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Surfactant-modified native soil in the treatment of oil field (Nimr) produced water

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ABSTRACT

In this study, we investigated the possibility to use surfactant-modified and unmodified native sand (Oman) for the treatment of oil field (Nimr) produced water. Dodecyltrimethylammonium (DDTMA) bromide was used to modify the sand properties. In our approach, surfactant was added to the contaminated water and the resulting aqueous surfactant solution was forced to percolate through the column packed with native soil. Thus, in this approach, soil modification by the surfactant molecules occurs during the water treatment process. Rejections of the crude oil aromatic components were estimated using a new and simple approach based on the measured total fluorescence emission ratio A_p/A_0, where A_p is the total fluorescence area of the permeate and A_0 the total fluorescence area of the untreated water. Our results from the packed column with unmodified native sand showed substantial rejection of aromatic hydrocarbons (~ 85%) only for the first individual 100 mL permeate sample collected. As the cumulative volume of permeate increases up to 1000 mL, the rejection decreases to less than 10%. When surfactant was added to the feed (contaminated Nimr water) at 10^{-4} M (below the surfactant CMC), complete rejection occurred only with the first individual 100 mL permeate sample collected, followed by a decrease in the rejection to about 45% rejection as the cumulative permeate volume reached 1000 mL On the other hand, when e surfactant was added above its CMC (5×10^{-4} M and 1×10^{-3} M), all individual 100 mL (10 separate individual 100 ml samples) were practically free of aromatics (~100% rejection). Thus, complete rejections occurred only at and above the surfactant critical micelle concentration. This concentration-dependent rejection of the aromatics was associated to the concentration-dependence of the surfactant onto the substrate surface.

Keywords: Surfactant, Rejection, Surfactant-modified soil, Adsorption, Aromatic components

1. Introduction

Considerable amount of water associated with the drilling of crude petroleum is produced daily by Petroleum Development Oman (PDO) and estimated to be about 4.5 million bpd [1]. Such huge volume of water is separated from the crude oil through a multistage separation process. However, the treated water still contains traces of oil and its discharge into the environment is strictly regulated. In Oman, governmental regulations require the injection of the treated oil-produced water into deep disposable zones [2], a very costly approach for the Sultanate. Petroleum Development Oman (PDO) has spent about US$ 120 million on produced water

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management during 2000–2008 for disposal into the deep reservoirs alone [3]. This has led PDO to investigate ways of treating oil field produced water for use as drinking water, irrigation etc. One approach was based on the use of reed bed-cultivated at Nimr [3]. Most of the contaminating oil was removed by the action of plant roots. However, concern remains that contaminants could enter in the human food chain. Accordingly, a second processing phase involving “solar dew” distillation technology was used to yield demineralized water to eliminate the food-chain risk. But the economic viability of the entire process has not been worked out [4]. A joint investigation by PDO and Sultan Qaboos University [4] was carried out using combined air-flotation and adsorption (anthracite and activated carbon) to remove oil. The process reduced the oil content from 100–300 ppm to less than 0.5 ppm. Such process, however, seems to be inappropriate in a large scale application. More recently [5], we showed that micellar enhanced ultrafiltration (MEUF) could be effective in reducing oil content to less than 0.5 ppm, but the cost of the membrane could be a serious limitation.

Extensive research is currently underway on the use of surfactant-modified clays and soils to treat water contaminated with organic pollutants [6–15], a promising approach justified by the fact that natural soils are ineffective sorbents for hydrophobic solutes due to their hydrophilic nature. This is due to the fact that the adsorption of hydrophobic solutes onto polar soil minerals is suppressed by the strong competitive adsorption of water. Accordingly, surfactants are used to modify the soil nature from hydrophilic to hydrophobic upon adsorption of the surfactant at the substrate surface. Surfactant adsorption onto solid minerals has been extensively studied and was shown to depend on many parameters: i) the nature of the substrate, ii) the molecular structure of the surfactant being adsorbed, and iii) the environment of the aqueous phase [16,17]. In particular, the mechanisms by which ionic surfactants may adsorb from aqueous solution onto an oppositely charged solid substrate is a complex process, during which adsorption of the surfactant may occur successively by ion exchange, ion pairing, and hydrophobic bounding. At low concentration, surfactant monomers are adsorbed by ion exchange and eventually form a monolayer with the hydrophilic surfactant head adsorbed on the surface and the hydrophobic surfactant tail oriented towards the aqueous phase, thereby modifying the soil surface from hydrophilic to hydrophobic. As the amount of surfactant increases, hydrophobic interaction among hydrocarbon tails causes the formation of bilayer (a hydrocarbon phase) that function as a powerful solubilizing medium [18,19] for organic compounds. At this stage, adsorption is usually complete, and in many cases this occurs in the neighborhood of the critical micelle concentration [16].

In the present study, our main objective is to demonstrate laboratory feasibility of using surfactant-modified Omani native soil (sand) in removing aromatic crude oil components from Nimr oil field (Oman) produced water. Our focus on aromatic crude oil components is justified by their known extreme toxicity even at very low concentrations and their adverse effect on human health [20,21]. To the best of our knowledge, most studies reported on the removal of organic solutes by surfactant-modified soils were carried out by pumping the contaminated water into the column packed with an already surfactant-modified soil. In our approach, surfactant will be added to the contaminated water and the resulting aqueous surfactant solution will be forced to percolate through the column packed with native soil. Thus, in this approach, soil modification by the surfactant molecules occurs during the water treatment process.

2. Experimental

2.1. Materials

Native soil (sandstone) from Dhank (Sultanate of Oman) was used in this study. The sand was sieved to obtain particle sizes in the range 100–200 mm. The sand was then washed with de-ionized water and heated at 120°C overnight. Dodecyltrimethylammonium (DDTMA) bromide (> 99% pure) was purchased from Acros Organics, USA. This cationic surfactant was used without further purification. Its critical micelle concentration (CMC) in distilled water is 1.6×10^{-2} M [22].

Produced water from Nimr oil field (South Oman) was provided by Petroleum Development Oman (PDO). The produced water, a turbid suspension of crude oil droplets, contains about 8.2 g/L total dissolved solids (TDS).

RF-5301PC spectrofluorimeter (Shimadzu, Japan) was used for measuring fluorescence spectra.

2.2. Procedure

2.2.1. Column leaching test

Column experiment was carried out at room temperature (Fig. 1). The porous plate inside the column beneath the soil prevented loss of soil during leaching. 200 g of sand was incrementally packed to a height of 15.5 cm in glass columns (3.5 cm diameter and 35 cm height), Next, distilled water was pumped into the packed column at a constant flow rate of 1.65 ml/min overnight to saturate the column. The feed solution (Nimr produced water with and without added surfactant) was pumped into the column at the same rate. Permeates were collected in individual 100 mL for analysis.

2.2.2. Chemical analysis

Aromatic compounds are known for their strong fluorescence emission. Therefore, fluorescence was used to estimate the relative concentration of aromatics in the non-treated oil field produced water and in the treated

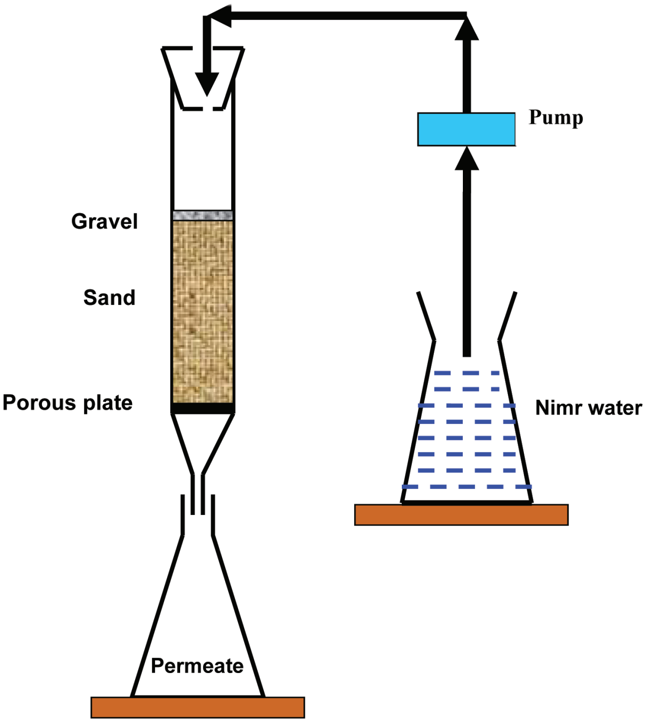

Fig. 1. Schematic representation of column leaching experiment.

water (permeate) from the area of their respective fluorescence spectra. All samples were excited at $\lambda_{exc} = 235$ nm.

2.2.3. Retention of aromatics

In all cases, the parameter which quantifies the efficiency of oil removal is defined by the percentage of rejection *R* factor (% *R*) as expressed by

$$\%R = \left[1 - \left(C_p / C_0\right) \times 100\right] \quad (1)$$

where C_p and C_0 refer to the analytical concentration of pollutants in the collected permeate and the non-treated produced water, respectively. However, the determination of C_p and C_0 in many complicated systems such as crude oil contaminated water can be a very time-consuming and challenging task. Accordingly, in this work we propose a simple and efficient method to estimate the rejection of crude oil aromatic components by fluorescence emission measurements from the untreated water and the treated water (permeate). In this approach, the ratio (C_p/C_0) is replaced by the ratio A_p/A_0, where A_p and A_0 are the total fluorescence area of the permeate and the feed solution (untreated Nimr water), respectively. This is because, under similar experimental conditions, total concentration of aromatic components in the permeate (C_p) and the corresponding concentration in the untreated Nimr water (C_0) can assumed to be proportional to the areas of their respective fluorescence spectrum

$$C_p = b \cdot A_p \text{ and } C_0 = b \cdot A_0 \quad (2)$$

where *b* is a constant (instrumental parameter). Substitution of Eq. (2) into Eq. (1) leads to

$$\%R = \left[1 - \left(A_p / A_0\right) \times 100\right] \quad (3)$$

The validity of Eq. (3) assumes that the total fluorescence area varies linearly with the concentration of the fluorescent species. Thus, fluorescence spectra were measured for untreated Nimr produced water diluted with distilled water to obtain different volume fractions (Fig. 2). Areas of the total emission intensity (A_t) were extracted from spectra shown in Fig. 2 and plotted versus untreated Nimr produced water diluted with distilled water at different mixture compositions in Fig. 3. Clearly, a linear relationship is observed, with an intercept at the origin A_r = 645.58, reflecting a residual emission even in the absence of aromatics at infinite dilution. In fact, residual emission intensity from distilled water was also observed (A_r = 598.281). Hence, the total emission intensity from the different samples appears to be the sum of two contributions, namely a contribution from the true fluorescence emission (A_f) from the excited singlet states (S_1) of the aromatic molecules to their corresponding ground states (S_0) and a contribution from scattering emission (A_{sc}) intensity. Accordingly, the true fluorescence area could be estimated from the following relation

$$A_f = A_t - A_{sc} \quad (4)$$

Plot of the true fluorescence A_f vs. Nimr produced water concentration is shown in Fig. 3 (inset). An excellent linear fit (R^2 = 0.99687) is observed with an intercept at the origin equal to zero, suggesting correctness of assumptions made in Eq. (2). Therefore, in this study, the

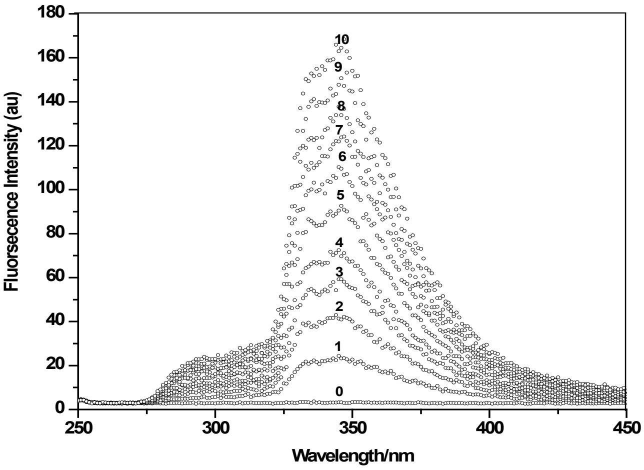

Fig. 2. Fluorescence spectra for diluted Nimr produced water: distilled water (0), 10% (1), 20% (2), 30% (3), 40% (4), 50% (5), 60% (6), 70% (7), 80% (8), 90% (9) and 100% Nimr water (10).

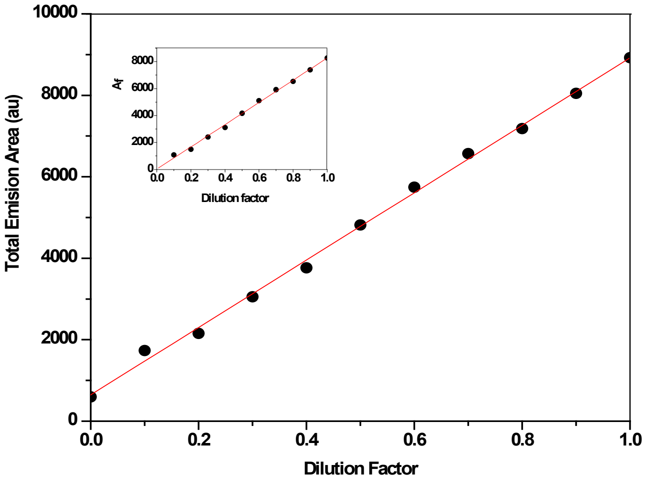

Fig. 3. Calibration curve showing the variation of the total emission (A_t) area vs. dilution factor. Inset: variation of the true fluorescence emission (A_f) with dilution factor.

percentage of rejection (% R) was calculated from the true fluorescence of the sample (corrected from scattering) by using Eq. (3).

3. Results and discussion

3.1. Retention of aromatic components by native sand

In this experiment, we investigated the rejection of aromatic components from Nimr oilfield produced water with unmodified native sand (200 g, 100–200 μm). Permeates were collected in ten individual 100 mL samples. All fluorescence spectra are presented in Fig. 4. True fluorescence areas ($A_f = A_t - A_0$) were extracted from these spectra and rejections of aromatic pollutants were calculated according to Eq. (3) and are shown in Fig. 5. Interestingly, the first 100 mL permeate sample showed a significant rejection of 83.95%. However, the rejection capacity of the natural sand was reduced to 8.52% as the amount of cumulative volume of collected permeate is increased from 100 to 1000 mL. Two mechanisms were proposed to account for the sorption of hydrocarbon solutes in soil–water systems. First, the sorption might be attributed to the adsorption of aromatics onto the soil surface [16]. The second mechanism could be associated with a partition process involving hydrophobic interactions between soil organic matter (OM) and the aromatic pollutant, in which the OM acts as a natural solubilizing medium for the pollutant. In fact, X-ray fluorescence analysis (Table 1) shows that the sand may contain as much as 6.11% natural organic matter. The decrease in pollutant retention with the increase in cumulative volume of permeate is probably due to the decreasing capacity of the soil OM in solubilizing aromatic molecules and to the saturation of soil surface with the adsorbed aromatic molecules.

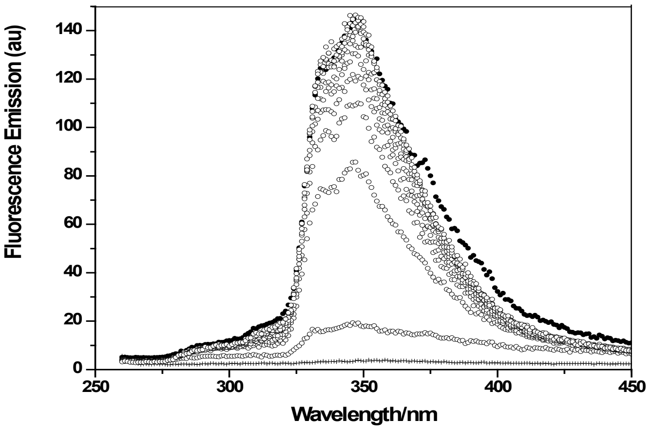

Fig. 4. Fluorescence spectra for: untreated Nimr water (•), successive individual 100 mL permeate samples (o) and distilled water (+) treated with unmodified native sand (200 g, 100–200 μm).

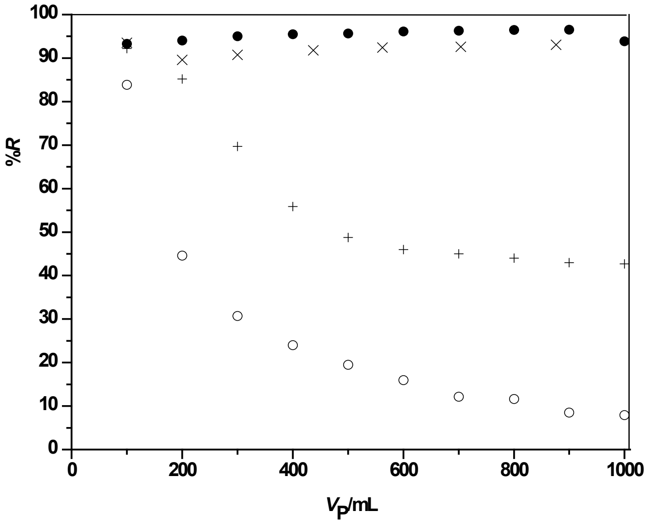

Fig. 5. Variation of the percent rejection of aromatic components with cumulated volume of permeate collected in the treatment of Nimr oil field produced water with: unmodified native sand (o), DDTMA (10^{-3} M)-modified sand (•), DDTMA (5×10^{-4} M)-modified sand (×), and DDTMA (10^{-4} M)-modified sand (+), 200 g sand (100–200 μm).

3.2. Retention of aromatic components by surfactant-modified sand

Surfactant adsorption onto solid surfaces is strongly influenced by the surfactant concentration. In particular, a plateau adsorption generally occurs at or near the critical micelle concentration (CMC) and is characterized

Table 1
X-ray fluorescence (XRF) analysis for the native sand collected from Dhank, Oman

Compound	% wt.
SiO_2	64.11
Al_2O_3	5.63
Fe_2O_3	1.81
CaO	13.81
MgO	6.43
SO_3	0.08
K_2O	1.00
Na_2O	0.98
Mn_2O_3	0.01
TiO_2	0.01
P_2O_5	0.01
Cl	0.00
Total*	93.89

*The remaining 6.11% may be organic matter (OM)

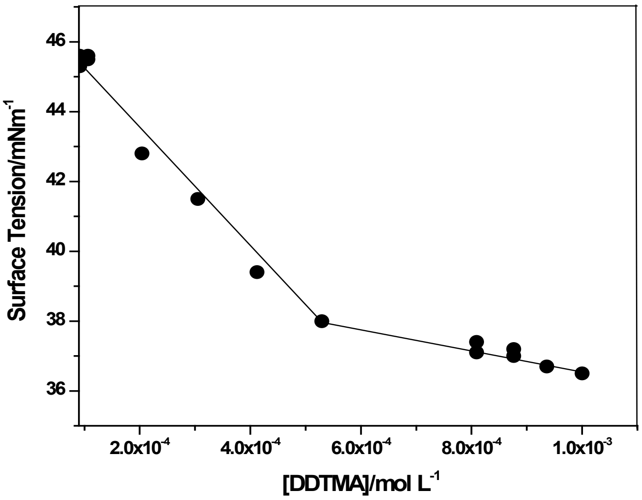

Fig. 6. Variation of surface tension with DDTMA concentration in Nimr oil field produced water at 23°C.

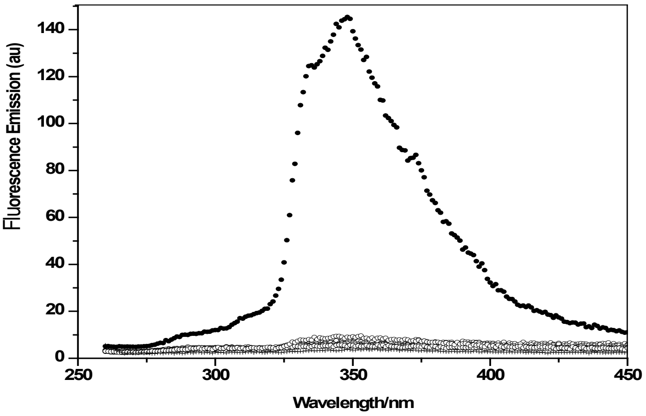

Fig. 7. Fluorescence spectra for: untreated Nimr water (•), successive individual 100 mL permeate samples (o) and distilled water (+) treated with DDTMA (10^{-3} M)-modified sand (200 g, 100–200 μm).

by no increase in adsorption with increasing surfactant concentration. The critical micelle concentration (CMC) of DDTMA in distilled water is reported to be 1.6×10^{-2} M at 25°C [22]. However, the presence of electrolyte in Nimr water may affect drastically the CMC [23]. Accordingly, we estimated the CMC of DDTMA in Nimr water from the variation of surface tension with surfactant concentration (Fig. 6). As shown in this figure, the micelle formation in Nimr water occurs at 5.3×10^{-4} M, considerably less than the CMC value of the surfactant in distilled water (1.6×10^{-2} M). This depression in the CMC is attributed to the decrease in the electrical repulsion between the surfactant cationic head groups in the micelles in the presence of electrolyte [23].

In this experiment, dodecyltrimethylammonium bromide (DDTMA) was added to the untreated Nimr produced water at a concentration of 10_{-3} M, concentration above its CMC. Permeates were collected in successive individual 100 mL samples to get a total volume or 1000 mL. All fluorescence spectra are presented in Fig. 7. Rejections of aromatic components of the crude oil in Nimr water were calculated according to Eq. (3) and are plotted in Fig. 5. Interestingly, almost complete rejections (~100%) were observed in the presence of the surfactant. This drastic increase in surfactant-modified rejection of aromatics can be attributed to the known fact that soils with cation-exchange capacity (CEC) might be modified by ion exchange with large surfactant molecules to increase their organic matter contents, thereby providing additional organophilic moiety favorable for the sorption of organic contaminants. Furthermore, surfactant tails can interact with each other (hydrophobic–hydrophobic bounding) and form a hydrophobic bilayer that can also provide a powerful partition medium for organic pollutants. Hence, this significant surfactant-induced rejection enhancement may be attributed to the combined effect of the two mechanisms mentioned above, namely ion exchange and hydrophobic–hydrophobic interactions.

3.3. *Effect of surfactant concentration on the rejection*

The above experiment was repeated at the surfactant CMC (5×10^{-4} M) and below the CMC (10^{-4} M). Permeates were collected in individual 100 mL samples. Fluorescence spectra from these treated samples are given in Fig. 8 (5×10^{-4} M) and Fig. 9 (10^{-4} M). Plots of R% vs. cumulative volume of permeate collected (V_p) are displayed in Fig. 5. Interestingly, rejections observed with surfactant system

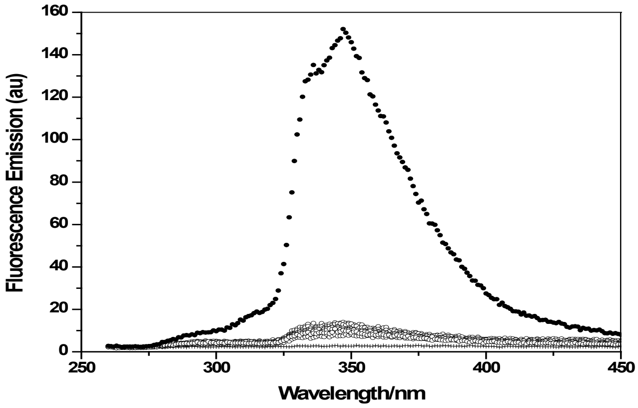

Fig. 8. Fluorescence spectra for: untreated Nimr water (•), successive individual 100 mL permeate samples (o) and distilled water (+) treated with DDTMA (5×10^{-4} M)-modified sand (200 g, 100–200 μm).

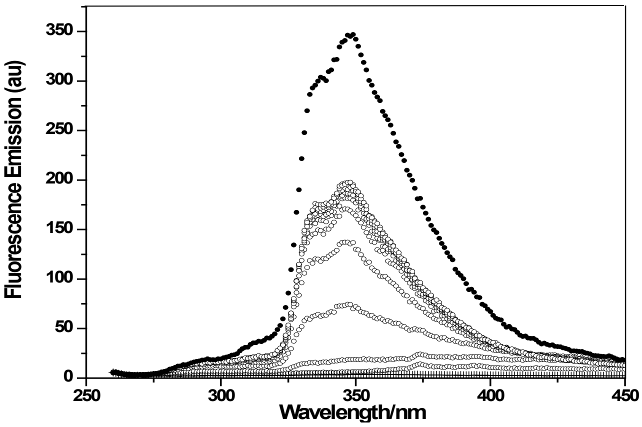

Fig. 9. Fluorescence spectra for: untreated Nimr water (•), successive individual 100 mL permeate samples (o) and distilled water (+) treated with DDTMA (10^{-4} M)-modified sand (200 g, 100–200 μm).

at the CMC were similar to those observed with the surfactant system above the CMC (10^{-3} M). On the other hand, at 10^{-4} M surfactant concentration (below the CMC), a relatively high rejection (~90%) was observed only with the first individual 100 mL permeate sample collected, followed by a decrease by a decrease as the cumulative permeate volume is increased to reach a limiting value (~50%) at V_p around 600 mL. These results clearly indicate that maximum rejections can be achieved only above the surfactant critical micelle concentration. It is, therefore, essential to use surfactants characterized by low CMCs in order to reduce the amount of surfactant required in a large scale water treatment process. It is also interesting to note the invariance of the rejection at a critical cumulative volume of permeate (V_p) for surfactant system below the CMC and in the absence of surfactant (Fig. 5). This invariance may be attributed to the occurrence of an equilibrium between adsorption and desorption of aromatic solutes onto the solid substrate. Previous studies showed that hexadecyltrimethylammonium bromide (HDTMA) held at ion-exchange sites was resistant to desorption, whereas the sorption of surfactant held via hydrophobic bonding was more readily desorbed [24,25]. Current work on the dynamic adsorption–desorption of DDTMA onto the native sand is in progress in our laboratory.

Finally, it is worth to note that highest rejections were obtained with surfactant systems above the critical micelle concentration. This appears to indicate that hydrophobic–hydrophobic interaction among surfactant hydrocarbon plays a major role in the rejection efficiency. This interaction causes the formation of bilayer (a hydrocarbon pool) that function as a powerful solubilizing medium for the aromatic solutes [18,19]. At this stage, surfactant adsorption reaches a plateau, and in many cases this occurs in the neighborhood of the critical micelle concentration [16]. Accordingly, surfactant systems having very low critical micelle concentrations can be suitable for low-cost water treatment processes.

4. Conclusion

Rejection of aromatic hydrocarbon components from produced oil field (Nimr) water by native and surfactant (DDTMA)-modified native sand was investigated. Excellent rejections (~100%) were achieved at surfactant concentrations at/and above the critical micelle concentration (5×10^{-4} M and 1×10^{-3} M). In the absence of surfactant (unmodified native sand) and in the presence of surfactant below its CMC (1×10^{-4} M), the rejection first decreases with the cumulative volume of permeate collected (V_p) and then reaches a plateau (10% with native sand and 50% surfactant-modified sand), at a particular value of V_p. Surfactant concentration is therefore a vital parameter for a successful surfactant-enhanced water treatment process. In particular, surfactant systems above the critical micelle concentration (CMC) can be very effective in solute rejection. Clearly, surfactant-modified soils could be successfully used to enhance removal of aromatic components from contaminated oil field produced water.

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