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SEPARATION SCIENCE AND TECHNOLOGY, **35**(12), pp. 1973–1978, 2000

TECHNICAL NOTE

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

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ABSTRACT

This paper describes the use of α-olefinsulfonates (AOS) in the removal of the pesticide 2,4-dichlorophenoxyacetic acid from aqueous solutions by adsorptive micellar flocculation (AMF). The removal occurs by adsorption of the pollutant during flocculation of AOS micelles in the presence of Al^{3+}. AOS is the second surfactant found to be susceptible to use in AMF.

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

INTRODUCTION

Adsorptive micellar flocculation (AMF) has been described in recent works (1–4). AMF is a separation technique based on a particular case of cation adsorption onto the surface of micelles. In this case, adsorption of Al^{3+} cations forces the flocculation of micelles with the secondary effect of binding any suitable solutes (anionic pollutants, for example) to the micellar flocculate. The flocculate can be removed from solution by filtration, which is a very attractive option for the separation of water-soluble pollutants. The potential recovery of valuable chemicals from process water and the recycling of the surfactant add to the interest of the technique.

The overall process may be regarded as a continuous adsorption of pollutant from the effluent stream. The process is an obvious alternative to MEUF

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(micellar enhanced ultrafiltration): both cause binding of a solute to an aggregate, preventing it from crossing a barrier and releasing a treated effluent which 1) contains the unbound pollutant, 2) contains surfactant at a concentration equal to its cmc, and 3) yields a waste with a high concentration of pollutant and surfactant. The main differences are: 1) the waste is more concentrated in micellar flocculation (and semisolid) than in MEUF, which is an advantage of AMF; and 2) the effluent from AMF contains unused flocculant, which is a waste and a pollution, which is a disadvantage.

There are still some limitations to the process. First, it has been reported until now only in the presence of Al^{3+}, which raises some environmental and health concerns. Second, while SDS (1, 2) behaves very well as an adsorbent, it is fairly susceptible to biodegradation and chemical decomposition, and therefore from the point of view of inventories, alternatives should be sought. Because of this disadvantage AOS has been studied as an alternative. AOS is more resistant to precipitation in hard waters, chemically more stable, and less biodegradable. However, it is still highly biodegradable, and the release of traces ot AOS in the treated effluent should not be controversial.

MATERIALS AND METHODS

High purity aluminum sulfate was purchased from PROBUS, Spain. It was specified to be 98% pure, and used as received. AOS (an anionic surfactant composed of a mixture of hydroxyalkanesulfonates and alkenesulfonates with hydrocarbon chain lengths between 14 and 16) was kindly provided by KAO Corporation, Spain. It was supplied as a aqueous paste with a surfactant content about 35% in weight. The contents of nonsurfactant organic compounds and inorganic salts was less than 1% w/w to the surfactant content. The product was used as received, as the purpose of the research is to ascertain its usefulness in a technological, large-scale application which would make purification economically impractical. AR grade 2,4-dichlorphenoxyacetic acid (2,4-D) from Merck-Schuchardt was used as the test pollutant.

Stock solutions of the various compounds (aluminum sulfate, AOS, 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 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 0.45 μm Whatman cellulose nitrate membranes.

2,4-D was analyzed by high-performance liquid chromatography with a reverse HPLC column C18 and a spectrophotometric detector. The wavelength was set at 236 nm, and the solvent used was a 50:49:1 (v/v) mixture of acetonitrile, water, and acetic acid. AOS was analyzed by double-phase volumetric titration following the Hyamine method (ISO 2271-1972), using AR grade

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Hyamine 1622 (Carlo Erba, Italy) as standard and a mixed indicator of Blue Acid 1 (Merck Darmstadt) and Dimidum Bromide (PROBUS, Spain), both AR grade.

RESULTS

Figure 1 shows that [AOS] remaining in solution after flocculation becomes constant within 10 minutes. The illustration shows the overall surfactant and Al^{3+} concentrations. While in a previous work (3) it was shown that the flocculation ratio of NaDS became constant within 2 minutes, here the flocculation ratio varies with time and both total [AOS] and [Al^{3+}]. The experiments were performed in the presence of 50 ppm of 2,4-D, and it was observed that the flocculation ratio remained constant after 60 hours. Because of the differences between floccculation curves for NaDS and AOS (Fig. 2), the $[AOS]_{residual}$ after flocculation are very similar across the flocculation region. AOS has a broader flocculation region than NaDS (5), and the flocculation ratio (ratio between the residual surfactant in solution and the total surfactant concentration) is less sensitive to surfactant concentration than in the case of NaDS. Additionally, the lower and upper flocculation limits are more pronounced than in the case of NaDS. The first conclusion is that the flocculation rate is lower than in the case of NaDS. However, the contact time required to reach flocculation equilibrium with an adequate choice of concentrations of pollutant and Al^{3+} (about 5 minutes for 0.05 M AOS) is good as a minimum

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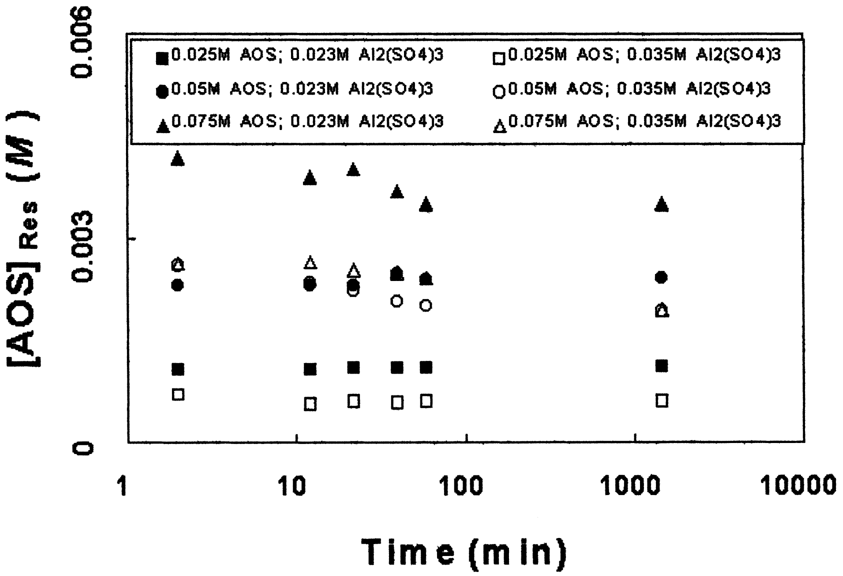

FIG. 1 Residual surfactant concentration in solution. The experiments were performed in the presence of 50 ppm of the pesticide 2,4-D.

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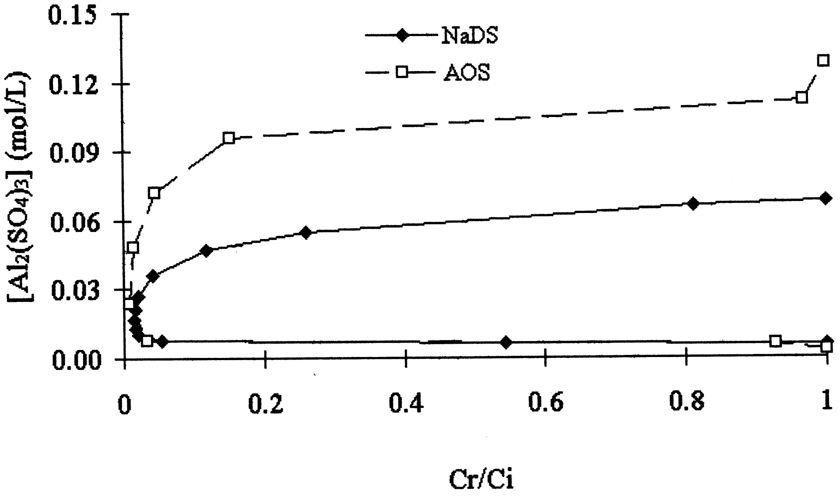

FIG. 2 A comparative plot of the flocculation ratios of NaDS and AOS in front of the concentration of aluminum salt. The experiments were performed in the absence of pesticide and with a surfactant concentration of 0.05 M in both cases.

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contact time for a continuously operated adsorber. As the residual surfactant concentrations are similar from the point of view of release with the effluents and loss of reagent, the product is comparable to NaDS.

Figure 3 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 ppm. The best

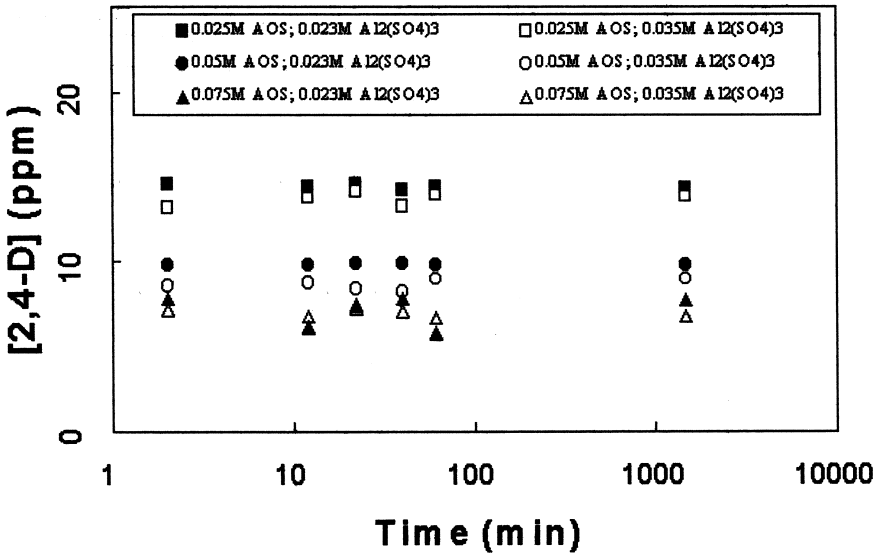

FIG. 3 Residual 2,4-D concentration left in solution after flocculation and subsequent filtration of AOS.

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results presented in the figure (about 7–8 ppm of 2,4-D left in solution) are comparable with the best in a previous work with NaDS (about 4–5 ppm) of residual 2,4-D). The flocculation of AOS has been performed in conditions of high flocculation in all cases, while in previous work with NaDS pollutant capture was studied in conditions of total and partial flocculation. In experiments with NaDS within the high flocculation region, the residual 2,4-D concentration was kept below 12 ppm. For AOS the range of residual [2,4-D] is between 7–8 and 15 ppm. This means that AOS is slightly less effective. By comparing Figs. 1 and 3 it can be seen that the experiments with higher AOS concentrations (0.075 M) led to a lower 2,4-D residual concentration. This is obvious because the concentration of flocculate (adsorbent) is higher than in the other experiments. It can also be seen that the nonequilibrium condition of the flocculation process affects the pollutant capture ratio during the initial minutes. Some dispersion exists for both 0.046 and 0.07 M [Al^{3+}]. This was not the case with NaDS even though the concentrations of 2,4-D and the analytical method were the same. The fluctuation in residual 2,4-D value shown in Fig. 3 may be attributed to dynamic factors. As flocculation takes place by itself while pollutant capture is subsidiary to it, the fact that changes with time of the sorption process only take place when such changes occur in the flocculation process suggests that flocculation is the controlling process from a kinetic point of view.

The results in Fig. 4 were obtained after an equilibration time of 1 hour. As in previous work, a separation parameter α was calculated for various combi-

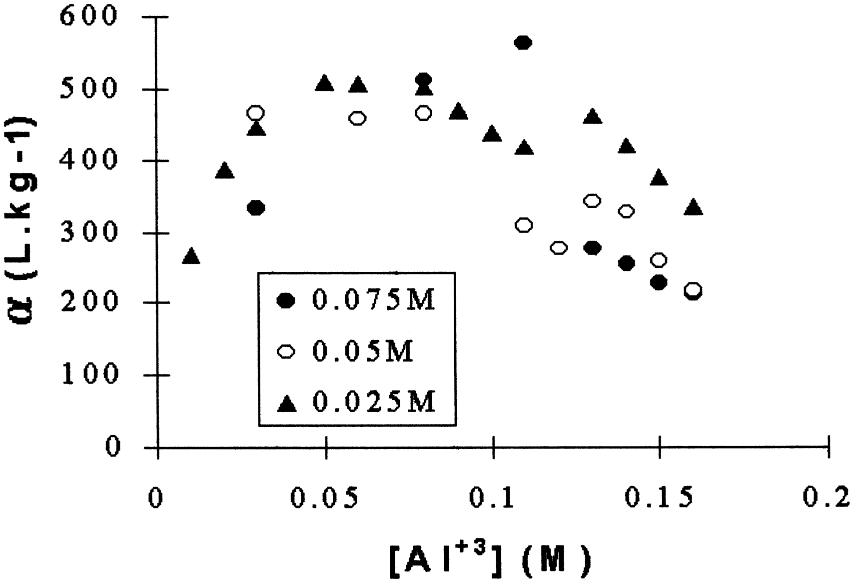

FIG. 4 The ratios between surfactant-adsorbed 2,4-D and the 2,4-D in water plotted against the overall Al^{3+} concentrations.

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nations of AOS, Al^{3+}, and 2,4-D. Total [AOS] were 0.05 and 0.07 M, $[Al^{3+}]$ ranged from 0.03 to 0.13 M, and [2,4-D] were 50 and 300 ppm. The separation parameter was defined as:

$$\alpha = [\text{2,4-D}]_{\text{sorbed}}/[\text{2,4-D}]_{\text{residual}}$$

No values are found above 600, while for NaDS some values above 1500 were obtained. However, again the process of removal of a compound like 2,4-D from aqueous solutions by micellar flocculation seems more attractive than alternatives like admicellar solubilization (6). Since the octanol/water partition coefficient for 2,4-D is 6.2 (3), that AOS flocculates are on average at least 50 times more efficient than admicelles.

CONCLUSIONS

The kinetics of flocculation and pollutant capture of AOS differ slightly from those of NaDS. While flocculation kinetics is slower, and the separation parameter reaches lower values, its stronger resistance to degradation makes it reasonable to assume it could be an useful alternative to NaDS in a closed-loop industrial application of waste treatment by micellar flocculation.

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