 10, 20, and 30 minutes. The flotation time was the same for each test, at 20 minutes. At the end of the process, the volume of the pulps was measured and the recovery of PAH\textsubscript{tot} was calculated.

In the second set of the flotation tests, the process was performed to determine the effect of Tween 80 at a test concentration of 0.5% (V/V%), on the flotation kinetics of PAH\textsubscript{tot} during the conditioning step. Each 5 min, 5 mL of samples were taken until 30 min of stirring and the concentrations of PAH\textsubscript{tot} were measured.

The third set of the flotation tests was performed to study the effect of ethanol on the flotation kinetics of PAH\textsubscript{tot} during the conditioning step and its effect on both conditioning and flotation times. Three flotation tests were carried out at the conditioning times of 5 min, 10 min, and 20 min, respectively, with the initial concentrations of PAH\textsubscript{tot} in the three samples of PW of 4.68 mg/L, 4.69 mg/L, and 10.48 mg/L. Tween 80 and ethanol were added at a test concentration. The flotation time was the same for each test: 20 min. For each 2 min of flotation time, 5 mL of samples were taken until the end of the process and the concentrations of PAH\textsubscript{tot} were measured.

The details of the flotation steps carried out on the PW sample are illustrated by the diagram represented in Fig. 1.

Data Analysis

UV–visible spectroscopy was used for qualitative and quantitative analysis as per the methods of Weide et al. and Monakhovaet et al. [20, 21] by measuring the UV absorbance of a sample containing PAHs to quantify the total PAHs (PAH\textsubscript{tot}) via calibration as described by Mistry [22]. The calibration curve for naphthalene was established by obtaining optical densities on a series of dilutions made from the 100 mg/L solution in water-96% ethanol mixture (V/V%) at a wavelength of 220 nm [8, 22] (coefficient of regression, R\textsuperscript{2} = 0.996), measured on a Single Beam UV-Vis Spectrophotometer (SHIMADZU Model SpectroScan 30, Biotech Engineering Management Co, Ltd, UK).

Samples were filtered onto a filter paper of 1 µm. The dilutions were made on 0.5 mL of samples and transferred into glass pill dispensers to which were added 0.5 mL of 96% ethanol in order to form water-96% ethanol mixtures (V/V%) for analysis by UV-Vis spectroscopy; similarly, we established the naphthalene calibration curve in water-96% ethanol (V/V%). Samples were calculated from concentration dosages determined from optical densities measured at a wavelength of 220 nm, on the calibration curve for naphthalene.

Concentration analysis is carried out for the recovered PAH\textsubscript{tot}. Calculating the removal efficiency of PAH\textsubscript{tot} is done as a percentage of weight [23], as:

Table 1. Main physical and chemical characteristics of PW.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.13 - 6.78 at 25ºC</td>
</tr>
<tr>
<td>Density</td>
<td>1576 kg/cm\textsuperscript{3} at 25ºC</td>
</tr>
<tr>
<td>Conductivity</td>
<td>83.62 mS/cm at 20ºC</td>
</tr>
<tr>
<td>Turbidity</td>
<td>92.67 FTU</td>
</tr>
<tr>
<td>Suspended Matters</td>
<td>562 mg/L</td>
</tr>
<tr>
<td>Hydrotimetric title</td>
<td>12.8 meq/L</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>0 mg/L</td>
</tr>
<tr>
<td>Full alkalinity</td>
<td>10 mg/L</td>
</tr>
<tr>
<td>COD</td>
<td>734 mg/L O\textsubscript{3}</td>
</tr>
<tr>
<td>Cl\textsuperscript{−}</td>
<td>1015.3 mg/L</td>
</tr>
<tr>
<td>NaCl</td>
<td>1673.1 mg/L</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+}</td>
<td>0.042 mg/L</td>
</tr>
<tr>
<td>Pb\textsuperscript{2+}</td>
<td>4.91 mg/L</td>
</tr>
<tr>
<td>Cr\textsuperscript{6+}</td>
<td>0.135 mg/L</td>
</tr>
<tr>
<td>Ag\textsuperscript{−}</td>
<td>0.0613 mg/L</td>
</tr>
<tr>
<td>Ba\textsuperscript{2+}</td>
<td>0.91 mg/L</td>
</tr>
<tr>
<td>Li\textsuperscript{+}</td>
<td>0.0185 mg/L</td>
</tr>
<tr>
<td>TOC</td>
<td>93.83 mg/L</td>
</tr>
<tr>
<td>PAH\textsubscript{tot}</td>
<td>3243 mg/L</td>
</tr>
</tbody>
</table>
where $C_i$ and $C_p$ are concentrations of PAH$_{tot}$ in the PW and the pulp, respectively, and $V_i$ and $V_p$ are volumes of the PW and the pulp, respectively.

The Kinetics Study of Flotation of PAH$_{tot}$

To describe the kinetics of PAH$_{tot}$ flotation, mathematical models such as first-order and Higuchi model were used [24]. The criterion for selecting the most appropriate model was based on a goodness-of-fit test.

First-order:

$$\ln \left( \frac{C_i}{C_f} \right) = -kt$$

where $k$ (min$^{-1}$) is the flotation rate constant;

Higuchi Model:

$$\frac{C_i}{C_f} = K_H t^{0.5}$$

where $K_H$ is the flotation rate constant for the Higuchi Model, $C_i$ (mg/L) is the concentration of the PAH$_{tot}$ at any time, $C_f$ (mg/L) is the final concentration of the PAH$_{tot}$ at the end of the flotation process, beyond which the concentration of the PAH$_{tot}$ does not change appreciably.

Results and Discussion

Effect of Conditioning Time on the Recovery of PAH$_{tot}$

Conditioning time is the contact and mixing time between PAHs and flotation reagents. Since generally an increase in conditioning time can enhance and benefit the flotation process, the effect of conditioning time was determined. The stirring speed was chosen to be 750 rpm because at this speed we observed that the majority of particles were kept in suspension without an overly turbulent pulp froth interface, and no frother was added. Fig. 2 shows that the conditioning step before injection of air in the flotation cell, mainly after the addition of Tween 80 (collector), at a test concentration of 0.5%, acts directly on the flotation process. At 10 min of conditioning of the pulp, no flotation of PAHs was observed. It may be that 10 min were not sufficient for the formation of PAH-Tween 80 aggregates, or PAH-Tween 80 aggregates were formed but did not attach to the bubbles.
The increase in the conditioning time from 10 to 20 or even 30 min caused a measurable increase in PAH\textsubscript{tot} recovery. The uniform distribution of Tween 80 molecules within the pulp, before injection of air bubbles, and their adsorption onto the surface of PAH\textsubscript{tot} molecules was favored with increasing conditioning at 20 min and 30 min a PAH\textsubscript{tot} recovery of 31.8% and 93.67%, respectively, which has been calculated as described previously [8]. These results show that the time required for the Tween 80 molecules to adsorb onto the PAH surfaces and to make them hydrophobic, during the conditioning step, was to be around 30 min. Longer conditioning times were usually more effective, because PAHs molecules have more opportunity for contact with both Tween 80 molecules and bubbles.

Wang et al. [25] and Firouzi et al. [26] reported that the typical induced air bubble diameter is approximately between 100-1000 µm. This implies that IAF has a greater bubble-rise velocity. The greater bubble-rise rate could, however, have an adverse effect on recovery. This is because faster-rising bubbles may redisperse the PAH-Tween 80 complex aggregates, on the one hand, and increase the contact time between PAH-Tween 80 aggregates and bubbles because of the increased induction time. On the other hand, it may have a direct effect on the conditioning time. To decrease bubble diameters and improve recovery, researchers have opted for the addition of frothers or/and inorganic salts [26, 27].

Furthermore, the natural presence of NaCl at greater concentration in this real oilfield effluent, at 1673.1 mg/L (Table 1), probably challenges the bubble diameters produced by IAF machine. Studies carried out by several researchers have demonstrated that some salts have been proven to affect the surface tension of bubble and inhibit bubble coalescence above a certain concentration [27]. Xu et al. [27] have reported that in the presence of NaCl, the surface tension of air bubbles decreased, which leads to a decrease in their size. In this study, the effect of NaCl (naturally present in PW) on PAH recovery has not yet been addressed.

**Effect of Tween 80 on the Flotation Kinetics of PAH\textsubscript{tot} during the Conditioning Step**

Flotation depends on the surface characteristics of the oil; its overall effectiveness is greatly increased when chemical agents are used. Tween 80 was used in this study as collector at test concentration. The major reason for using Tween 80 is its ability to enhance the solubility of hydrophobic organic compounds by partitioning them into the hydrophobic cores of Tween 80 micelles [28]. A set of flotation tests has been established to investigate the role of Tween 80 on the flotation kinetics of PAHs during the conditioning step.

However, any emulsion must first be broken and the oil droplets grown before the flotation process takes place. The emulsion destabilization is brought about by adding Tween 80 [29]. The data (Fig. 3) showed that the addition of Tween 80 affects the flotation kinetics of PAH\textsubscript{tot} molecules during the conditioning step well before the introduction of air bubbles.

In the absence of Tween 80, the quantification of PAH\textsubscript{tot} in the samples collected at the surface of the pulp did not show any difference in the PAH\textsubscript{tot} concentrations with time (Fig. 3). Effectively, heavy oil has a density close to that of water and tends to form a stable emulsion [1]. In addition, because of the complexity of the PW medium (Table 1), it was probable that PAH molecules, which were either trapped by the organic matters or at the free state in PW, have a low tendency to reach the water-air interface (the surface of the pulp).

Tween 80 affects the interfacial tension between PAHs and water [28]. The Tween 80 molecules have no residual electric charge. Therefore, their adsorptions onto PAHs were governed by hydrophobic interactions [30]. According to the obtained results, the addition of Tween 80 had led to the formation of a soluble PAH-Tween 80 aggregate with hydrophobic end, created by the hydrocarbon chain of Tween 80, oriented at the water-air interface [31], which explains the accumulation of PAH molecules at the water-air interface during the first 20 min and stabilization until 30 min of the conditioning step.
Ethanol contains the hydrophilic group OH, which has strong hydrophilic properties and is very weakly-adsorbed on minerals (with the exception of naturally hydrophobic compounds such as PAHs) [18]. Ethanol molecules concentrate at the surface layer of air bubbles, which reduces their sizes and leads to an increase in the specific area air-water for the molecules attachment [32]. Small bubble size is important in controlling the number of bubbles that may be attached to particles. Also, large bubbles could break the PAH-Tween 80 aggregates and produced turbulence, preventing its flotation [33].

Effect of Ethanol on the Flotation Kinetics of PAH$_{tot}$ at Different Conditioning Times

Ethanol contains the hydrophilic group OH, which has strong hydrophilic properties and is very weakly-adsorbed on minerals (with the exception of naturally hydrophobic compounds such as PAHs) [18]. Ethanol molecules concentrate at the surface layer of air bubbles, which reduces their sizes and leads to an increase in the specific area air-water for the molecules attachment [32]. Small bubble size is important in controlling the number of bubbles that may be attached to particles. Also, large bubbles could break the PAH-Tween 80 aggregates and produced turbulence, preventing its flotation [33].
Experiments were carried out to study the effect of ethanol (frother) on the conditioning time and recovery of PAHs. Our results showed that recovery rates improved when a frother was used (Fig. 4). The addition of ethanol in the flotation pulp significantly increases the kinetics of the flotation of PAHs. The presence of ethanol reduced the flotation time of PAH$_{tot}$ from 20 min [8] to 12 min. Researchers have reported that large bubbles have a strong rise velocity, hence contact between the PAH molecules and the bubbles in the pulp was practically low [33]. Indeed, the diminution of the flotation time of PAH$_{tot}$ can be explained by the fact that the use of ethanol had led to the production of finer bubbles due to lowering the surface tension of the pulp [34]. This led to the reduction of the induction time, that is, they have allowed colliding PAH-Tween 80 aggregates and bubbles to establish contact more rapidly [32, 34] for all three flotation tests at different conditioning times. However, after 12 min of aeration (flotation step), it was noticed that the concentration of PAH$_{tot}$ in the concentrate was almost constant for all three flotation tests at different conditioning times. Researchers have reported that large bubbles have a strong rise velocity, hence contact between the PAH molecules and the bubbles in the pulp was practically low [33]. Indeed, the diminution of the flotation time of PAH$_{tot}$ can be explained by the fact that the use of ethanol had led to the production of finer bubbles due to lowering the surface tension of the pulp [34]. This led to the reduction of the induction time, that is, they have allowed colliding PAH-Tween 80 aggregates and bubbles to establish contact more rapidly [32, 34] for all three flotation tests at different conditioning times. However, after 12 min of aeration (flotation step), it was noticed that the concentration of PAH$_{tot}$ in the concentrate was almost constant for all three flotation tests 2 and 3 until the end of the process, which was due to the stability of the froth above the flotation cell. Finally, high bubble density had promoted good flotation of PAH$_{tot}$ by increasing the probability of PAH-bubble encounter and by making more bubbles available for attachment to each particle.

For flotation test 1 (5 min) we observed after 12 min of flotation a notable decrease of PAH$_{tot}$ concentrations (compared to tests 2 and 3 with longer conditioning times), which remained low during the next 4 min before stabilization until the end of the process. This sudden decrease of PAH$_{tot}$ concentrations was due to the instability of the froth. The contact PAH-bubble was unstable; the PAH$_{tot}$ molecules fall down in the bottom of the flotation cell. Although there is not a general theory to describe the behavior of the froth [32], it is apparent that the use of a frother in IAF led to further stabilizing the foam layer [34]. The detachment of PAH molecules following the flotation process can probably be explained by the fact that the conditioning time (5 min) was not sufficient to distribute uniformly the ethanol molecules in the PW before introducing bubbles, and that just after the introduction of air and the important turbulence existing in the flotation cell, the ethanol molecules did not all adsorb on the surface layer of the bubbles. But this was done gradually during the flotation, which was justified by the stability of froth after 16 min of flotation until the end of the process. In general, the frother determines the rate of flotation in almost every flotation system and the selection of the frother must always be in agreement with flotation kinetics [35].

According to this, as mentioned earlier, the first-order flotation kinetics and the Higuchi model were employed to determine the mathematical model, which corresponds to describing the effect of ethanol on the flotation kinetics of PAH$_{tot}$ at different conditioning times. The data was plotted in Fig. 5 for comparison. It can be seen from Fig. 5a) that the first-order flotation kinetics showed a slower – and consequently more variable – flotation rate over time for the three set flotation tests at different conditioning times. It was in point of fact observed that the variations were linear with the correlation coefficients of 0.9721, 0.9593, and 0.9792 for, respectively, 5, 10, and 20 min of conditioning.

The kinetics of flotation of PAH$_{tot}$, in the same conditions described by the Higuchi model (Fig. 5b), showed a higher flotation rate (k) over time for the three set flotation tests at different conditioning times. The increasing trend of k with conditioning time indicates an improved PAH$_{tot}$ recovery with a decrease in flotation time (Fig. 4). We observed that the variations at 5, 10, and 20 min of conditioning were linear with high correlation coefficients of 0.9897, 0.9881, and 0.9998 for, respectively, 5, 10, and 20 min of conditioning. Da Silva et al. [36] reported that the separation of oil from synthetic oilfield PW by IAF obeyed first-order kinetics. Compared to the results obtained with the first-order kinetics, we emphasize again that the flotation kinetics of PAH$_{tot}$ into the real oilfield PW by IAF responds to the Higuchi model for each flotation test [8].

Conclusions

IAF was applied on a real oilfield effluent (PW) to remove PAHs. This study evaluated the importance of the conditioning step on the removal efficiency of PAHs from PW, and the role of both Tween 80 and ethanol on efficiency of this process. The results confirm that the crucial role of this step is the flotation process. As discussed above, electrolytic salts are known to reduce bubble diameters, thus the natural presence of NaCl in PW at considerable concentration probably affects the bubble sizes. This suggests that the presence of NaCl may improve the removal efficiency of PAHs from PW by IAF. The conditioning step before the flotation process is important in the case of PAH$_{tot}$ recovery from PW. The applied conditioning times in the presence of Tween 80 resulted in PAH$_{tot}$ recovery of 93.67%. The addition of ethanol as frother reduced both the conditioning time from 30 min to 10 min and the flotation time from 20 min to 12 min. These data indicate that less alcohol may be necessary to reduce processing time than was used previously, which is beneficial from an economic standpoint. A detailed study of flotation kinetics in the presence of ethanol based on the flotation of PAH$_{tot}$ at different conditioning times showed that the process followed the Higuchi model.

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Conflict of Interest

The authors declare no conflict of interest.

References
