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TECHNICAL NOTE

Removal of 2,4-D from Aqueous Solutions by Micellar Flocculation

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ABSTRACT

This paper describes removal of the pesticide 2,4-dichlorophenoxyacetic acid from aqueous solutions by sorption on aggregates formed by flocculation of micelles of the anionic surfactant sodium lauryl sulfate with aluminum sulfate. The micelles aggregate in a single floc containing all the micellar surfactant, and this floc is sufficiently consistent to be removed by filtration. This example illustrates the potential of micellar flocculation as a water treatment technique.

Key Words. Anionic; Surfactant; Separation; Micelle; Pesticide

INTRODUCTION

Recent work (1) has reported that micelles of the anionic surfactant sodium lauryl sulfate (NaDS) may be forced to flocculate in the presence of Al^{3+}. The flocculation forms a single aggregate which holds all the micellar surfactant and is sufficiently consistent to be filtered with ease from the solution. Furthermore, the aggregate often shows buoyancy. Micelles flocculate because of binding of Al^{3+} cations to the surface of micelles. Because of the high charge/size ratio of this cation, the ζ-potential of the micelles is reduced to zero or near zero after the addition of an adequate amount of Al^{3+} salt. This is unlike the case of binding of other cations like Ca^{2+}, where the ζ-potential of NaDS micelles is reduced only moderately and becomes constant at a value of approximately −40 mV (1). As micelles remain stable, the outcome of adding

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Ca^{2+} to a NaDS solution is precipitation of CaDS when the surface of the micelle becomes saturated in Ca^{2+} and any further excess of the cation meets the solubility product of the surfactant. The flocculate redissolves at high Al^{3+} concentrations by the existence of Al^{3+}/DS^{-} aqua complexes (1), in a similar way as reported in the literature for other cation–anionic surfactant systems (2, 3). Microscopic photography and x-ray diffractometry show that the aggregate obtained by micellar flocculation consists of small fragments of liquid crystal dispersed in an amorphous matrix (1). Such aggregates possess an ability never shown by surfactant precipitates: They may capture organic solutes dissolved in water. We show this by describing the removal of the pesticide 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solutions by NaDS/Al^{3+} flocculates. The most interesting features of this phenomenon are that the sorption process is fast (a few minutes) and the ratio between the concentration of pollutant remaining in solution and the weight ratio (removed pollutant/removed surfactant) is higher than in other techniques like adsolubilization. Therefore, micellar flocculation may be a potentially competitive alternative to other surfactant-based separation processes.

MATERIALS AND METHODS

The following reagents were used: High purity aluminum sulfate was purchased from PROBUS, Spain. It was specified to be 98% pure, and used as received. Sodium lauryl sulfate (NaDS) was kindly provided by KAO Corporation, Spain. It was a technical grade product with a conversion of no less than 97%, with less than 2% free alcohol and 1% sodium sulfate relative to the surfactant. The product was used as received. AR grade 2,4-dichlorophenoxyacetic acid (2,4-D) from Merck-Schuchardt was used as a test pollutant.

Stock solutions of the various compounds (aluminum sulfate, NaDS, and 2,4-D) were prepared and allowed to reach thermal equilibrium at 25°C. Appropriate volumes of these were mixed in 200 mL volumetric flasks and brought to the final volume with Milli-Q water. The samples were thoroughly shaken and kept at 25°C for an appropriate time (usually 1 hour) before filtration. The flocculate was removed by vacuum filtration through 45 μm Whatman cellulose nitrate membranes.

The pesticide and surfactant were analyzed in samples taken from the filtrate, and the amounts of surfactant and pesticide removed were calculated by mass balance. The pH remained between 3.4 and 3.3. The difference in pH for the case of micellar flocculation in the absence of 2,4-D was no more than 0.1 pH unit (1). The pH was not buffered in order to prevent interference of the buffer system with the flocculation process.

The analyses were performed by the following methods: 2,4-D was analyzed by a reverse high-performance liquid chromatography (HPLC) column C18 and a spectrophotometric detector. The wavelength was 236 nm, and the solvent used was a 50:49:1 (v/v) mixture of acetonitrile, water, and acetic acid. NaDS was analyzed by double-phase volumetric titration following the Shell method (ISO 2271-1972), using AR grade Hyamine 1622 (Carlo Erba, Italy) as the standard and a mixed indicator of Blue Acid 1 (Merck, Darmstadt) and Dimidum Bromide (PROBUS, Spain), both of AR grade.

RESULTS

Figure 1 shows that the flocculation ratio, defined as [residual NaDS]/[initial NaDS], reaches a constant value in less than 2 minutes. The illustration key show the overall surfactant and Al^{3+} concentrations. These experiments were performed in the presence of 50 ppm of 2,4-D. Although it is not plotted in the figure, after 48 hours the ratio still remained constant. The flocculation of surfactant micelles reaches a stationary flocculation ratio value within 2 minutes. At $[Al^{3+}] = 0.046$ M the residual surfactant concentration is very low in the absence of 2,4-D (1), while at $[Al^{3+}] = 0.07$ M the residual surfactant concentration is higher. However, the residual NaDS concentrations in the absence of 2,4-D are lower than in its presence. This suggests that the pollutant interferes to some effect with the flocculation phenomenon. A second

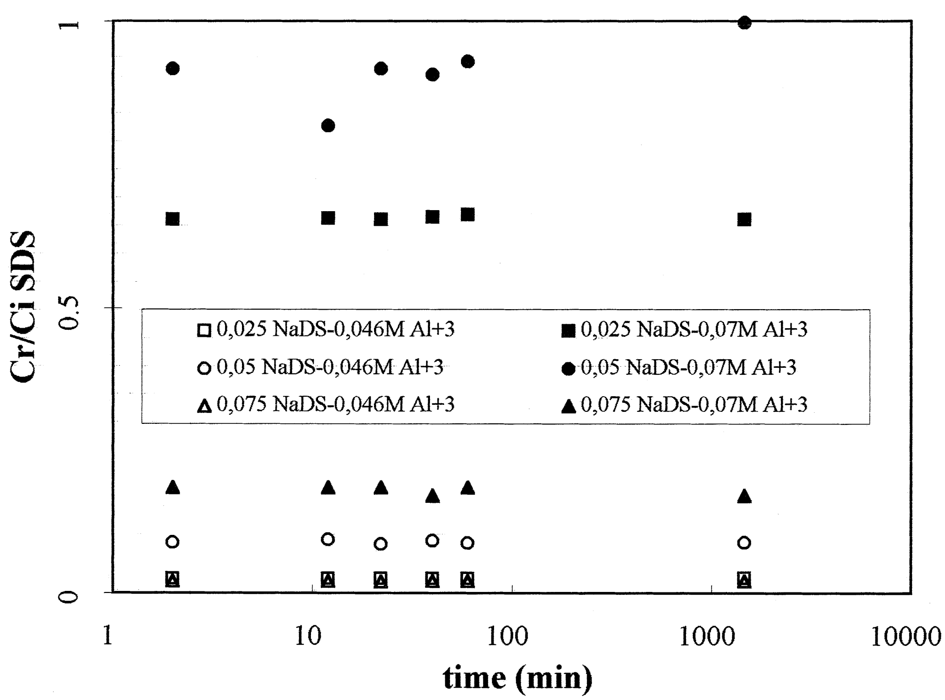

FIG. 1 Flocculation ratio of the surfactant, defined as the ratio between the residual NaDS concentration (C_r) and the initial NaDS concentration (C_i). The experiments were performed in the presence of 50 ppm of the pesticide 2,4-D.

fact is the existence of maxima of surfactant solubility at [NaDS] = 0.05 M. This is not observed in the case of flocculation of NaDS in the absence of 2,4-D, where the residual surfactant concentration has a minimum value at a total NaDS concentration of 0.05 M (1).

Figure 2 shows the amount of 2,4-D left in solution after flocculation and filtration of the surfactant flocculate. The initial [2,4-D] was 50. For high flocculation ratios ([Al^{3+}] = 0.046 M), the residual [2,4-D] decreases with the amount of flocculate generated. A lower 2,4-D value is found after flocculation of a NaDS solution initially 0.075 M. At [Al^{3+}] = 0.07M, the residual [2,4-D] decreases substantially only for the higher NaDS concentration. Again, even up to 48 hours the residual 2,4-D concentration remained constant.

The results shown in Fig. 3 were obtained after an equilibration time of 1 hour, which is considered more than enough to consider that equilibration had been reached. A separation parameter α was calculated for various combinations of total [NaDS] and [Al^{3+}] tested. Separation parameter α has been defined similarly to partition coefficients in work on adsolubilization (4, 5) as

$$\alpha_{FW} = \frac{[2,4\text{-D}]_{sorbed}}{[2,4\text{-D}]_{residual}}$$

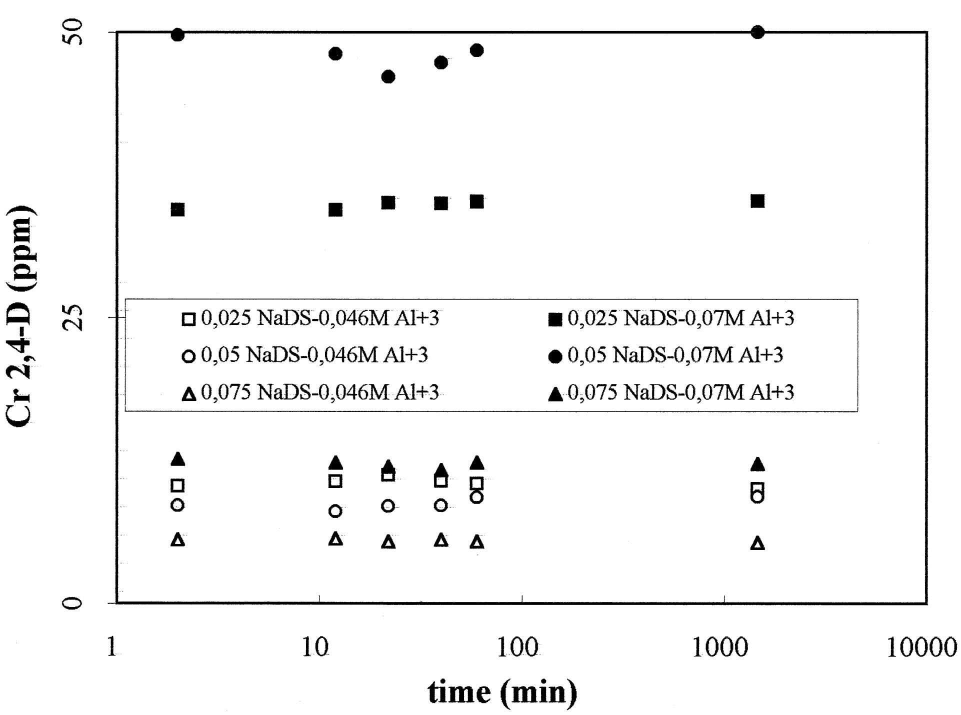

FIG. 2 Residual 2,4-D concentration left in the solution after flocculation and subsequent filtration of NaDS.

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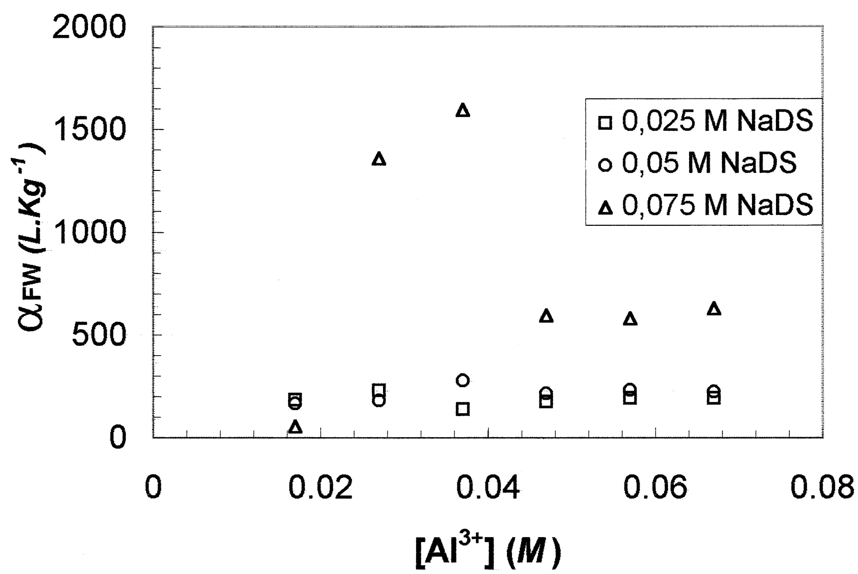

FIG. 3 The ratios between surfactant-sorbed 2,4-D and the 2,4-D in water plotted against the overall Al^{3+} concentrations added to cause flocculation.

where $[2,4\text{-D}]_{sorbed}$ is the concentration in milligrams of 2,4-D per gram of flocculated NaDS. pK_a for 2,4-D is 2.8, below the pH of the solutions in the various experiments, which remained between 3.4 and 3.3. Therefore, the pesticide in its dissociated form. The octanol/water partition coefficient for 2,4-D was determined in previous work (6) as 6.2. The octanol/water partition coefficient is a good index for the solubility of nondissociated polar organic solutes in the nonpolar cores of NaDS micelles, and it has been found that for values below 1000 of this coefficient, there is also a good agreement between the octanol/water partition coefficient and the partition coefficient for solubilization in NaDS micelles and admicelles (5).

The difference of two orders of magnitude between the partition coefficient for flocculate/water and octanol/water systems suggests that the high affinity of the solute for the flocculate in this case is related to the ionized form of the surfactant. The ionized form of 2,4-D is predominant under the experimental conditions, and the solubility in a nonpolar medium (like nonpolar portions of liquid crystal fragments) should lead to a much lower degree of separation.

CONCLUSIONS

Micellar flocculation may provide the basis for separation techniques targeted on water-soluble organic compounds due to its high affinity for these compounds. The sorption process is fast for both micelle flocculation and solute sorption.

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