

Physicochemical Characterization and Kinetic Study of Flotation Process Applied to the Treatment of Produced Water

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Abstract

Produced water (PW) discharged into the Mediterranean basin is a mixture of organic and inorganic materials of high toxicity and risk to the marine environment. This PW had a high water mineralization and significant amounts of suspended matter (SM). The detected levels of heavy metals, especially Ag^+ , Ba^{2+} and Pb^{2+} cations, were not negligible. The values of chemical oxygen demand (COD 735 mg/L) and total organic carbon (TOC 93.83 mg/L), which were very high, confirmed the presence of large concentrations of polycyclic aromatic hydrocarbons (PAHs) which were identified by infrared analysis. The total concentration of polycyclic aromatic hydrocarbons (PAH_{tot}) in the PW sample was about 3.243 g/L. This can be treated by flotation in a very acidic medium at pH=2, in the presence of a neutral collector (Tween 80) at 0.5%, with an optimum cleaning efficiency of 93.67%, without necessarily generating the production of polluted sludge, in about 20 min, optimum time of flotation found. A study of flotation kinetics based on PAH_{tot} recovery was carried out. It showed that the process followed Higuchi model. At the end of the treatment, all effluents were corrected from the acidic pH to the neutral pH, before to be discharged into the sea.

Keywords: Produced water; Polycyclic aromatic hydrocarbons; Flotation; Kinetic; Environment

Introduction

Drilling and extraction operations which aim to maximize the production of oil and gas can be offset by the production of large quantities of water contaminated with organic and inorganic pollutants [1-3]. Produced water (PW) is the name given to the co-product generated when water or groundwater in the subsurface formations or reservoirs is brought to the surface during the production of conventional energy resources (oil and gas) and unconventional (coal gas and shale gas) [4]. The composition of PW is both complex and highly variable, of the organic constituents, polycyclic aromatic hydrocarbons (PAHs) are often regarded to contribute significantly to the environmental risk [5]. The inertness of these compounds, their low water solubility and strong lipophilic character lead to very high accumulation levels and persistence in the environment, so their elimination is considered as a priority in many countries [6]. Generally, PAHs are considered as hazardous chemicals because they can bioaccumulate in the food chain, and are carcinogenic, mutagenic and teratogenic to humans and other animals [7]. Because of the carcinogenic potential of several of them, the United States Environmental Protection Agency (USEPA) has listed as priority pollutants 16 PAHs in wastewaters and 24 PAHs in soils, sediments, hazardous solid wastes, and groundwater [8]. Since 1959, the oil port of Bejaia (North-East of Algeria) in the south of the Mediterranean sea, is the largest in Algeria, at this level, PW is the result of water concentrations in oil and condensates derived from Haoud El Hamra oilfields (Hassi Messaoud, south of Algeria). During storage in tanks, liquid hydrocarbons are separated from water by the difference in density. Before being discharged into the Oued Seghir River, which flows into the Mediterranean sea, PW is first collected in the concrete settling basin downstream the petroleum reservoirs. After natural settling, the oil is collected in the tray and the water released into the peripheral canal in order to undergo final settling. Research work on PW in different oilfields in the world has shown that the range of variation of the content of organic and inorganic pollutants present in PW exceeds that imposed by regulation.

The concentration of total organic carbon (TOC) varies between 0-1500 mg/L, Pb^{2+} between 0.002-8.8 mg/L, Ag^+ between 0.001-0.15 mg/L and Cr^{6+} between 0.02-1.1 mg/L [1]. So, there is an urgent need to develop effective, economic and green methods to simultaneously

remove organic and inorganic pollutants in these effluents, and to supervise the final effluents for reuse or environmental purposes [9]. Many technologies have been developed for the removal of petroleum pollutants [10-12], including biological treatment [13,14], membrane separation [15], flotation [16]. Among these methods, flotation is widely used because of its high rate of separation at short residence time and low operating cost [17].

In this context, the aim of this work is to give an overview on the physicochemical quality of PW, located in the Bejaia Marine Terminal (BMT), which is discharged into the Mediterranean basin, and to involve the use of induced air flotation as an appropriate treatment process for the recovery of oil, precisely PAHs. A commercially available surfactant (Tween 80) was used as both a collector and frother. Effects of pH of PW on the flotation of PAH_{tot} were studied in detail. First-order kinetic and Higuchi models for PAH_{tot} recovery were proposed.

Materials and Methods

Chemicals

Sulfuric acid (H_2SO_4), hydrochloric acid (HCl) 35-37%, sodium hydroxide (NaOH), hexane (C_6H_{14}) and nonionic collector (Tween 80) were obtained from BIOCHEM Chemopharma, Montreal. Ethanol ($\text{C}_2\text{H}_6\text{O}$) 96 Vol% was obtained from SIGMA-ALDRICH. Carbon tetrachloride (CCl_4) was obtained from PROLABO. Naphthalene (C_{10}H_8), anthracene ($\text{C}_{14}\text{H}_{10}$) and phenanthrene ($\text{C}_{14}\text{H}_{10}$) were obtained from PANREAC QUIMICA SA, Espana.

Sites and sampling

PW was sampled from a hydrocarbon storage tank at the Bejaia

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Marine Terminal (BMT) in amber glass bottles. A part of these samples was acidified with 1% H₂SO₄ to prevent the precipitation of heavy metals as oxides, in order to preserve them during one month. The other part was stored in the rough, without acidification, and was depended on the treatment by flotation.

Infrared analysis of dissolved PAHs

The crude samples had first to undergo a liquid-liquid extraction with CCl₄ to isolate PAHs dissolved in the organic phase, which were analyzed by infrared spectrometry.

Analysis of SM

SM contained in PW had a diverse composition and may contain significant quantities of heavy metals and PAHs. For this, we have needed to isolate SM from water by drying and filtration (To avoid the destruction of organic matters by heating).

After drying: a volume of 100 ml of PW was evaporated to dryness in an oven at 105°C for 24 h. After a complete evaporation of water, SM constituting solid residues was characterized by X-ray diffraction (PANalytical model) and infrared spectrometry, in order to identify organic (PAHs) and inorganic (heavy metals) pollutants. This method is destructive to certain organic compounds which are sensitive to heat.

After filtration: the SM was vacuum-filtered and retained, on a filter paper of 1 µm, previously dried in an oven at 105°C for 24 h and weighed before being characterized by different techniques: scanning electron microscopy (SEM) coupled with the chemical energy dispersion microanalysis (EDAX, FEI Quanta 200), the X-ray diffraction (XRD) and infrared spectrometry (FTIR), to identify the different mineralogical phases as well as the minerals, the morphology and the structure of the chemical compounds existing in SM. The filtrate was passed through a filter of 0.45 µm, before undergoing a liquid-liquid extraction with hexane to isolate the PAHs in the organic phase, and quantify the sole minerals in the aqueous phase by atomic absorption (Aurora Instruments), by targeting heavy metals such as lead. Further chemical analyses were made by flame photometry (SHIMADZU) and colorimetry (SpectroScan 50) to assay barium and lithium, on the one hand, and hexavalent chromium complexed with diphenylcarbazide, on the other.

Flotation tests

About 1 L of PW was introduced in a stainless steel tank, with a capacity of 1.5 L, of a Denver-type flotation cell, D-12 model and METSO brand. The first parameter of flotation which had to be optimized in this work was the pH which we varied from 2 to 11, by adjusting it and bringing it with an HCl solution (1N) to acid pH, and with a NaOH solution (1N) to basic pH. PW was subjected to vigorous stirring (750 rpm), controlled by a central rotor equipped with baffles at the lower end, in order to ensure a good homogeneity during attrition. After 15 min, 5 mL of the nonionic collector (Tween 80) at 0.5% was added. After 30 min of stirring (conditioning time), the valve allowing the injection of well determined and controlled caliber air bubbles was opened. During the bubbling, the froth formed on the surface of the liquid is recovered for 20 min (flotation time). At the end of the treatment, the concentrate and the pulp were recovered in sealed vials, which were analyzed to determine the removal efficiency of PAHs from PW by flotation. Meanwhile, two reference tests were completed: the first was a blank test, performed on crude PW, without reagent addition (natural flotation), except the foaming (pine oil), which was added at the end of the conditioning scum to neutralize the froth formed during

stirring. The second test was also performed on crude PW, without adjusting the pH, but with the addition of a collector (Tween 80). At the end of each test, the volumes of the pulp and the concentrate of flotation were measured, then filtered through a filter paper of 1 µm. PAHs were separated by liquid-liquid extraction by mixing 10 mL of filtrate with 10 mL of CCl₄ (V/V).

An estimate of the concentration of the total polycyclic aromatic hydrocarbons (PAH_{tot}) was made by infrared analysis of the organic phase, with respect to naphthalene standards (5 mg/mL), anthracene (5 mg/mL) and phenanthrene (5 mg/mL) in CCl₄. The quantification of PAH_{tot} was performed on volumes of 10 µL of either the raw water sample, or the pulp and concentrates in comparison to the standards prepared in the same conditions and volume of solvent, and separately deposited on pellets KBr for infrared analysis, by measuring the absorbance of the out-of-plane of δ_{arom}(CH) bending, which was characteristic to PAH_{tot} and located at 795.509 cm⁻¹. The quantification method developed in this work can link the concentrations of PAH_{tot} in PW (C₀), in the pulp (C_p) and in the concentrate (C_c) of flotation, as determined in comparison with that of naphthalene standard 5 mg/mL, with a removal efficiency (R_{ep} %) by flotation, which was estimated using the three relations:

$$R_{ep} (\%) = \frac{(A_0V_0 - A_pV_p)}{A_0V_0} \times 100 \quad (1)$$

Where, V₀, V_p and V_c (mL): volumes, respectively, of the samples of the crude PW, pulp and concentrate. A₀, A_p and A_c: absorbance of PAH_{tot} in crude PW, pulp and concentrate, respectively, measured at the same wavenumber 795.509 cm⁻¹.

The contents of PAH_{tot} in the pulp (T_p) and in the concentrate (T_c) could also be calculated precisely according to the relations (2) and (3) respectively.

$$T_p (\%) = \frac{m_p}{m_0} \times 100 \text{ for pulps} \quad (2)$$

$$T_c (\%) = \frac{m_c}{m_0} \times 100 \text{ for concentrates} \quad (3)$$

If losses are negligible, the material balance would be expressed by equation (4):

$$T_p (\%) + T_c (\%) = \left(\frac{m_p}{m_0} \times 100\right) + \left(\frac{m_c}{m_0} \times 100\right) = 100 \% \quad (4)$$

Flotation kinetics study for the recovery of PAH_{tot} at pH=2

To study the flotation kinetic of PAH_{tot}, two models was used, first-order kinetic and Higuchi models, which correspond to the equations that are expressed as following:

First order

$$\ln \left(\frac{C_t}{C_f} \right) = -kt \quad (5)$$

Where C_t (mg/L) is the concentration of the PAH_{tot} at any time and C_f (mg/L) is the final concentration of the PAH_{tot} at the end of batch flotation, beyond which the concentration of the PAH_{tot} does not change appreciably. k (min⁻¹) is the flotation rate constant, which was calculated using Equation 5.

Higuchi model

$$\frac{C_t}{C_f} = K_H t^{0.5} \quad (6)$$

Where K_H is the rate constant for the Higuchi Model.

In this case, a flotation test was done on a sample of PW at pH=2 in the same operating conditions as the precedent tests. Except that, after injection of bubbles air, 5 mL of samples were taken in the foam formed on the surface of the tank, each interval of time of flotation process until 60 min, and transferred into sealed glass test tubes. Samples were filtered through a filter paper of 1 μ m. Then, dilutions were made on 0.5 mL of samples and transferred into glass pill dispensers to which were added 0.5 mL of ethanol in order to form water-ethanol mixtures (V/V) for analysis by UV-Visible spectroscopy, similarly it has been established the naphthalene calibration curve in water-ethanol (V/V). Absorbances were read at 220 nm, the wavelength of absorption of PAH_{tot} on the Ultraviolet range. Their concentrations were calculated using a naphthalene calibration curve with a correlation coefficient of $R^2=0.996$.

Results and Discussion

Physicochemical characterizations of PW

SEM coupled with EDAX of SM: On micrograph (Figure 1a) carried out with a lower magnification (X400), we noticed the presence of clear and white appearance grains probably corresponding to clay minerals and quartz crystal. With an average magnification (X800), we observed a very porous morphology of the grains on micrograph (Figure 1b). The examination of the micrograph (Figure 1c) with a higher magnification (X1600) showed that quartz crystals are elongated and trigonal kind, whereas at a much higher magnification (X3000, 20 μ m) we got the micrograph (Figure 1d) showing two distinct parts: one dark (S), corresponding to mineral crystals, and the other lighter and fluorescent (F), attributed to organic matters (OM) rich in PAHs and adsorbed by the clay phase.

The electronic spectra (Figure 2a) obtained by chemical microanalysis (EDX) revealed the existence of chloride and fluoride ions combined as Na crystals, Pd, Ca and K of noticeable levels and mixed with low carbon amounts. Whereas the fluorescent moiety (Figure 2b) contained more atoms of carbon belonging to polycyclic aromatic compounds, which appear to have precipitated with oxides of Fe, Ni and Si in significant percentages, thus probably giving the sample a fluorescent appearance.

XRD analysis of the SM: The sample is analyzed after the total evaporation of water with powder X-ray diffraction, in order to identify the different mineralogical phases making the crude PW suspension. This gave two aspects, reddish precipitate (B), containing white crystals (A) (Figures 3A and 3B). The diffractogram of the white crystals formed and isolated after evaporation (Figure 4A) were identified as NaCl. XRD analysis of the reddish precipitate (Figure 4B) showed that its composition was complex and rich in various metals, including heavy metals, such as Pb as sulphate $PbSO_4$, transition metals represented by Zn as oxide ZnO and noble elements such as Ag as chloride AgCl and bromide AgBr. Among these, there was also the presence of lighter elements such as carbons in solid and crystallized form presumably belonging to pyrogenic or fossil phases, and derived PAHs.

Physicochemical composition of PW: The results in Table 1

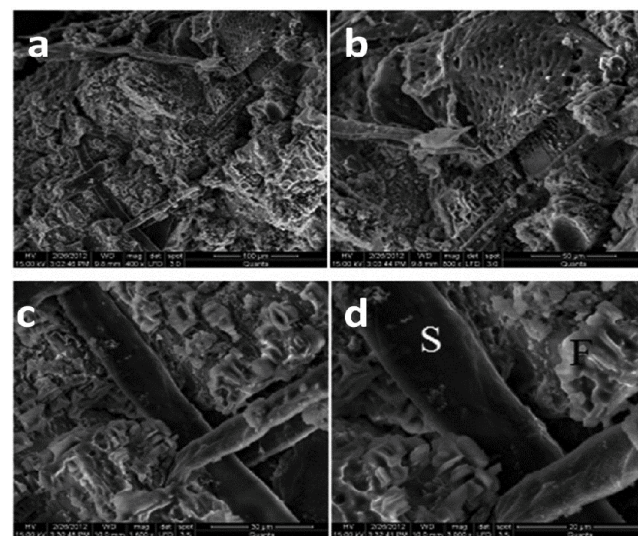


Figure 1: SEM micrographs of the SM of PW at different magnifications, a) X400; b) X800; c) X1600; d) X3000.

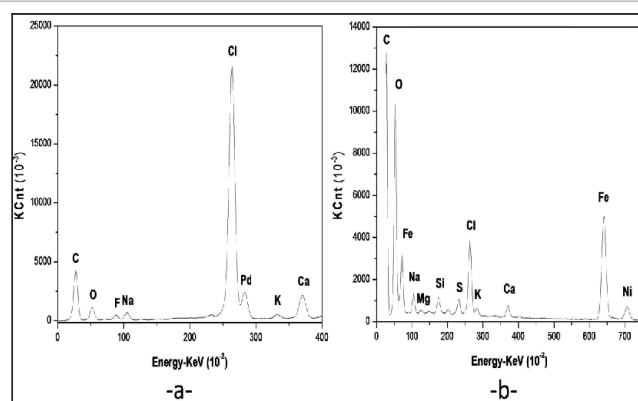


Figure 2: EDX microanalysis of: a) the dark side 'S' suspension for PW; b) the fluorescent portion 'F' of the SM from PW.

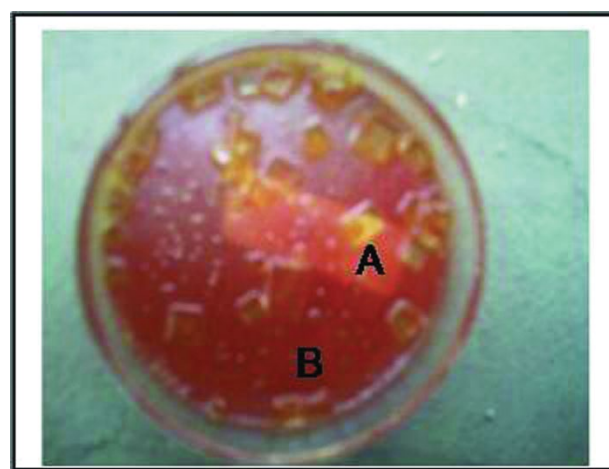


Figure 3: Photo representing the total SM after evaporation of the water, reddish and white containing NaCl crystals (A) stained with heavy metals and organic material (B).

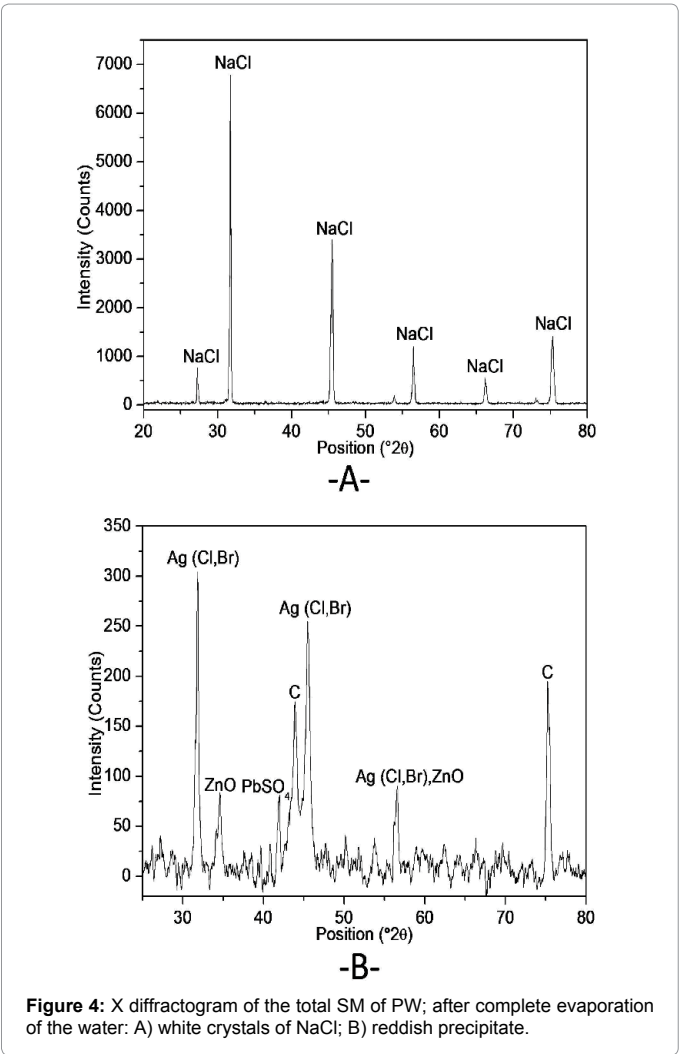


Figure 4: X diffractogram of the total SM of PW; after complete evaporation of the water: A) white crystals of NaCl; B) reddish precipitate.

Parameters	Value
pH	5.13-6.78 at 25°C
Density	1576 kg/cm³ at 25°C
Conductivity	83.62 mS/cm at 20°C
Turbidity	92.67 FTU
SM	562 mg/L
Hydrotimetric title	12.8 meq/L
alkalinity	0°F
Full alkalinity	1°F
COD	734 mg/L O ₂
Cl ⁻	1015.3 mg/L
NaCl	1673.1 mg/L
Fe ³⁺	0.042 mg/L
Pb ²⁺	4.91 mg/L
Cr ⁶⁺	0.135 mg/L
Ag ⁺	0.0613 mg/L
Ba ²⁺	0.91 mg/L
Li ⁺	0.0185 mg/L
TOC	93.83 mg/L
PAH _{tot}	3243 mg/L

Table 1: Main physical and chemical composition of PW.

showed that PW had an acidic character; pH (5.13 and 6.78) was within an interval more or less close to the lowest recommended limits of industrial waste discharges (5.5-8.5) [18]. Conductivity (83.62 mS/cm) was significantly higher, this showed that the water was rich in dissolved minerals. The chemical oxygen demand (COD) value (734 mg/L) was very important due to the presence of high concentrations of OM (93.83 mg/L), which were particularly assigned to PAHs. The amount of SM (562 mg/L) was far beyond the maximum limit values of the parameters of industrial waste established by local regulations in force in the report of the Minister of Education (respectively: 120 mg/L, 20 mg/L, 20 mg/L and 30 mg/L) [18]. The concentrations of heavy metals such as Pb²⁺ (4.91 mg/L), Cr⁶⁺ (0.135 mg/L) were relatively high and exceeded the standards, respectively 1 mg/L and 0.1 mg/L [19].

The concentration of Ag⁺ (0.0613 mg/L) was very important compared to the concentration established by the Predicted Environmental Concentration (PEC) in the aquatic environment which ranged from 0.03 µg/L to 1 µg/L [20]. The barium concentration (0.91 mg/L) in produced water was much higher than that required by the regulation of sea water, which ranged from 2 µg/L to 63 µg/L, with an average concentration of about 13 µg/L [21]. The most abounding elements were sodium and chlorides, which showed that PW had a character close to that of brackish water. Lithium is not considered toxic, since its concentration was low.

Flotation tests

IR spectrum (Figure 5a) of the organic phase of PW extracted in CCl₄, revealed the existence of high concentrations of polycyclic aromatic compounds, identified by a narrow, intense band at 795.509 cm⁻¹, corresponding to the out-of-plane deformation of the vibration of the aromatic CH bending [22]. Two stretching bands assigned to the valency vibration of the conjugated double bonds of the aromatic rings, at 1620 cm⁻¹ and at 1450 cm⁻¹, for a structure having a symmetry and specific to polycyclic aromatic compounds (the case of naphthalene) were also observed in the spectrum [19]. A strong and broad absorption band between 3600 cm⁻¹ and 3300 cm⁻¹ was attributed to the elongation of the OH group of hydration water. Infrared spectrum (Figure 5b) of the standards at 5 mg/mL of naphthalene, anthracene and phenanthrene, showed the appearance of an IR absorption band common to the three compounds: narrow and intense at 795.509 cm⁻¹, assigned to the out-of-plane deformation of the vibration of the aromatic CH bending [22]. This band was also observed at the same wavenumber for the organic phase of PW extracted in CCl₄ (Figure 5a), which confirmed the existence of a significant amount of PAHs. The infrared spectrum of the organic phases in CCl₄, concentrates and pulps of blank flotation and after addition of neutral collector (Tween 80) at 0.5%, respectively, were shown in Figures 5c and 5d. We observed the appearance of the same narrow absorption band and substantially of the same intensity at 795.509 cm⁻¹, characteristic of PAHs derivatives.

Despite the difference between the value of the pH of the water tank initially levied (5.13 at 6.78) (Figure 5c), and the pH of the flotation test set at 8 (Figure 6a), we also noticed that we obtained substantially the same IR absorption band, where intensities at 795.509 cm⁻¹ were at the same importance. Contrary to the flotation tests at pH=2 (Figure 6b) and at pH=11 (Figure 6c), we noticed that the intensities of IR absorption bands at 795.509 cm⁻¹ were much higher in the concentrates, unlike the pulps.

Nevertheless, Figure 7 showed that the flotation residues in the pulps and in the concentrates, which may contain significant amounts of PAHs, were significantly larger at basic pH than at acid pH. These

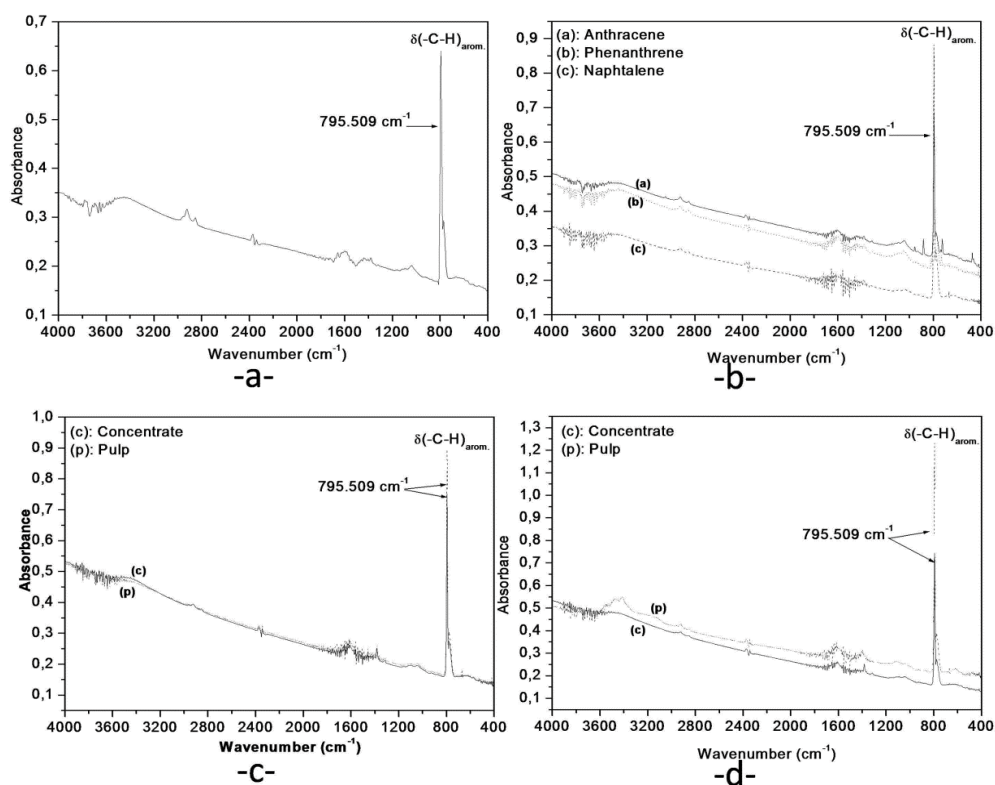


Figure 5: Infrared spectrum of the organic phase in CCl_4 of: a) produced water; b) standards at 5 mg/mL of naphthalene, anthracene and phenanthrene; c) concentrate and the pulp of flotation without collector addition and without pH adjustment (blank test); d) concentrate and the pulp of flotation with addition of collector (Tween 80 at 0.5%) and without pH adjustment.

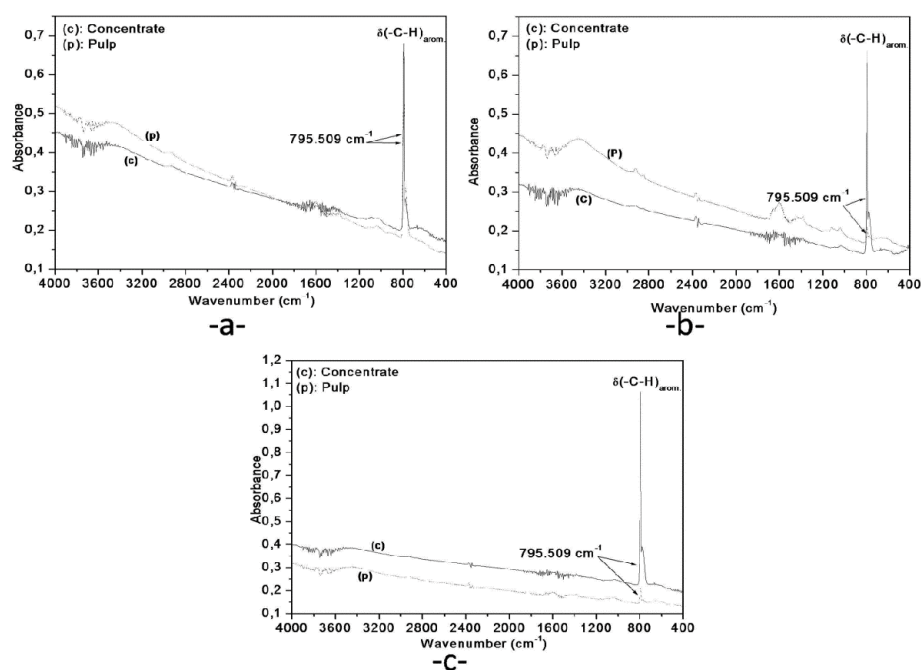


Figure 6: Infrared spectrum of the organic phase in CCl_4 of the concentrate and the pulp with the addition of the collector (Tween 80 at 0.5%) at: a) pH=8; b) pH=2, c) pH=11.

results showed that the basic pH have enhanced the formation of SM which were turned, at the end of the flotation treatment, into large quantities of sludge, where these formed flotation residues would not completely float, but precipitated in the bottom of the flotation tank. This confirms that PAHs, which tend to be adsorbed on the solid residues [23], rich in clay minerals and metals characterized by SEM coupled with EDX and XRD, and OM, have precipitated with a large amount of OM. At very basic pH (pH=11), the mass of the flotation residues was higher in the pulp compared with the flotation residues in the concentrate (Figure 7).

This explains the importance of the recorded removal efficiency at this pH, which was optimal and was estimated at 94.09% (Figure 8a), as well as a low content in PAH_{tot} in the pulp (5.9%) (Figure 8b). These results were in agreement with the excess negative charge, in particular, which was induced by a high concentration of OH^- ions, on the one hand, and, on the other hand, by the deprotonation of the aromatic rings of PAHs, which caused the formation of an excess of negative charges delocalized along the aromatic rings. Therefore, the negative charge of SM surface tended to further precipitate the metal cations and minerals which have sedimented more and enhanced the adsorption of OM. At strongly acidic pH (pH=2), the mass of flotation residues was rather the same in the concentrate and in the pulp, but at relatively lower amounts than those obtained with the flotation test at pH=11 (Figure 7).

The removal efficiency (Rep) of PAH_{tot} in PW, recorded at pH=2 is 93.67% (Figure 8a), which allowed us to conclude that the flotation of PAH_{tot} was also very effective in the highly acidic medium, due to the molecular state of PAH, which were more hydrophobic and have more affinity to the neutral collector (Tween 80). PAH_{tot} content in the pulp was of 6.33%, but was, in contrast, higher in the content reaching about 25.5% (Figure 8b), we can say that, in the concentrate, about 67% of PAH_{tot} were adsorbed on the flotation residues (about 326.9 mg for the concentrate and 263.3 mg for the pulp), which caused considerable losses in the quantification.

Flotation kinetic study for the recovery of PAHs

The calibration curve represented in Figure 9 has allowed us to quantify the PAH_{tot} in the concentrate of flotation and to follow the flotation kinetics which was modeled thereafter.

The variation of the concentration of PAH_{tot} from the float with flotation time, at pH=2 and a constant dose of collector (tween 80 at 0.5%), is shown in Figure 10. It was observed that the concentration of PAH_{tot} increases with time of flotation and approached an asymptote. It can be noted that the increase in the concentration of PAH_{tot} was marginal if the flotation time was extended beyond 20 min. Hence, 20 min may be considered as the optimum flotation time of PAH_{tot} where their concentration reached was about 9.7 mg/L.

The near constancy of the concentration of PAH_{tot} indicates that the separation process is purely governed by the mixing of air and PAH_{tot} and the interaction between PAH_{tot} and collector. Hence, the collectors form micelles. Free collectors release PAH_{tot} from the organic matters (OM) by reducing the surface tension between solid-liquid (OM-PAH) interfaces. Some PAH_{tot} is trapped within the micelles and some are attached to the rising air bubbles.

As mentioned earlier, two models for the flotation of PAH_{tot} were proposed, first order kinetics and Higuchi model. According to the Equation 5, a plot of $\ln\left(\frac{C_i}{C_f}\right)$ versus t should result in a straight line. The values of $\frac{C_i}{C_f}$ were plotted against time and it was indeed observed that

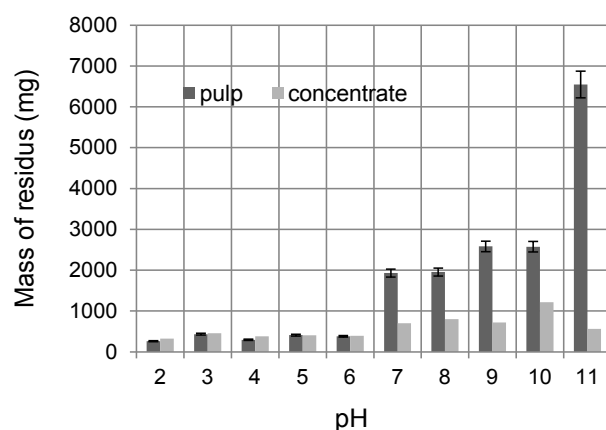


Figure 7: Mass of flotation residues in the pulp and in the concentrate depending on pH.

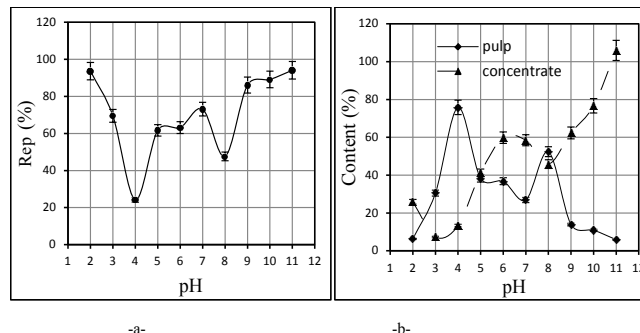


Figure 8: a) Removal efficiency of PAH_{tot} depending on pH; b) PAH_{tot} content in pulp and concentrate of flotation depending on pH.

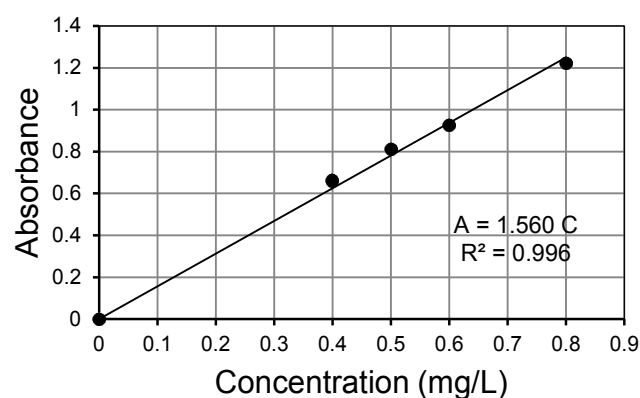


Figure 9: Calibration curve of PAH_{tot} in water/ethanol (V/V), UV spectroscopy at 220 nm.

the variations were linear with a high correlation coefficient $R^2=0.971$ (Figure 11a).

While, according to the Equation 6, a plot of $\frac{C_i}{C_f}$ versus $t^{0.5}$ should result too in a straight line, and it was too observed that the variations were linear with a very high correlation coefficient $R^2=0.986$ (Figure 11b). This has proved that the flotation kinetics of PAHs responds to Higuchi model much more than the first order kinetics.

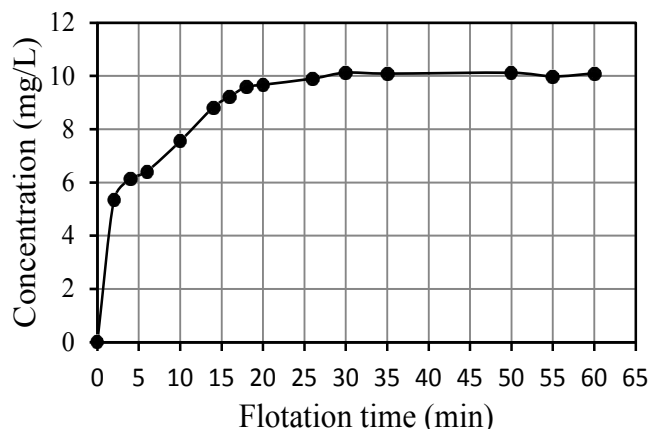


Figure 10: Variation of the concentration of PAH_{tot} in the concentrate with flotation time, at pH=2, UV spectroscopy at 220 nm.

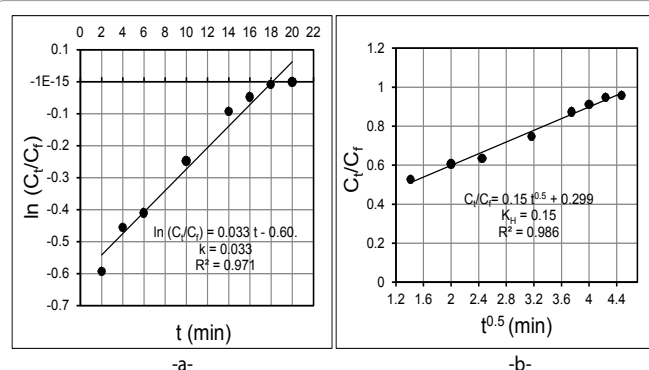


Figure 11: a) First-order kinetics and b) Higuchi model of flotation of PAH_{tot} at pH=2, UV spectroscopy at 220 nm.

Conclusions

The present study reveals that produced water (PW) localized in Bejaia Marine Terminal (BMT) was loaded with organic pollutants, especially polycyclic aromatic hydrocarbons (PAHs), and heavy metals, with concentrations exceeding that imposed by regulations, hence the need to treat this PW before reuse or discharge into the Mediterranean basin. The flotation treatment applied to this PW had been optimized, and the results showed that the best removal efficiency (93.67%) of total polycyclic aromatic hydrocarbons (PAH_{tot}) is obtained at strongly acidic medium (pH=2). In addition, the flotation process at a strongly acidic pH would not lead to the formation of solid residues. In contrast, at strongly basic pH (pH=11), we noticed that, despite a maximal removal efficiency (94.01%) of PAH_{tot}, this basic medium created competition between the flotation process and the flocculation-coagulation mechanism, which generated substantial amounts of sediments and sludge loaded with organic and inorganic pollutants, leading to the formation of matrices which were even more dangerous than aqueous medium, especially to the marine environment. The optimum time of flotation of PAH_{tot} was found to be around 20 min. It has been found that the flotation kinetics of PAH_{tot} follows much the Higuchi model.

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