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"Gheorghe Asachi" Technical University of Iasi, Romania

EFFECT OF NONIONIC SURFACTANTS ON THE REMOVAL OF PAH FROM CONTAMINATED SOIL

Razika Khalladi[1]*, Nadji Moulai-Mostefa[1], Fatiha Bentahar[2]

[1]Laboratory of Materials and Environment, University of Medea, Ain D'heb, Medea 26001, Algeria
[2]Laboratory of Transfer Phenomena, USTHB, Bab Ezzouar, BP 32 EL Alia, Algiers 16111, Algeria

Abstract

In this study, a soil washing process in the presence of a nonionic surfactant solution of Tween 80 or Triton X-100 was investigated. Sandy soil was contaminated in the laboratory with naphthalene (10 mg/kg and 5000 mg/kg) and anthracene (25 mg/kg and 200 mg/kg), then washed with surfactant solution. A preliminary water washing step showed the performance of water in the removal of the two polycyclic aromatic hydrocarbons (PAH), especially naphthalene. The effect of Tween 80 and Triton X-100 was significant beyond the critical micellar concentration (CMC), where a concentration of 7 or 10CMC showed a great efficiency in removing PAH. Also, the effect of these surfactants was shown remarkably affected by the pH and the ionic strength.

Key words: hydrocarbon, PAH, soil remediation, surfactant

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1. Introduction

The contamination of soils and groundwater by polycyclic aromatic hydrocarbons (PAH) is a widespread environmental problem and the removal of such hydrophobic compounds from contaminated area is becoming a major concern. Commonly known by their toxic and carcinogenic effects, the PAH are released into the environment as a result of incomplete combustion of fossil fuels or by accidental discharge during the transport, use, and disposal of petroleum products (Costes and Druelle, 1997). Now widely used, the consumption of polycyclic aromatic hydrocarbons has greatly increased. Wild and Jones (1995) estimate that 90% of PAH emitted into the environment are stored in soils and groundwater. Hence, their fate in the environment has become a topic of great importance because these compounds are highly toxic even at low concentrations.

PAH possess low water solubility and are strongly adsorbed to soils and sediments. Therefore, the natural attenuation of PAH by biodegradation or volatilization is very slow, resulting in their persistence in environment for long periods of time (Laha et al., 2009; Li et al., 2016). According to Butler and Hayes (1998) and Rao and Paria (2009), surfactants can increase hydrophobic organic compounds solubility in the water phase through micellar solubilization and can improve their mobilization due to interfacial tension reduction. Up to now, various remediation techniques have been developed; among them, the soil washing processes with surfactant solutions are the most used (Liang et al., 2017). These processes are based on the decrease of the interfacial tension at the soil/organic phase and water/organic phase interfaces (Mao et al., 2015). According to Guha et al. (1998), surfactants are more efficient above their critical micelle concentration (CMC), where micellar aggregates can be formed by an auto association of surfactant monomers.

Actually many surfactants are commercially available, but a lot of them are not suitable for PAH contaminated soil remediation. Some could become potential contaminants in soil or groundwater and

* Author to whom all correspondence should be addressed: e-mail: r_khalladi@yahoo.fr; Phone/Fax: (213) 25 59 45 40

might also be expected to influence the behavior of other pollutants. Abdul et al. (2008) evaluated the suitability of ten surfactants for washing contaminated sand. They conducted batch tests for solubilization capacity and pollutant removal. The results showed that effectiveness of surfactant differs depending on the system properties (contaminant nature, contamination rate, surfactant concentration, soil structure).

The use of surfactants for the remediation of contaminated soils has been studied by many authors (Abdul et al., 1990; Mulligan et al., 2001; Paria, 2008; Pantsyrnaya et al., 2014). However, due to the complexity of phenomena observed in a soil/PAH/surfactant system (micellization, adsorption, solubilization, and mobilization), the dependence of surfactant efficiency on system properties and the continuous increase of hydrocarbon consumption, this field is still a matter of interest and merits investigation.

The objectives of this study are: i) to investigate the effect of the presence of two nonionic surfactants on the PAH removal from polluted soil, ii) to evaluate the dependence of surfactant efficiency with the pH and the ionic strength. The experimental results can be used to understand the performance of the chosen surfactants in the removal of Naphthalene and Anthracene and to provide valuable information about the behavior of such systems.

2. Materials and methods

2.1. Materials

PAHs used in this study were Naphthalene (Naph) of analytical grade purchased from Biochem chemopharma and Anthracene (Anth) (purity 97%) product of Alfa Aesar GmbH. The nonionic surfactants used were polysorbate 80 called Tween80 (TW80) obtained from Biochem chemopharma, and the octylphenol polyoxyethylene known as Triton X-100 (TX100) purchased from Prolabo. The surfactants were used as received without further purification. The solubility enhancement of PAH by TX100 and TW80 was evaluated by the molar solubilization ratio (MSR), which is often used to quantify the solubilization enhancement by surfactants (Ahn et al., 2008; Paria, 2008). The MSR was calculated according to Edwards et al. (1991) and Guha et al. (1998). Selected physicochemical properties of these compounds are presented in Table 1.

2.2. Preparation of solutions

Surfactant solutions were prepared by dissolving the relevant surfactant in distilled water. PAH standard solutions were made by dissolving the solute in distilled water containing 10% methanol. These solutions were stored in a refrigerator at 4°C and used within a week. Methanol and acetone were obtained from Sigma Aldrich with purity 99%, and KCl was of analytical reagent grade.

2.3. Preparation of soil samples

The soil sample for the experiments was collected according to a standard procedure (AFNOR X31100) from a non-contaminated area located in Bordj-El-Kiffan near Algiers. The soil was air dried, homogenized and sieved to remove large particles (> 0.8 mm), then rinsed by acid solution followed by distilled water to avoid microbial contamination. It was then sterilized by autoclaving at 105°C for 24 hours.

The texture of soil was sandy, containing 94% sand, 2.9% silt and 2.4% clay. The average size of particles determined according to the standard procedure AFNOR X 31-107 was 238 µm. The soil had a neutral pH (6.10±0.06) with low organic matter content (8.5±0.2%). Organic matter content was calculated from the weight difference after charring at 550 °C in the furnace for 2 h. The pH of soil was determined according to the standard procedure AFNOR X 31-103. Soil analysis by X-ray fluorescence (Panalytical MagixPro) revealed the presence of different inorganic compounds (42% SiO_2 and 19% of CaO).

2.4. Contamination of soil

A quantity of PAH was dissolved in a corresponding volume of acetone, and then mixed with a defined mass of soil (mass/volume rate equal 2). The mixture was stirred for 1 h under 100 rpm on a rotary shaker. The completely solvent-wet soil was then evaporated at room temperature with intermittent manual mixing in a hood.

The PAH-contaminated soil in the closed box was stored in a refrigerator at 4°C. The loss of PAH by volatilization or degradation was negligible within 5% and 3% of Naph and Anth respectively. This result was confirmed by control tests left for a week under a hood at (24 ± 3°C).

Table 1. Properties of PAH and surfactants

Compounds	***MW***	***S_w(mol/L)***	***$logK_{ow}$***	***MSR_{TW80}***	***MSR_{TX100}***	***CMC***
Naphthalene	128.2	$2.34.10^{-4}$	3.37	0.620	0.369	
Anthracene	178.2	$2.52.10^{-7}$	4.45	0.047	0.002	
TW80	1310					$0.14.10^{-4}$
TX100	628					$0.20.10^{-3}$

In this work, the contamination rates studied are 10 mg/kg of dry soil and 5000 mg/kg of dry soil for Naph, and 25 mg/kg of dry soil and 200 mg/kg of dry soil for Anth. In the following parts all the contamination rates are expressed as mass percentages.

2.5. Soil washing

One gram of contaminated soil was added to a 50 mL Erlenmeyer flask which was then filled with 25 mL of surfactant solution at different concentrations. The mixture was stirred for 60 min by an orbital reciprocating shaker at 200 rpm. Soil washing was performed with duplicates for the same conditions. The experimental conditions are given in Table 2. In the case of surfactant washing process, all results are obtained after 1 hour of treatment.

2.6. Analytical method

The soil within the washed solution was permitted to settle. Liquid phase, 15 mL, was centrifuged at 4000 rpm during 20 min. After that, 1 mL of methanol was added to 9 mL of the supernatant collected by a syringe. PAH were analyzed by a UV Lambda25 spectrophotometer (Perkin Elmer Instrument). Naphthalene and Anthracene were detected at 219 nm and 252 nm respectively. Residual concentration of soil was computed as the difference from the initial concentration and the final one.

3. Results and discussion

3.1. Effect of water washing

The evaluation of PAH extracted with water was tested for more than one washing operation. Fig. 1 shows the values of the removal efficiency (R_E) obtained after one, two, three and four steps of washing with water.

It was shown that water contribution in the elimination of the two PAH from soil was less than 10%. Where, the major part was achieved after two washes corresponding to 20 minutes. From a precedent study (Khalladi et al., 2009), it was seen that the effluent concentration of hydrophobic hydrocarbons increased with time, and then became constant. Hence, these results demonstrated the existence of a mobile fraction of PAH, that water can easily remove. Urum et al. (2004) reported that a preliminary water washing step can remove approximately 40% of oil present in sandy soil. Thus, in spite of its little effect in the whole process, the contribution of water in the extraction of PAH is moderately significant, especially in the case of soils highly contaminated with PAHs.

Accordingly to the results of Fernandez and Luque de Castro (2000), the use of water in the remediation of highly contaminated soil as a first treatment solution was shown of great interest. Based on the observed performance of water in the removal of PAH, and in order to decrease the surfactant consumption, the following surfactant washing experiments were realized on contaminated soil previously washed with water during 20 minutes.

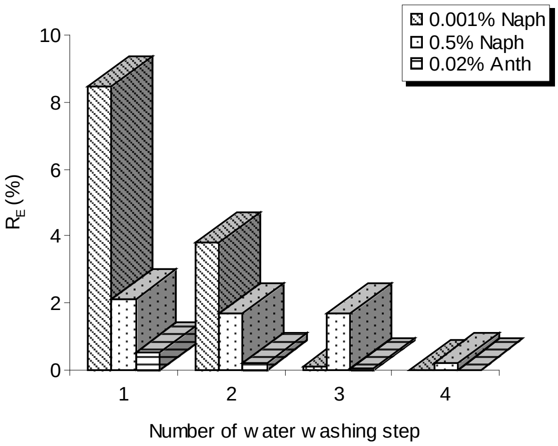


Fig. 1. Effect of water on PAH removal

3.2. Effect of surfactant concentration

In the overall process, the total removal efficiency (R_{tot}) value represents the combined effect of water and surfactant in the removal of PAH. Thus, to study only the effect of surfactant in the remediation of soil, the efficiency of removal by surfactant (R_{TA}) was chosen instead of R_{tot}. The effects of the type and the concentration of surfactant on the removal of anthracene and naphthalene from soil are illustrated on Fig. 2.

Examination of histograms indicate proportionality "logically expected" between the elimination of PAH and the surfactant concentration. In fact, the proportionality obviously observed beyond the CMC shows that the increase of the number of micelles leads to increased extraction efficiency of PAH molecules from soil.

Comparing histograms (a) and (b) with (c) and (d), shows that the values of naphthalene elimination efficiency are greater than those of anthracene with both surfactants. This result is probably related to the appreciable difference between the solubility of naphthalene and anthracene (Table 1).

Furthermore, Fig. 2 shows that the Tween 80 is more efficient than the Triton X-100 in removing both naphthalene and anthracene. This result is in accordance with the MSR values presented on Table 1.

According to Ahn et al. (2008), the MSR represents the ability of a surfactant to solubilize a hydrophobic substance. And the higher the MSR is the more efficient is the surfactant. Thus, the behavior of the two surfactants indicates that the solubilization of anthracene and naphthalene is more favorable with TW80 than with TX100. Also, the lower CMC of the TW80 compared to that of the TX100, can justify the relatively higher efficiency of Tween 80.

Table 2. Experimental parameters

Studied parameter	*Value of parameter*	*Conditions*
Effect of water	1, 2, 3 and 4 washing	10 min/wash, pH=6.5, 200 rpm
Effect of surfactant concentration	TW80, TX100 1CMC -10CMC	pH=6.5, 200 rpm
Effect of pH	pH=3.1, pH=6.5, pH=9.0	1CMC, 5CMC, 10CMC, 200 rpm
Effect of ionic strength	0 or 3.5 g/L of KCl	1CMC, 10CMC, 200 rpm

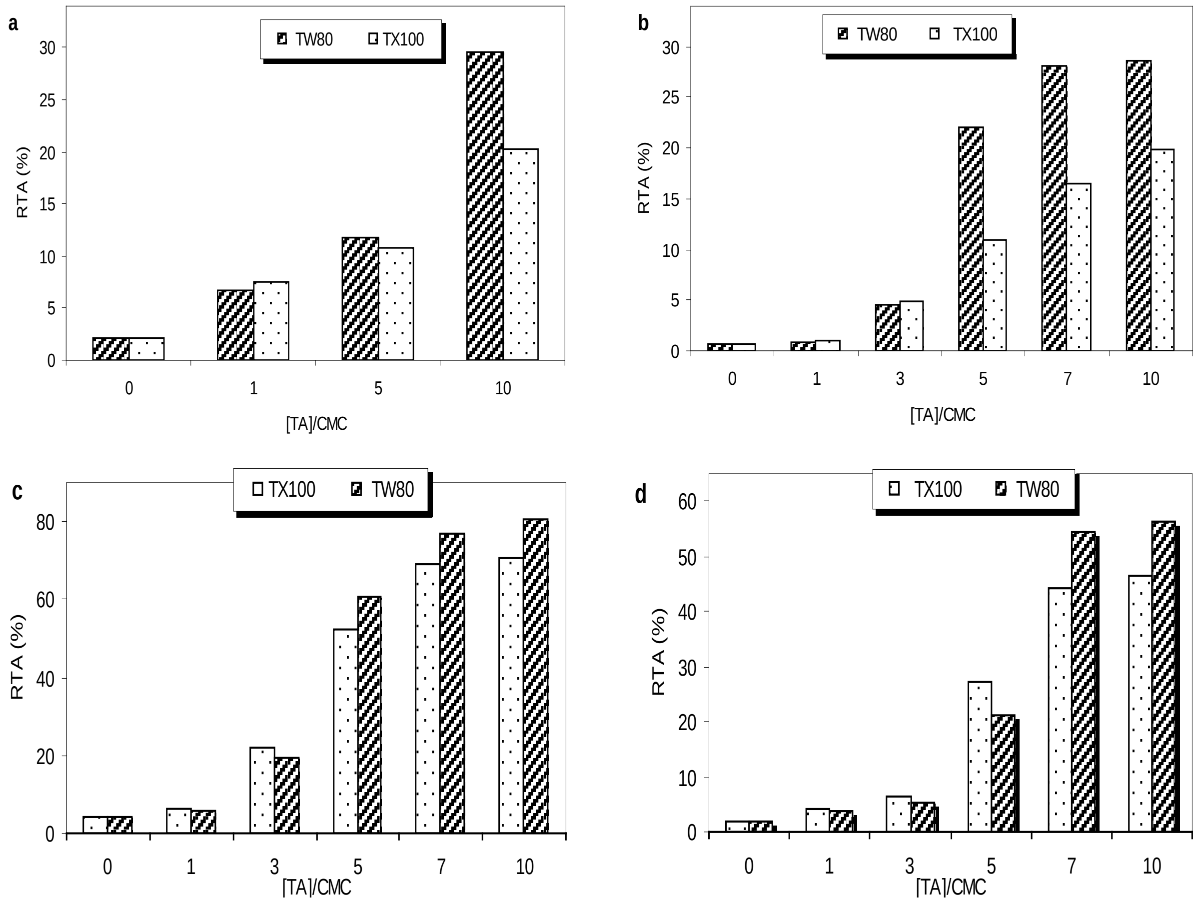


Fig. 2. Effects of type and concentration of surfactant on the removal of PAH: (a) 0.0025% Anth., (b) 0.02% Anth (c) 0.001% Naph, (d) 0.5% Naph

However, according to the surfactant concentration we observe that the nonionic surfactants are acting in two different ways. For low surfactant concentrations (≤ 3CMC), the TX100 presents an efficiency slightly higher than that of the TW80. And beyond 3CMC we find the opposite.

3.3. Effect of pH

According to previous studies conducted by Perineau and Gaset (1981) and Shen et al. (2004), the nonionic surfactants are practically stable at a pH varying from 2.0 to 11.0 and the probability of their degradation over the course of the experiment is unlikely. The effect of pH on the effectiveness of TX100 and TW80 in the elimination of anthracene from a soil contaminated with 0.0025% Anth is shown on Fig. 3.

It was noted that the elimination of anthracene from soil is remarkably enhanced by raising the pH. Indeed, the values of R_{tot} obtained at acidic pH for both surfactants are smaller than those obtained at neutral pH. However, at alkaline pH we note that the removal of the PAH was increased by 3 to 10% when varying the pH from 3.1 to 9.0. Similarly Bhandari et al. (2000) have found that the removal efficiency of total hydrocarbons by a commercial nonionic surfactant increases from 66 to 73% by increasing the pH from 7.0 to 12.0. The removal of anthracene from soil at an alkaline pH was shown for both TW80 and TX100 very favorable at a concentration of 5CMC and 10CMC and less favorable for a solution of 1CMC.

The difference between the behavior at low- and high surfactant concentrations was explained by Cao et al. (2008). Indeed, when it comes to small amounts, these researchers suggest that non-ionic surfactants show a greater tendency to adsorb to soil. Also, these researchers suggest that the prometryn desorption observed below the CMC in a TX100 solution is certainly due to the sharing of this compound between soil and surfactant adsorbed onto soil. Moreover, beyond the CMC the surfactant molecules dissolved in the solution allow a better dissolution of the PAHs molecules adsorbed on soil and those trapped in the pores.

In addition, Chen et al. (2006) reported that Tween 80 adsorbed on soil will increase the sorption of PAH molecules while the dissolved Tween 80 increases the apparent solubility of PAHs. This is explained by the influence of these two processes on the partition coefficient of PAHs in soil-water in the presence of the surfactant.

Studying the effect of pH on the removal of this hydrocarbon we proposed the sorption of surfactant's molecules on soil as the principal process governing the efficiency of the surface agent. Laha et al. (2009) and Saichek and Reddy (2003) indicated in their investigations that the sorption of surfactants on mineral soils was appreciably influenced by the pH variation.

3.4. Effect of ionic strength

The ionic strength of the washing solution was tested using KCl as a model of monovalent electrolyte. The increase of the anthracene concentration in the effluent when using the KCL is presented in Fig. 4.

From these two figures, we find that the effect of salt on the behavior of TX100 and TW80 is similar. However, it should be noted that for a concentrated washing solution and a diluted one, the intensity of the effect of salt is not the same. For a washing solution 10CMC, we notice that the curves obtained in the presence and absences of KCl are nearly superimposed, with a slight deviation in the case of TW80. However, with a solution 1CMC we observe a significant difference between curves obtained with and without electrolyte. Yang et al. (2010) have found that the sorption of TW80 is positively influenced by increasing salinity of seawater. However in a previous study, Lee et al. (2005) reported that the increase of the ionic strength improves gradually the recovery rate of toluene by Tween 20, 60 and 80 respectively. The calculated values of the total removal efficiency obtained with a solution containing surfactant and KCl are given on Fig. 5.

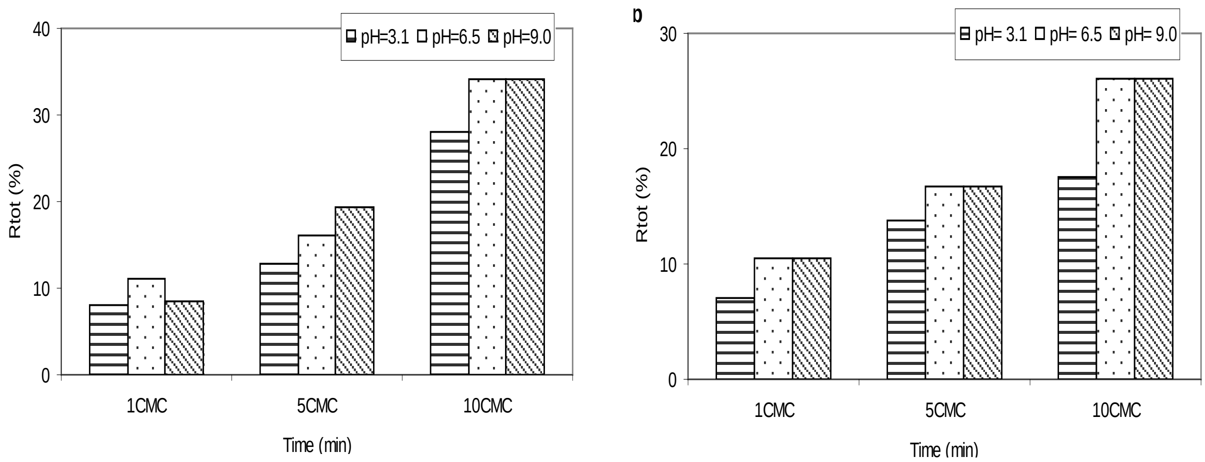
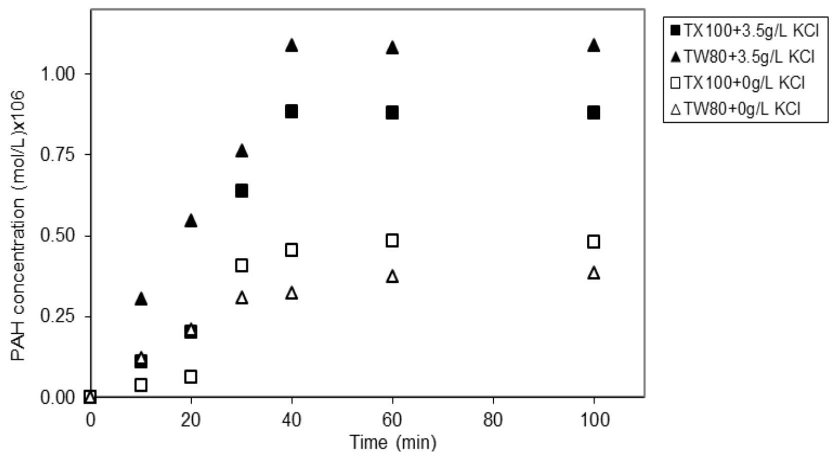
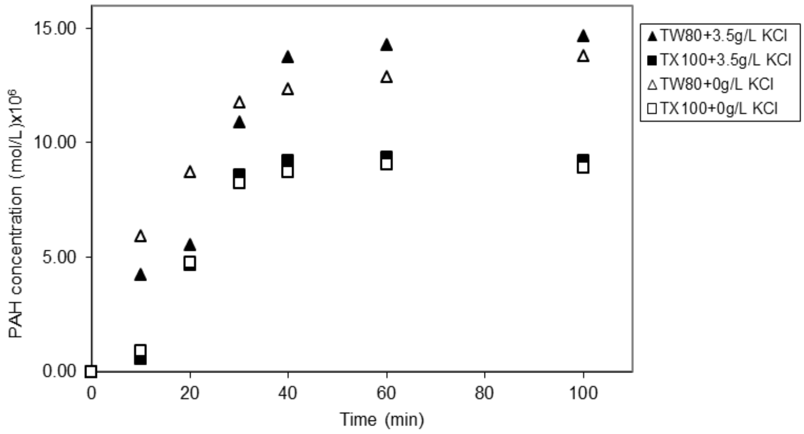


Fig. 3. Effect of pH on the anthracene removal from a 0.0025% contaminated soil (a) TW80, (b) TX100



(a)



(b)

Fig. 4. Effect of KCl on the PAH concentration in the liquid phase (0.0025% Anth) (a) with 1CMC, (b) with 10CMC

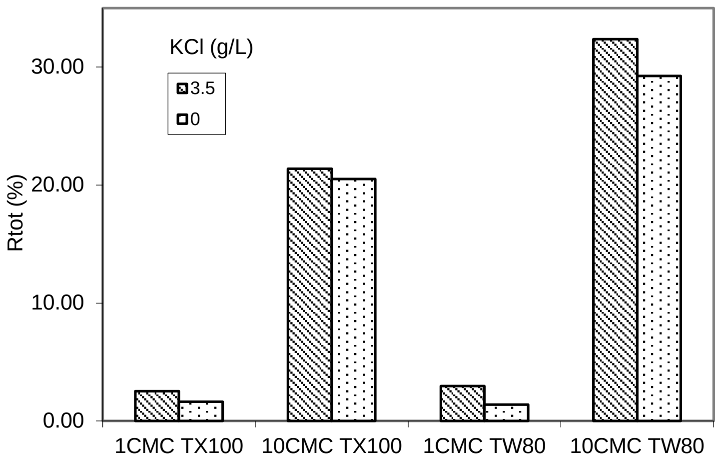


Fig. 5. Effect of KCl on the anthracene removal efficiency by TW80 and TX100 (0.0025% Anth)

For both TW80 and TX100, the R_{tot} values of anthracene in the presence of KCl are moderately high compared to those obtained in the absence of KCl. However, we find that for low as for high concentrations, the effectiveness of TW80 in the elimination of anthracene is improved, a little more than that of TX100 by the addition of KCl.

4. Conclusions

This study demonstrated that washing water process can eliminate approximately 10 % of PAH present in soil. So it will be of great importance in the remediation of highly contaminated soils, and can be suggested as a preliminary treatment. From the experimental results, it was noticed that TW80 is more efficient than TX100.

However beyond the CMC, TX100 is slightly more efficient than TW80. In addition, it was noted that the concentration of surfactant and the initial concentration of PAHs in soil have both a positive effect on the elimination of anthracene and naphthalene. The removal of anthracene with both TW80 and TX100 is remarkably enhanced at alkaline pH and slightly improved in the presence of KCl.

Nomenclature

CMC	Critical micellar concentration (mol/L)
log K_{ow}	Log decimal of the octanol-water coefficient
MSR	Molar solubilization ratio
MW	Molecular weight
R_E	Removal efficiency by water (%)
R_{TA}	Removal efficiency by surfactant (%)
R_{tot}	Total Removal efficiency (%)
S_w	Solubility of PAH in water (mol/L)

Abbreviations

Anth.	Anthracene
Naph.	Naphthalene
PAH	Polycyclic aromatic hydrocarbon
TW80	Tween 80
TX100	Triton X-100

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