# Removal of Safranine from Aqueous Solution by Using Adsorptive Bubble Separation Techniques

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**Abstract**: Safranine, a cationic dye, was removed from synthetic wastewater by ion flotation. Over 98% of safranine was removed from the solution in 10 min. A stoichiometric amount of surfactant (1 mol of surfactant to 1 mol of dye) was found to be most effective for safranine removal. The separation efficiency of safranine decreased with increasing concentration of NaNO<sub>3</sub>. Safranine was also removed by adsorbing colloid flotation technique using Fe(OH)<sub>3</sub> as the coagulant. Sodium lauryl sulfate was used as the collector, and over 97% of safranine was removed in 5 min. The separation efficiency decreased with increasing ionic strength of the solution. The deleterious effect of neutral salt was compensated somewhat with the aid of  $Al^{3+}$  as the activator. Both ion flotation and adsorbing colloid flotation may be applicable in the removal of safranine from wastewater.

Keywords: Safranine, ion flotation, adsorbing colloid flotation.

Ion flotation technique<sup>1</sup> is a process in which an ionic solute, called the colligend, is removed from aqueous solution by adding surface-active collector ion of a charge opposite to that on the colligend, and then bubbling the air through the solution. When the bubbles reach the surface of the aqueous solution, a foam is formed in which a solid phase is deposited. The applicability of ion flotation as a technique to treat dyes in wastewater has been investigated for dyes of only two kinds- direct blue<sup>2</sup>, and auramine<sup>3</sup>. The removal of safranine from an aqueous solution by ion flotation was studied. Because safranine can cause some environmental problem, the search of a simple and effective removal method is necessary.

The adsorbing colloid flotation technique has been applied in removing various inorganic species from aqueous solutions<sup>4-5</sup>. This technique involves the addition of a coagulant (ferric or alum nitrate) to produce a floc. The dissolved inorganic species are adsorbed onto the floc particle and/or coprecipitated with it. A surfactant is then added, adsorbs onto the floc particle, and renders it hydrophobic. On bubbling air through the solution, the floc is adsorbed on the rising bubble and carried out from the solution by the foam. In this paper we also attempted to remove safranine by adsorbing colloid flotation.

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Chung Shin LU et al.

## **Experimental**

The apparatus for ion flotation and adsorbing colloid flotation was similar to that described earlier<sup>6</sup>. For the ion flotation runs, sodium lauryl sulfate (NLS) was added to the sample solution to form the dye-surfactant complex, the pH of the solution was adjusted, the solution was poured into the separation column, and the timer was started. The rate of air flow was adjusted before the sample solution was poured into the column. For the adsorbing colloid flotation runs,  $Fe(OH)_3$  was added to the sample solution, and the pH was adjusted to produce the floc. Safranine was adsorbed on or coprecipitated with the floc. NLS was added to render the floc hydrophobic, and the solution was then poured into the column for separation. All runs were made with 250 mL of test solution that contained  $7.1 \times 10^{-5}$  mol/L safranine. The concentrations of dye in the sample solutions were determined using a UV/Vis spectrometer (Perkin Elmer Lambda 25).

## **Results and Discussion**

Figure 1

The effect of surfactant concentration on the ion flotation of safranine is shown in Figure **1.** It was found that a 1:1 mole ratio of surfactant to dye is enough for an effective separation with approximately 98.3% removal in 10 min. A large excess of surfactant dosage resulted in a lower removal efficiency; this is presumably due to the competition for the bubble surface by the excess surfactant ion with the dye-surfactant complex. A similar effect was observed on the solvent sublation of magenta-NLS<sup>7</sup>, direct red-HTA<sup>8</sup>, acid red-HTA<sup>9</sup>, methyl violet-DBS<sup>10</sup> and ion flotation of direct blue<sup>2</sup>. This finding was quite different from the solvent sublation results for methylene blue and methyl orange studied by Wilson et al.<sup>11</sup>, who found that the rate of removal of methylene blue and methyl orange increased with increasing concentration of surfactant, when it was in much excess of the stoichiometric amount. This contradiction is probably due to the difference in the formation constant of the different surfactant-dye complexes and also due to the difference in the mole ratio of the dye and surfactant of the complexes.



of safranine<sup>a</sup>

Effect of NLS dose on ion flotation Figure 2 Effect of NaNO<sub>3</sub> on ion flotation of safranine<sup>a</sup>



<sup>a</sup>pH=6, rate of air flow was 180mL/min, duration of air flow was 15, 10, 5 and 3 min from top down.

<sup>a</sup>Molar ratio of NLS to dye was 1, pH=6, rate of air flow was 180 mL/min, duration of air flow was 15, 10, 5 and 3 min from top down.

100 80 40 20 2 3 4 5 6 7 8 9 pH

Figure 3 Effect of pH on adsorbing colloid

flotation of Safranine<sup>a</sup>

 ${}^{a}$ [Fe<sup>3+</sup>]=1.8×10<sup>-3</sup> mol/L, [NLS]=3.5×10<sup>-4</sup> mol/L, rate of air flow was 120 mL/min, duration of air flow was 20, 15, 10, 5 and 3 min from top down.

**Figure 5** Effect of NaNO<sub>3</sub> on adsorbing colloid flotation of safranine<sup>a</sup>



<sup>a</sup> [Fe<sup>3+</sup>]= $1.8 \times 10^{-3}$  mol/L, pH=5, rate of air flow= 50mL/min, [NLS]=  $2.1 \times 10^{-4}$  mol/L, duration of air flow was 20, 15, 10, 5 and 3 min from top down.

<sup>a</sup> [Fe<sup>3+</sup>]= $1.8 \times 10^{-3}$  mol/L, pH=5, rate of air flow= 50mL/min, [NLS]=  $2.1 \times 10^{-4}$  mol/L, [NaNO<sub>3</sub>]=0.4mol/L, duration of air flow was 20, 15, 10, 5 and 3 min from top down.

The effect of neutral salt (NaNO<sub>3</sub>) on the rate of removal of safranine-NLS complex by ion flotation is shown in **Figure 2**. The separation efficiency decreased somewhat with the addition of neutral salt, presumably due to the competition for collector between the colligend and the ions of salt<sup>4-5</sup>. Wilson *et al.*<sup>11</sup>, also observed the inhibiting effect of neutral salts on the solvent sublation of both methylene blue-tetradecyl sulfate and methyl orange-HTA dye-surfactant complexes.

Another series of experiments were performed using the adsorbing colloid flotation technique to remove safranine from aqueous solution. The effect of pH on the adsorbing colloid flotation of safranine with  $Fe(OH)_3$  floc is shown in **Figure 3**. Sodium lauryl sulfate was used as the collector and frother. It was found that the rate of removal was rapid at a pH range of 5-7; over 91% of safranine was removed in 15 min. The rate of separation and separation efficiency decreased significantly, if the pH of the solution was too low, probably due to incomplete formation of Fe (OH)<sub>3</sub> floc at lower pH.

The effect of surfactant dosage on the separation efficiency of adsorbing colloid flotation of safranine is shown in **Figure 4**. NLS concentration at  $2.1 \times 10^{-4}$  mol/L was

Figure 4 Effect of NLS on adsorbing colloid flotation of safranine<sup>a</sup>



<sup>a</sup>[Fe<sup>3+</sup>]=1.8×10<sup>-3</sup> mol/L, pH=5, rate of air flow was 120 mL/min, duration of air flow was 20, 15, 10, 5 and 3 min from top down.

**Figure 6** Effect of Al<sup>3+</sup> on adsorbing colloid flotation of safranine <sup>a</sup>



Chung Shin LU et al.

sufficient for an effective separation. At a greater concentration of surfactant  $(3.5 \times 10^{-4} \text{ mol/L})$ , the rate of separation of safranine is smaller, presumably due to the competition of the bubble surface by the excess surfactant ion with the Fe(OH)<sub>3</sub> floc.

The effect of NaNO<sub>3</sub> on the separation efficiency of adsorbing colloid flotation of safranine is shown in **Figure 5**. The separation efficiency decreased with increasing ionic strength of the solution, presumably due to a decrease of the surface potential of the floc by the adsorption of the anion (nitrate ion) in the solution, such that the surface potential of the floc was no longer positive enough for a sufficient amount of anionic surfactant to be adsorbed. It was found that only 68.5% of safranine was removed in 10 min from a solution containing 0.4 mol/L of NaNO<sub>3</sub>.

We attempted to use  $Al^{3+}$  as the activators for the removal of safranine from solution containing 0.4 mol/L of NaNO<sub>3</sub> by adsorbing colloid flotation. The results are shown in **Figure 6**. Effective separation with 94.7% removal of safranine was achieved in 10 min when  $3.8 \times 10^{-4}$  mol/L of  $Al^{3+}$  was added. The effect of  $Al^{3+}$  as the activator is presumably due to the increase of the surface potential of the floc by the adsorption of  $Al^{3+}$  species on the Fe (OH)<sub>3</sub> floc (or by forming a mixed precipitate), such that a sufficient negatively charged surfactant (NLS) can be adsorbed onto the surface of the floc, thus render the surface of the floc hydrophobic. This results in an effective separation.

### Conclusion

Safranine was removed effectively from synthetic wastewater by ion flotation; over 98% of safranine was removed from the solution in 10 min. The separation efficiency increased with increasing rate of air flow and decreased with increasing concentration of NaNO<sub>3</sub>. Adsorbing colloid flotation of safranine with Fe(OH)<sub>3</sub> floc and NLS is effective with 97% removal of safranine in 5 min. The deleterious effect of neutral salt on the adsorbing colloid flotation of safranine is compensated by use of  $Al^{3+}$  as activator, which increases the surface potential of the floc as a result of the adsorption of  $Al^{3+}$  species.

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