Use of Surfactants to Enhance the Removal of PAHs from Soil

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ABSTRACT

The efficiency of soil remediation is often limited by the low aqueous solubility of Polycyclic Aromatic Hydrocarbons, PAHs. Surfactants can then be used to enhance the removal of PAHs from soils. The dissolution of pure solid deposit of benzo(a)pyrene, B(a)P, has shown that cationic surfactants are the most efficient to increase the aqueous solubility of B(a)P, when compared to neutral or anionic surfactants. In this paper we compare by using soil suspension washings, the efficiency of two surfactants (i) a cationic surfactant, the benzyldimethyl dodecylammonium bromide, BDDA, and (ii) a neutral one, the t-octylphenoxypolyethoxy ethanol, triton X-100. The losses of surfactant, by adsorption on soil or precipitation, were measured together with the release of B(a)P, chosen as a model molecule, representative of all the PAHs. The efficiency of surfactants used in blend was then compared to the efficiency of surfactants alone.

Keywords soil ; PAHs ; surfactant

INTRODUCTION

Contamination of soils by organic pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs) is a crucial environmental concern due to the toxic and carcinogenic character of many of PAHs. The low aqueous solubility, less than 1 mg/L and the hydrophobicity of the PAHs induce strong interactions with soil especially with the organic matter. Surface active agents are then used to increase the aqueous solubility of PAHs and to improve their desorption from soil.

The molar solubilization ratio parameter (MSR) expresses the number of moles of the organic solute solubilized per mole of surfactant in micellar phase and then characterizes the efficiency of the surfactant towards a given solute. This parameter is usually measured in excess of organic phase by dissolution of a pure solid deposit by surfactant solutions. The pseudo aqueous solubility linearly increases with the surfactant concentration in micellar phase, the slope leading to the MSR value. The MSR values not only depend on the molecular properties of the surfactant, including the hydrophile/lipophile balance (HLB) parameter and the charge, but also on the molecular properties of the organic solute. Contrary results have been reported with aromatic compounds. Using five no ionic polyoxethylene surfactants, Yeom et al [1] showed an inverse relationship between the MSR values and the HLB in the case of phenanthrene, anthracene, benzo(a)pyrene (B(a)P) and pyrene. Grimberg et al [2] found that the solubilization of phenanthrene by various no ionic surfactants could be related to the HLB, when the solubilization capacity was expressed in mass ratio, but this relationship was no longer valid on a molar basis. Others results indicated that both the length of the alkyl chain and the number of ethoxy groups influenced the solubilization of phenanthrene [3]. The MSR values of aromatic hydrocarbons may exhibit a maximum value as a function of the HLB parameter. Such a behaviour was attributed to the existence of two competitive processes: (i) a loss of solubilization capacity with increasing HLB (ii) an enhancement by electron donor-acceptor EDA complexation, the delocalized π e- having a donor character [4]. As a consequence there are two potential sites of solubilization of PAHs : the inner hydrophobic core of micelles and the surface solubilization site due to specific interactions. In the case of aromatic solute, Gadelle et al [5] showed that cationic and non ionic surfactants have a similar solubilization capacity because of a specific interaction between the positive charge and the aromatic e-. By

comparing the efficiency of two surfactants differing by their polar head, it can be shown that surface solubilization represented 70 % of the total amount of benzo(a)pyrene solubilized by the cationic surfactant [6].

Release of soil-bound PAHs by surfactant is even a more complex talk. Surfactants interact with soil component by adsorption or precipitation leading to a decrease of the aqueous concentration of the surfactant in soil washing experiments. Furthermore the composition and the size of micelles are sensitive to their physico-chemical environment. The aggregation number of ionic surfactants may rise sharply with the ionic strength, for instance. Thus, soluble compounds from soils may affect the solubilization capacity of the surfactants due to micellar counterion binding.

There are only a few data about the PAHs release by surfactants from weathered, industrial contaminated soils [1,7]. However, the contamination age appears to be inversely correlated with the extend of mobilization, because diffusion process may control the release rate [7]. The interactions of surfactants with the soil matrix were usually poorly described. The influence of soluble compounds from soils on the solubilization capacity of surfactants was never discussed.

In this paper, we present experimental data on the solubilization of soil-bound PAHs by two surfactants (BDDA and Triton X-100) used alone or in blend. The global soil/surfactant interaction was taken into account by measuring the surfactant concentration in the water phase and an effective critical micellar concentration of surfactants in soil suspensions. The solubilization capacity of surfactants was measured in soil suspensions and then compared to their capacity measured in a pure solution. At the end we tested the influence of the adsorption of BDDA on soil on the further solubilization of PAHs by Triton X-100.

MATERIALS AND METHODS

Soils

PAHs-contaminated soil was taken from a pile on a manufactured gas plant site at Rouen (France). The initial content of total PAHs was 2880 mg/kg. Among others pollutants were cyanides (220 mg/kg) together with inorganic compounds such as Fe (10.4 g/kg) and Al (5.6 g/kg). The sand, silt and clay fractions were 57, 27, 16 % w/w respectively, the organic content was 36.4%.

Surfactants

Triton X-100 (t-octylphenoxypolyethoxy ethanol) and BDDA (benzyldimethyl dodecylammonium bromide) were purchased from Sigma Chemical Co. They were used without any purification.

PAHs Analysis

Separation and quantification were obtained by injections of 20 µl sample in HPLC through a 7125 Rheodyne valve. Elution of PAHs was then achieved onto an analytical column Supelcosil LC-PAH (15 cm x 4.6 mm *id;* Supelco, Saint-Quentin Falavier, France) with a Varian 9010 pump delivering a solvent system composed of acetonitrile and water. Elution began with 45% acetonitrile, followed by a linear increase to 55% acetonitrile over 5 min, another increase to 100% acetonitrile over 30 min, and then a plateau of 10 min, before a return to the initial conditions. The flow rate was 1.5 mL/min. UV absorbance (254 nm) was monitored with a variable wavelength detector (Varian 9050).

Surfactant Analysis

The surfactant concentrations were measured by HPLC analysis fitted with an analytical column TSK ODS-80 TM (25 cm x 4.6 mm *id*). Elution proceeded at 1.0 mL/min. It began with pure water over 3 min, followed by a linear increase to a 50-50 acetonitrile/ethanol mixture over 7 min, and by an isocratic phase of 8 min. UV absorbance was monitored at 277 nm for Triton X-100 and 262 nm for BDDA.

Determination of the Effective Critical Micellar Concentration

The effective critical micellar concentration (CMC_{eff}) was derived, in the case of BDDA, from the variation of the conductivity of soil suspensions with the initial surfactant concentration and by the variation of the surface tension in the case of Triton X-100. For each surfactant, mixtures of a surfactant solution of variable concentration and a soil suspension (200 g/L) were prepared and stirred during 24 h. The conductivity or the surface tension of the supernatant were measured after centrifugation at 2500 g for 10 min.

Soil Washing Experiments

A soil suspension (200 g/L) was stirred with an aqueous surfactant solution of variable concentration. The contact time was

varied. After centrifugation and filtration through a Whatman 0.2 µm membrane, the HPLC analysis of the supernatant gave the B(a)P concentration released from soil by the surfactant. The measurement of the BDDA and Triton X-100 concentrations [S] by HPLC analysis made it possible to derive the MSR values characterizing the efficiency of the surfactant by:

$$MSR = [PAHs] / ([S] – CMC) \quad (1)$$

where CMC was critical micellar concentration in water. Concentrations were expressed in mole/L.

RESULTS

Interaction Soil Surfactant

The two surfactants have an aromatic ring and a similar alkyl chain containing 12 C, the alkyl chain of BDDA is linear while those of Triton X-100 is branched, they also differ by their charge.

These discrepancies at the molecular level greatly affect the behaviour of surfactant in water solution. The CMC value of Triton X-100 is ten-fold lower than the value of BDDA due to the electrostatic repulsion between the polar heads in the case of cationic surfactant. In the same time, BDDA had a higher solubilization capacity of B(a)P than Triton X-100, as indicated by the values of the MSR parameter: 0.0001 for the Triton X-100 and 0.005 for the BDDA [6]. The high efficiency of BDDA was attributed to the existence of a specific interaction between the aromatic rings of PAHs and the cationic charge brought by the surfactant molecule.

The discrepancies at molecular scale also affect their behaviour in a soil suspension. Adsorption of BDDA was high as expected due to its cationic charge, while those of Triton was moderate as shown in Figure 1.

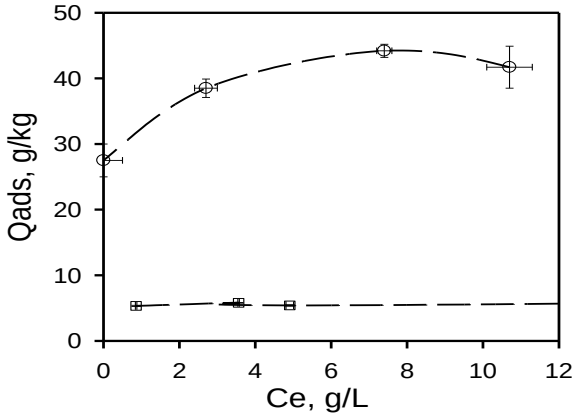

FIGURE 1 Adsorption isotherms of BDDA (circle) and Triton X-100 (square) on contaminated soil. The concentration of the suspension was 200 g/L and the contact time was 24 h.

In order to get a better insight into soil-surfactant interaction we determined a CMC_{eff} for each surfactant in soil suspensions. For the cationic surfactant, the variation of the conductivity, minus the initial conductivity of soil, exhibited two straight lines as a function of the initial surfactant concentration (Figure 2a).

The crossing point of these two lines gave the CMC_{eff}. As expected the value, equal to 6.9 g/L was higher that the CMC measured in water due to the losses of surfactant by adsorption on soil particles.

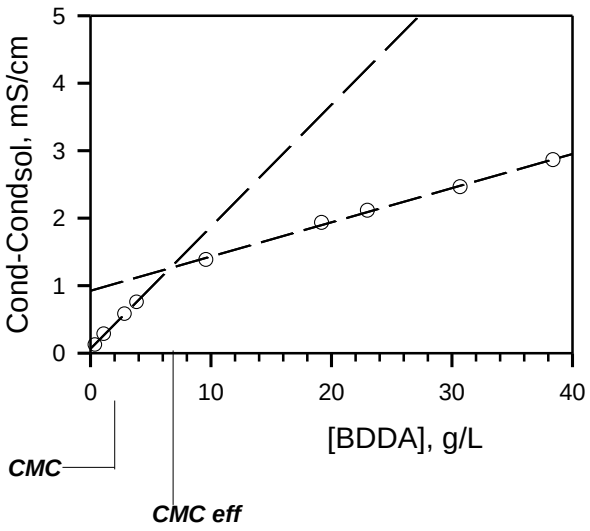

FIGURE 2a Variation of the conductivity of a soil suspension (200 g/L) with the initial concentration of BDDA. The contact time was 24 h.

The variation of the surface tension with the initial concentration of the neutral surfactant is shown in Figure 2b. The CMC_{eff} derived from this curve was also larger than the CMC value in water. It may be due to sorption of surfactant on soil [8]. But in our experiments, that discrepancy remains still difficult to explain because adsorption or precipitation of Triton X-100 were not dominant phenomena, as evidenced by the adsorption isotherm. Then, the occurrence of interactions between Triton X-100 and compounds arising from the soil organo-mineral matrix solubilized by the surfactant (*ie* soil organic matter) could imply the formation of a complex micellar phase.

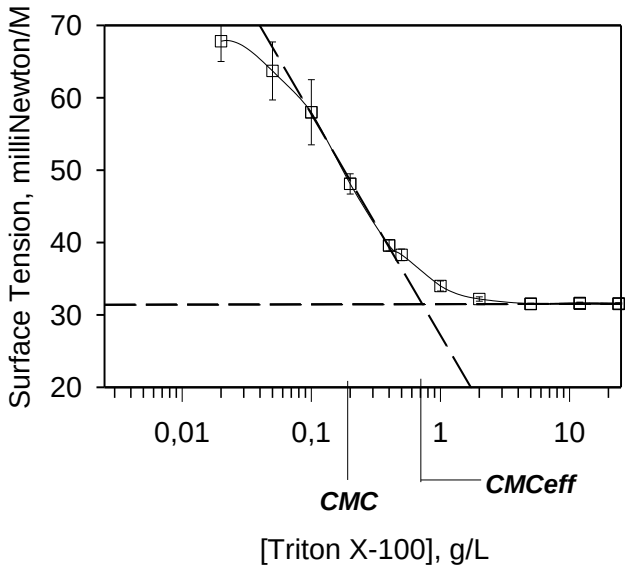

FIGURE 2b Variation of the surface tension with the logarithm of the initial Triton X-100 concentration in a soil suspension at 200g/L and a contact time of 24 h.

In both cases, significant solubilization of PAHs was only detected when the initial surfactant concentration is larger than the CMC_{eff}.

Release of Benzo(a)Pyrene

The following experiments were focused on the comparison of BDDA and Triton X-100 both in term of efficiency and in term of kinetic towards the solubilization of B(a)P from soil, the losses of surfactants being measured in the same time.

The release of B(a)P by Triton X-100 and BDDA are represented in figure 3 by the variation of the MSR parameter with time, where the MSR values were derived using equation 1. The initial concentration of BDDA and Triton X-100 were respectively 20 g/L and 60 g/L.

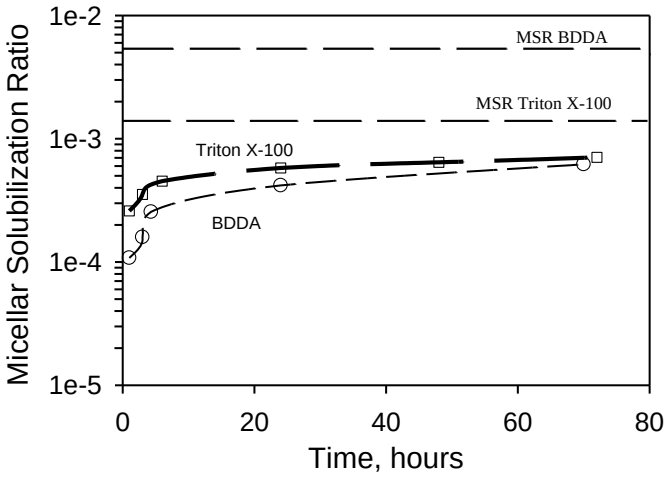

FIGURE 3 Time variation of the MSR parameter. The dotted lines represent the MSR values measured in pure solutions for each surfactant as indicated on the plot.

Results obtained with both surfactants obeyed the same kinetics, the curves reached a pseudo plateau value after 24 h and lead to close values of the MSR parameter. The MSR measured by using Triton X-100 tended to the value determined in water solution, while the efficiency of the BDDA was reduced by a factor 5 compared to the MSR value in water. From this comparison it can be deduced that the ionic environment provided by the soil suspension affected the micellar phase and reduced the solubilization capacity of the cationic surfactant.

Influence of BDDA adsorption on the efficiency of Triton X-100

A pre-treatment step of soil by BDDA was added to the soil washing experiments to test a potential synergetic effect between the two surfactants. The soil suspensions were in contact with a BDDA solution during 24 h. Surfactant concentration ranged from 0.5 g/L to 20 g/L. After that, a given volume of supernatant was withdrawn and used to dissolve an appropriate amount of Triton X-100 to reach a final concentration of 60 g/L. The percent of B(a)P solubilized was then recorded at different times as represented in Figure 4 for the different concentrations of BDDA.

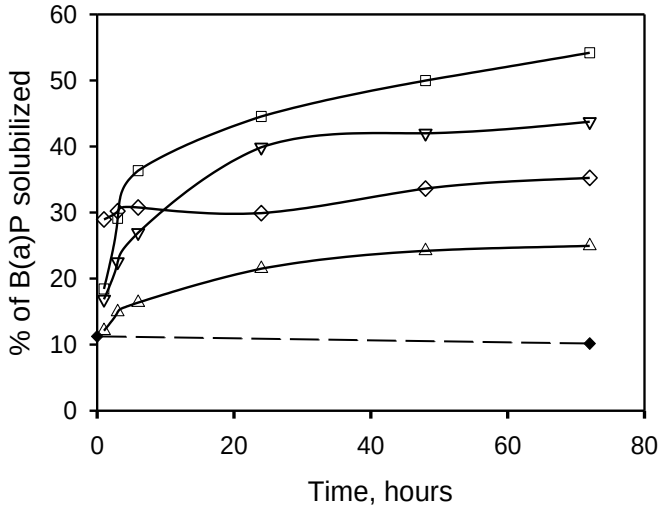

FIGURE 4 Amount of B(a)P solubilized by triton X-100 (60 g/L) after a pre-treatment step using BDDA at 0.5 g/L (∇), 5 g/L (Δ) and 20 g/L (◊). The square (□) represents the solubilization without any pre-treatment and υ the solubilization by BDDA at 20 g/L.

Clearly, the adsorption of BDDA reduced the amount of B(a)P solubilized. This reduction was more and more important as the BDDA concentration was high. The amount of Triton X-100 adsorbed on soil decreased with the BDDA concentration used during the pre-treatment step as indicated in Figure 5. The adsorption of BDDA on soil changed the soil reactivity towards the Triton X-100 and inhibited its further adsorption.

A mass efficiency ratio ρ was defined as the mass of B(a)P solubilized divided by the initial mass of surfactant added. The ρ value measured at 24 h was equal to 0.0002 with Triton X-100 at 60 g/L or BDDA at 20 g/L. It was reduced to 0.0001 with a mixture of BDDA (20 g/L) and Triton X-100 (60 g/L) showing a net antagonistic effect between the two surfactants. This effect was not due to a decrease of the Triton X-100 in micellar phase because the pre-treatment of soil with BDDA reduced the adsorption of Triton X-100, but was rather due to an increase of the soil/PAHs interaction by the BDDA.

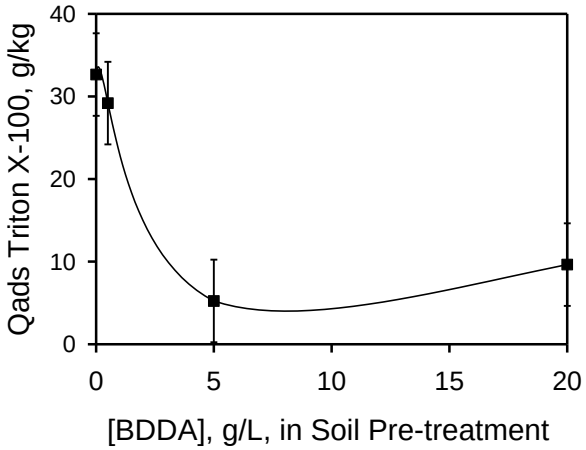

FIGURE 5 Variation of the amount of Triton X-100 adsorbed on soil in g/kg with the concentration of BDDA used during the pre-treatment of soil.

CONCLUSION

Indeed, the aqueous solubility of B(a)P has been increased by using surfactant solutions. The cationic and neutral surfactants, which are used in this work, had a different behaviour in soil suspension, the cationic being more adsorbed on soil than the neutral one. However they led to the same efficiency towards the B(a)P both in term of molar solubilization ratio and in term of kinetic. An antagonist effect has been evidenced between the two surfactants. The adsorption of the cationic surfactant on soil reduced the availability of B(a)P towards the Triton X-100.

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