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Separation of Organic Dyes from Wastewater by Using Colloidal Gas Aphrons

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Abstract

Auxiliary chemicals used in the preparation of water-based dyes have been reported to pose problems in conventional wastewater treatment processes. The dye manufacturing industries have to find alternate wastewater treatment processes to remove dyes from their waste effluents. This paper investigates a novel method of separation of dyes by flotation using colloidal gas aphrons (CGAs). The results indicate that this is an effective method for the separation of synthetic dyes from wastewater. The mechanism of removal has been shown to be ion coupling of the oppositely charged species of the surfactant forming the CGA and the dye and flotation of the ion–dye complex on the surface of CGA microbubbles.

Key Words: Colloidal gas aphrons; Separation; Organic dyes; Surfactants; Flotation

INTRODUCTION

One of the problems of effluents from dye manufacturing industries is the color imparted to wastewater. Conventional wastewater treatment processes are inadequate in removing dyes from effluents. This paper presents an alternative method for removing these dyes, and therefore the color, from industrial wastes using colloidal gas aphrons.

Colloidal gas aphrons are dispersions of very small microbubbles (usually of diameters in the range of 25 to 125 μm) distributed in an aqueous

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medium. Colloidal gas aphrons were first reported in 1971 by Sebba under the name of "micro gas dispersions" (*1*, *2*). Since then they have been utilized in various separation processes. Colloidal gas aphrons are gas bubbles encapsulated in a soapy film, but are quite different from conventional air bubbles and soap bubbles (*1*). These bubbles show colloidal features like their ability to stand suspended in solution for considerable time. These dispersions contain up to 50–65% by volume of gas phase, but the viscosity of the suspension and its flow characteristics are close to water, which enable them to be pumped from one location to another.

Due to the special properties of CGAs, they have been used in many areas of separations technology. The use of CGA suspensions for the removal of heavy metals from the aqueous phase has been reported by Ciriello et al. (*3*). Roy and Amedee (*4*) reported the application of CGA suspensions to remove heavy metals and organics from drilling fluids. Shea and Barnett (*5*) removed a commercial dye, Remazol Golden Orange 3-G, from water using CGAs. Numerous other applications of CGAs have been described by Sebba (*9*).

The purpose of the present research study was to investigate the applicability of colloidal gas aphrons in separating organic dyes from wastewater by flotation.

EXPERIMENTAL

Surfactants

Caballero et al. (*6*) reported that the concentration of the surfactant used for the production of CGAs can influence the process of flotation. It can influence not only the quantity of surfactant added to the column but also the stability of the colloidal gas aphrons. When the surfactant concentration reaches a critical value, the hydrophobic tails of the surfactant will cluster together inside the structure with the hydrophilic heads exposed to water to form an entity called a micelle. The concentration of the surfactant at which micelles are formed is known as the critical micellar concentration (CMC) (*7*). CGAs tend to be less stable at surfactant concentrations less than the CMC (*6*). For ionic surfactants, concentrations just above the CMC were found to be more appropriate. In the present work, the CGA suspensions were generated by using a surfactant concentration of 350 ppm for a cationic surfactant (hexadecyltrimethyl ammonium bromide, HTAB) which was slightly higher than the reported CMC, and 500 ppm for an anionic surfactant (sodium dodecyl benzene sulfonate, NaDBS) which was equal to the CMC. The structure and properties of HTAB and NaDBS used in this research are shown in Table 1.

TABLE 1
Structure and Properties of HTAB and NaDBS

	HTAB	NaDBS
Structure	$CH_3—(CH_2)_{15}N^+(CH_3)_3Br^-$	$CH_3—(CH_2)_{10}—CH_2—C_6H_4—SO_3^{2-}H^-Na^+$
Molecular weight	364.6	348.5
CMC[a] (m*M*)	0.9	1.5
Nature	Cationic	Anionic

[a] CMC is the critical micellar concentration, i.e., the concentration at which surfactants form self-aggregates called micelles (*7*).

CGA Generation

CGA suspensions can be produced by using any water-soluble surfactant with the gas phase being air or slightly soluble gases like nitrogen, oxygen, or carbon dioxide. In the present case, air was the chosen gas phase for CGA generation.

The method used to produce the CGA suspension for this research was first introduced by Sebba (*8*). Based on this method, a unit was fabricated in our laboratory to produce CGA suspensions (Fig. 1). It consisted of a motor fitted on top of a cylindrical reactor and a flat disk mounted at the end of the shaft connected to the motor. The level of the surfactant solution was initially adjusted to a few centimeters above the spinning disk whose speed could be adjusted to 8000 rpm by a speed controller. Two rigid baffles were used to encompass the disk. The high speed of the disk created strong waves on the liquid surface, which struck the baffles. Upon reentering the solution, air was entrained as small microbubbles to form the CGA suspension.

Particle Size Analysis

Size distributions of the CGA suspension created by the generator were determined using a Particle Size Analyzer (Microtrac 7995-10, Leeds and Northrop Inc.). This instrument projected a laser beam through a transparent cell containing a stream of moving particles suspended in the liquid. Light rays striking the particles were scattered through angles that were inversely proportional to the particle size. The rotating optical filter transmitted light at a number of predetermined angles and directed it to a photodetector. Electrical signals proportional to the transmitted light flux values were processed by a microcomputer system to form a multichannel histogram of particle size distribution. The analyzer was able to record any objects, such as droplets, soil particles, and bubbles, in the particle size range between 0.7 to 300 μm.

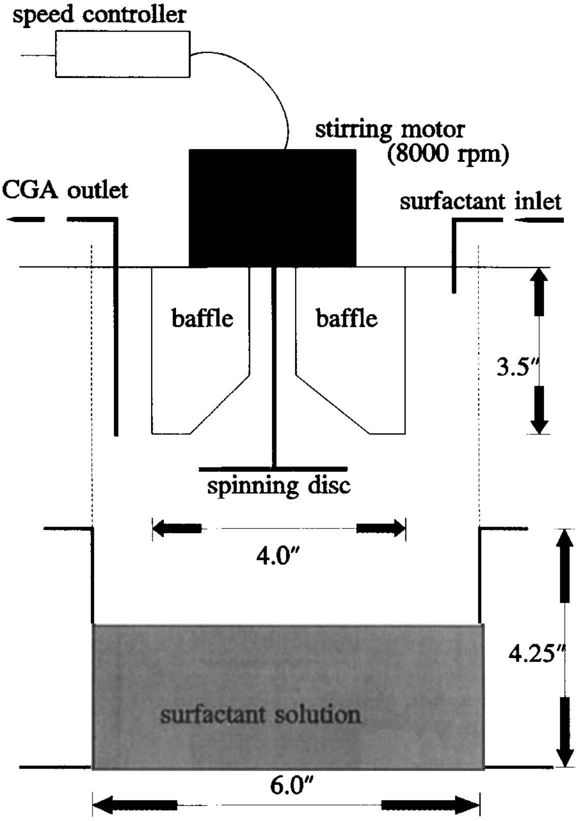

FIG. 1. Schematic of lab scale colloidal gas aphron generator.

Experimental Procedure for Flotation Using CGAs

CGA treatments were performed on two industrial sulfonate dyes, Cibacron-6B and Cibacron-4G. In addition, two other dyes, viz., methyl orange and methylene blue, were also studied. The two sulfonate dye solutions were supplied to us by a local industry and had the same composition but different concentrations and viscosities. The experiments on Cibacron-6B were performed at a dilution ratio of 1:2. In the case of Cibacron-4G, which was of very high concentration, a dilution ratio of 1:90 was chosen since this dilution gave an absorbance equal to that of the diluted Cibacron-6B so that a comparison could be made between these two dyes at fairly identical concentrations.

The entire experimental setup used for CGA treatment of the synthetic dyes is shown in Fig. 2. The surfactant reservoir for CGA was filled with either 350 ppm HTAB or 500 ppm NaDBS according to the dye to be treated. The flotation column was filled with the dye solution to be treated.

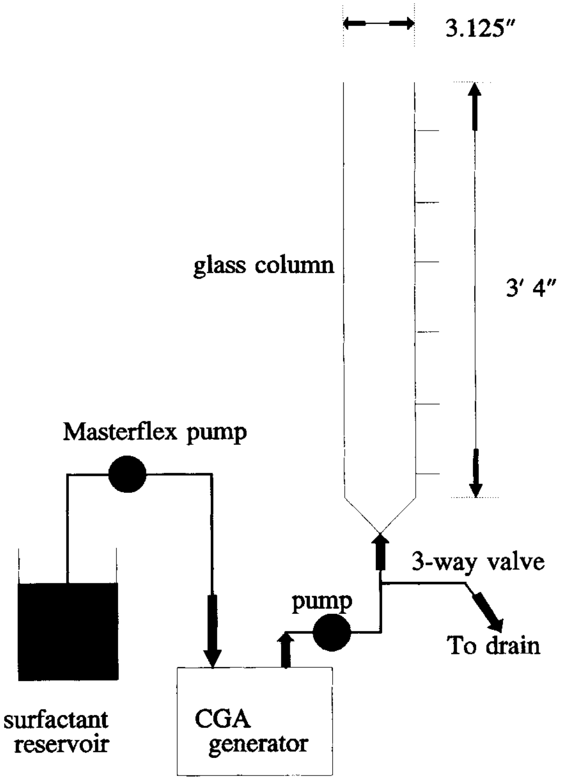

FIG. 2. Schematic of the experimental setup for flotation.

The CGA generator was started and run initially at 8000 rpm until sufficient CGA suspension was formed. The speed was then adjusted and maintained at 5800 rpm to prevent creaming (*10*), and the CGA suspension was injected into the column in short pulses using a peristaltic pump at the desired flow rate. The CGA suspension was allowed to rise in the column for 15 min. The dye was collected in the foam on top of the aqueous section and imparted a distinct color to the foam layer. Visual examination showed little or no backdispersion of the dye into the aqueous phase, and hence the foam layer was not removed from the top of the aqueous phase. The total volume of the solution was measured. A fresh batch of CGA solution was then passed through the solution. The procedure was repeated 3 times to treat methyl orange and methylene blue and 5 times to treat the two synthetic dyes, Cibacron-6B and Cibacron-4G. Aqueous samples were collected from the column after each run and analyzed to determine the UV absorbance. The passage of CGA suspension increased the overall volume of the aqueous phase. The effect of this dilution in the case of series CGA treatment was properly taken into account in determining the absorbance (concentration) of the dye in the sample and the percent removal from the original starting solution.

Absorbance Measurements

The UV absorbance of these dye samples was measured on a diode array UV-Visible Spectrophotometer (Hewlett-Packard Model 8452A). Both the sulfonate dye solutions contained several species contributing to the composite color. The absorption spectra of the sulfonate dyes showed several maxima corresponding to 500, 510, 520, 530, and 540 nm wavelengths. Hence all the samples collected after the CGA treatment on the sulfonate dyes were analyzed at all of these wavelengths to determine if one or more of the color-contributing species was selectively removed. However, the absorption spectra analysis of methyl orange and methylene blue dyes indicated absorbance maxima only at 490 and 590 nm, respectively. Hence, the samples collected after CGA treatment for methyl orange and methylene blue were analyzed for color removal only at those wavelengths.

RESULTS AND DISCUSSION

The results of the experiments on the removal of synthetic dyes are presented below. The following section discusses the particle size analysis, the selection of surfactants, CGA treatment of the four dye solutions, and the reduction in total organic contents of the aqueous phase by CGAs.

Particle Size Analysis

CGAs are more stable than conventional gas or soap bubbles due to the encapsulating surfactant film which prevents them from coalescing. It has been reported that there is a tendency for the suspension to cream due to the density difference between the liquid and gas phases. The driving force for creaming is the buoyancy, which allows the bubbles to rise to the top although at a much slower rate than conventional bubbles. However, creaming can be delayed or stopped if the CGA suspension is kept under continuous agitation (*10*). Agitation can convey a lateral movement to the bubbles which is greater than the buoyancy of the bubbles.

In our work, we first investigated the particle size distribution and stability of CGA suspensions. These were performed by using a particle size analyzer. The CGA suspensions produced from 350 ppm HTAB and 500 ppm NaDBS were analyzed for size range, mean diameter, and stability. The results of the particle size analysis performed on HTAB and NaDBS are presented in Figs. 3 and 4, respectively. Figure 3 indicates that the

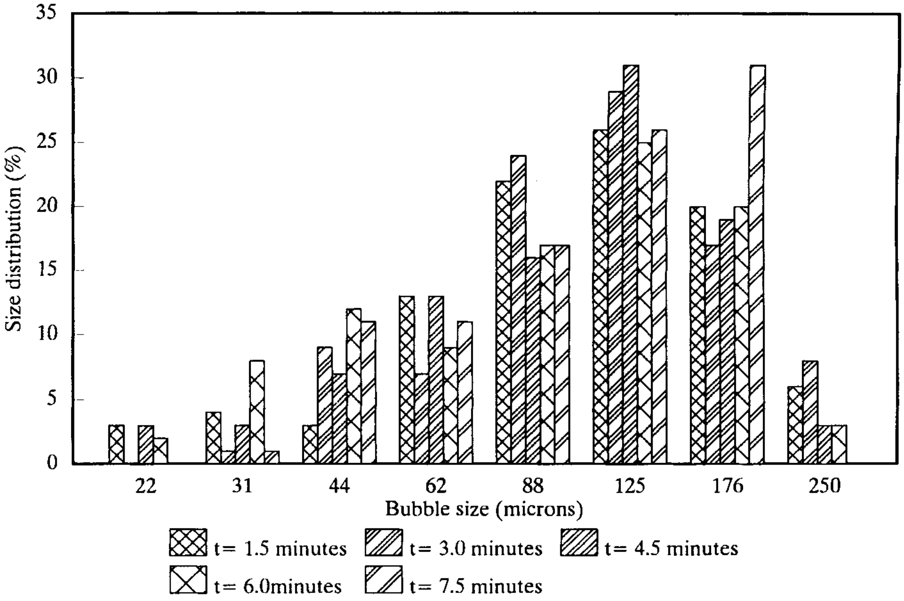

FIG. 3. CGA size distribution as a function of time for hexadecyl trimethyl ammonium bromide.

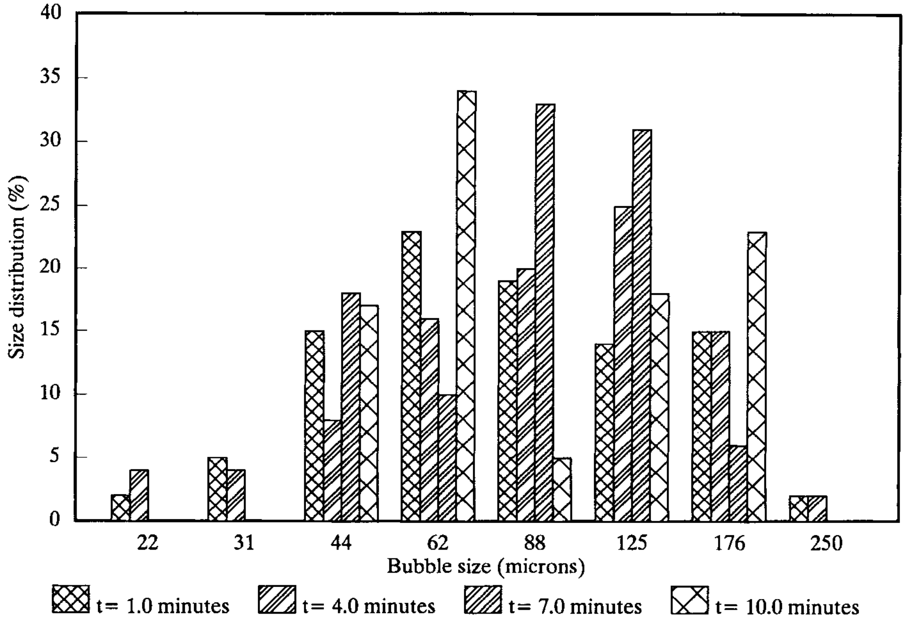

FIG. 4. CGA size distribution as a function of time for sodium dodecyl benzene sulfonate.

majority of CGAs produced from HTAB had diameters in the range between 44 and 176 μm with a mean diameter of 125 μm. Figure 4 shows that the CGA bubbles from the NaDBS surfactant had diameters in the range between 44 and 125 μm with a mean diameter of 88 μm. These figures also show that the size distribution of the bubbles remained fairly constant as time progressed. But most of the bubbles with larger and smaller diameters disappeared fast. The output from the particle size analyzer also provided a measure of the bubble volume in the sample (called DV fraction), which was monitored with time to determine the number of bubbles remaining in suspension. The results of the reduction in DV fraction of HTAB and NaDBS are presented in Fig. 5. The figure indicates that the DV fraction of the suspension decreases with time, which means that the ratio of bubble volume over sample volume decreased. The bubble volume decreased to about one-third of the original volume in about 6 min from HTAB CGAs and 12 min for NaDBS CGAs. A possible reason for this observation could be that bubbles smaller than 25 μm disappeared due to a high pressure inside the bubbles. Sebba (9) noted that the pressure

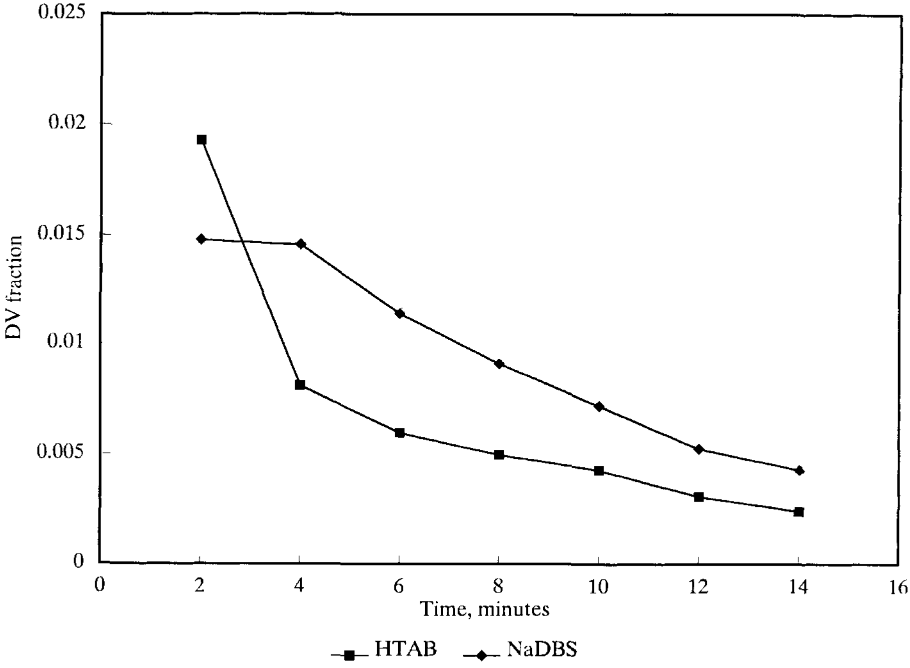

FIG. 5. Fraction of CGA bubble volume in the sample as a function of time for HTAB and NaDBS surfactants.

difference between the outer and inner surface of the bubbles is inversely proportional to the bubble diameter and that for bubbles with a diameter less than 25 μm the excess pressure inside the bubble is so high that the bubbles will tend to diminish in size by transferring their gas to larger ones, which have a smaller pressure. Very large bubbles would tend to disappear fast due to lack of proper mixing or agitation in the circulation chamber of the particle size analyzer. These bubbles would then rise to the surface due to their high buoyancy force and would become crowded, coalesce, and eventually disappear.

Selection of the Surfactant

The selection of a suitable surfactant for the treatment of a dye depends on the electrical charge of the dye to be treated. In the present case the two sulfonate dyes (Cibacron-6B and Cibacron-4G) and methyl orange were negatively charged while methylene blue had a positive charge. The CGA suspensions produced from both cationic and anionic surfactants were investigated on all four dyes to identify the best possible dye–surfactant combination. The removal of dissolved colloids and suspended particles from an aqueous solution by CGA treatment can occur by two different mechanisms. One mechanism is by "bubble-entrained floc flotation" in which relatively large particles are floated up by the buoyant action of a myriad of small bubbles (*10*). The second mechanism is called "ion flotation" in which charged species form an ion–surfactant complex with the oppositely charged surfactant molecules on the CGA microbubbles and the ion–surfactant complex is floated up to the surface (*11*). In our experiments, dye removals were obtained only when the surfactant and the dye solution to be treated had opposite charges. This observation supports the hypothesis that in these cases the mechanism of removal may be ion coupling of oppositely charged species followed by flotation. The efficiency of CGA treatment was determined based on the reduction in color as measured by the decrease in UV absorbance and the organic content of the samples after treatment.

Removal of Methyl Orange

The methyl orange solution was treated with CGA suspensions produced from 350 ppm HTAB in the column setup described earlier. The initial concentration of the methyl orange solution was 50 ppm (0.00015 *M*). The flow rate of CGA solutions into the column was maintained at 20 mL/min. An insoluble product with the color of the initial solution formed at the top of the liquid column, indicating the removal of the ion–surfactant complex formed between the ammonium ion of the surfactant and the sulfate group in the dye. The process was able to remove about 95% of

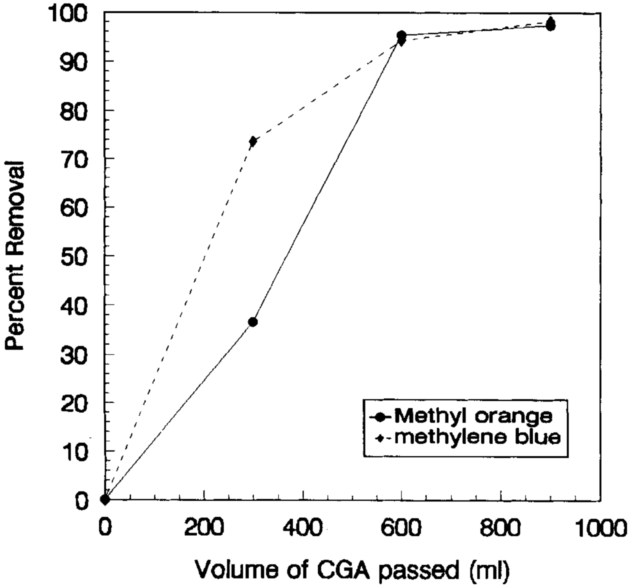

FIG. 6. Removal of methyl orange upon treatment with HTAB CGAs and methylene blue with NaDBS CGAs.

the methyl orange dye after passing about 600 mL of the CGA suspension (Fig. 6).

A study conducted by Caballero et al. (*6*) on methyl orange removal by the solvent sublation process using CGAs of HTAB surfactant at its CMC showed greater than 90% removal of methyl orange after passing the CGA suspension for 7 min at a flow rate greater than or equal to 20 mL/min. In their work they used an initial dye concentration of 2 ppm whereas in our case the initial concentration was 25 times larger. The trend of removal shows that in both the work of Caballero et al. (*6*) on solvent sublation using CGAs and in the present work involving simple flotation using CGAs, the rate of removal was initially slow but was followed by a rapid rate of removal.

Removal of Methylene Blue

Flotation experiments were performed on the positively charged methylene blue dye in the column setup described before. The initial concentration of methylene blue solution was 50 ppm (0.00013 *M*). The CGA suspensions were produced from 500 ppm NaDBS (an anionic surfactant) and the CGA flow rate to the column was maintained at 20 mL/min. The results presented in Fig. 6 show that about 95% methylene blue was removed after passing 600 mL of CGA suspensions through the column. In this case also, the mechanism of removal was due to ionic coupling. The formation of a thick blue colored product at the top of the surface of the liquid, leaving a clear liquid beneath, indicated the efficiency of ion flotation. Possible reasons for the slow kinetics of removal of dyes by ion flotation have been described by Clarke and Wilson (*11*).

Removal of Cibacron-6B

Before treatment of Cibacron-6B dye solution obtained from the industry, the solution was diluted to a ratio of 1:2. The CGA flow rate into the column was maintained at 2 mL/min. The results of this experiment, presented in Fig. 7, show that approximately 97% color removal was achieved at all the absorbance wavelength maxima after passing 200 mL of the CGA suspensions. The absorption spectra of the samples after treatment showed that there was no selective removal of the color-contributing species. The total time taken for 95% removal was longer compared to methyl orange and methylene blue. Caballero et al. (*6*) had observed that the process of removal using CGAs was slower for a pumping velocity less than 10 mL/min in their experiments on solvent sublation of dyes. A similar argument

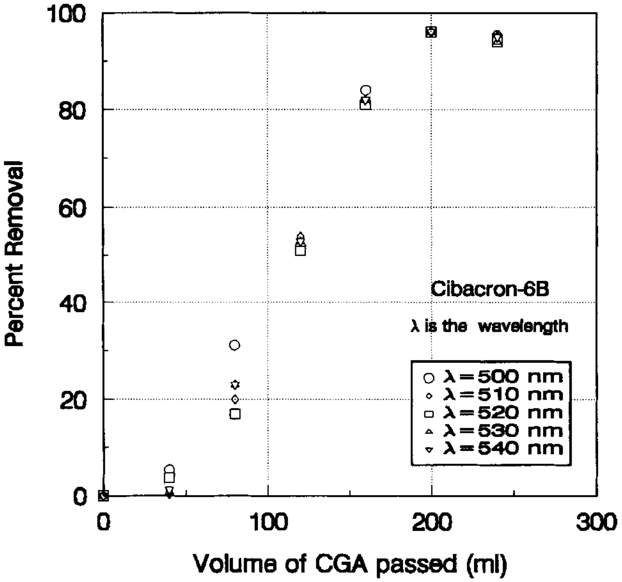

FIG. 7. Removal of Cibacron-6B dye using HTAB CGAs.

could explain the comparatively longer time taken for the removal in the present case. The effect of dilution may also have been a factor since the initial concentration of Cibacron-6B was 1100 ppm. The mechanism of removal was inferred to be ion coupling of the sulfate group of the dye and the ammonium group of the surfactant. The ion–surfactant complex was floated up to the surface of the liquid by the CGA bubbles. Here also, the trend of the removal was similar to methyl orange and methylene blue: an initial slow rate of removal followed by a rapid rate of removal.

Removal of Cibacron-4G

For the Cibacron-4G dye which had the same composition as Cibacron-6B, a dilution ratio of 1:90 was used on the raw waste supplied by the industry for the experiments since this dilution gave an initial absorbance value equal to that of Cibacron-6B. The flow rate of the CGA suspension to the column was increased to 5 mL/min. The time for removal of 97% of the dye was less for Cibacron-4G than for Cibacron-6B. This could be due to the increased flow rate of the CGA suspensions, which meant that as the flow rate increased, the rate of removal also increased. In this case also we observed an increase in time for 97% removal as compared to

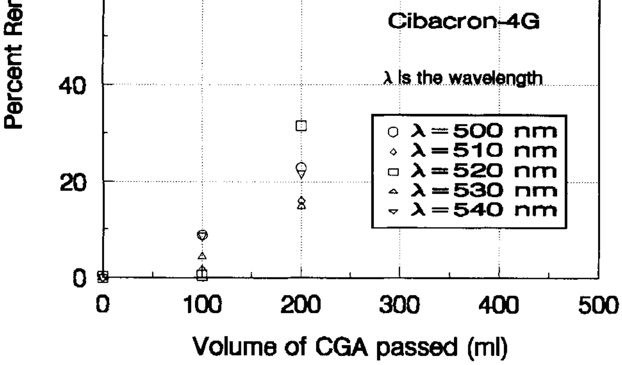

FIG. 8. Removal of Cibacron-4G dye using HTAB CGAs.

methyl orange and methylene blue. Here also the same mechanism of removal was inferred, namely, that the product of ion coupling between the surfactant and dye was floated up to the liquid surface by the CGA bubbles. Figure 8 shows that 97% removal was achieved by pumping about 300 mL of the CGA suspension. Here again, absorption spectra analysis did not show any selective removal.

Removal of Total Organic Content

For the sulfonate dyes, removal efficiency using the CGA suspension with respect to the total organic content was also determined. The samples collected after each experimental run were analyzed for chemical oxygen demand (COD), which is an indirect measure of the total dissolved organic carbon. From the results presented in Fig. 9 it is evident that significant reduction in the total organic content was possible. In the case of Cibacron-6B dye after passing 240 mL of CGA suspension, approximately 82% of the total dissolved organics were removed. The results presented in Fig. 9 shows that in the case of Cibacron-4G almost 86% of total dissolved organics were removed by the cationic surfactant after passing 400 mL of the CGA suspension.

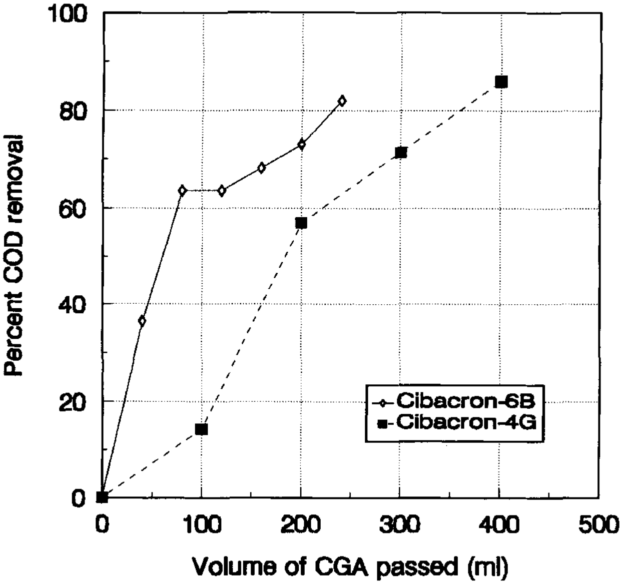

FIG. 9. Removal of total organic content from solutions of sulfonate dyes using HTAB CGAs.

In the case of the sulfonate dyes, an interesting observation was that there was an optimum amount of CGAs required for effective removal. This may be explained in relation to the mechanism of removal of dyes by CGA. As mentioned earlier, we infer that the removal mechanism of the dyes is through ion coupling of dyes with oppositely charged surfactant molecules on the CGA microbubbles and subsequent flotation of the dye–CGA complex. The process of settling of the aqueous phase after flotation seems to augment the separation of the dyes. The samples collected after the first series of CGA treatment were allowed to settle overnight. Visual observation showed that a large amount of colloidal particles had settled out. The percent removal (as measured by the decrease in UV absorbance) of the Cibacron-6B dye after the 24-h settling period seemed to increase for those samples that had 80 mL or more of CGA suspension passed through them, while for Cibacron-4G dye the increase in percent removal was noticed only for samples that had 300 mL or more CGA suspension passed through them (Figs. 10 and 11). This indicates that additional removal of the dyes is possible upon further settling of the suspended colloids

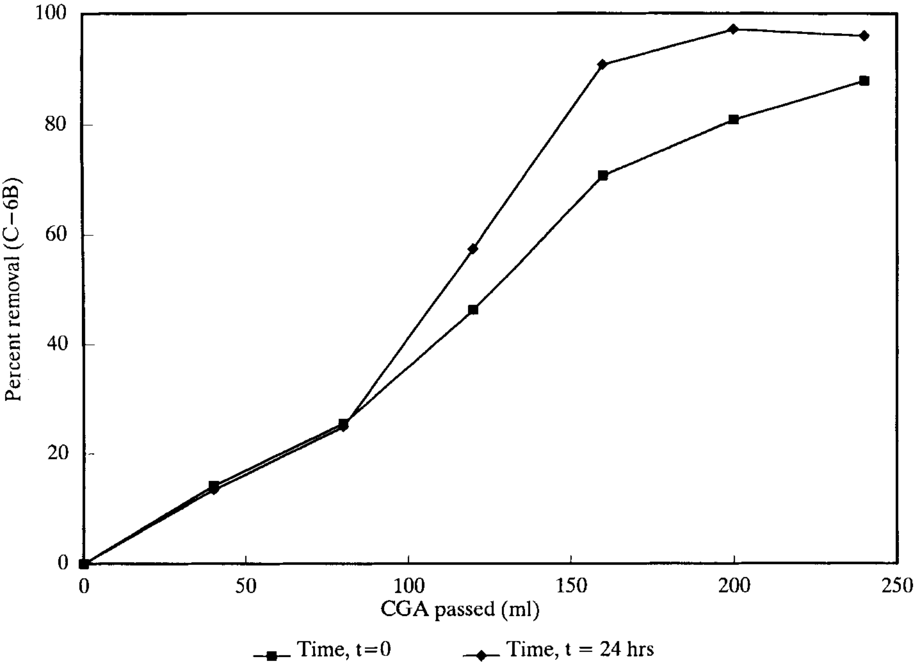

FIG. 10. Percent removal of Cibacron-6B using HTAB CGAs after flotation (samples designated t = 0 h) and subsequent settling (samples designated t = 24 h) of the suspended colloids.

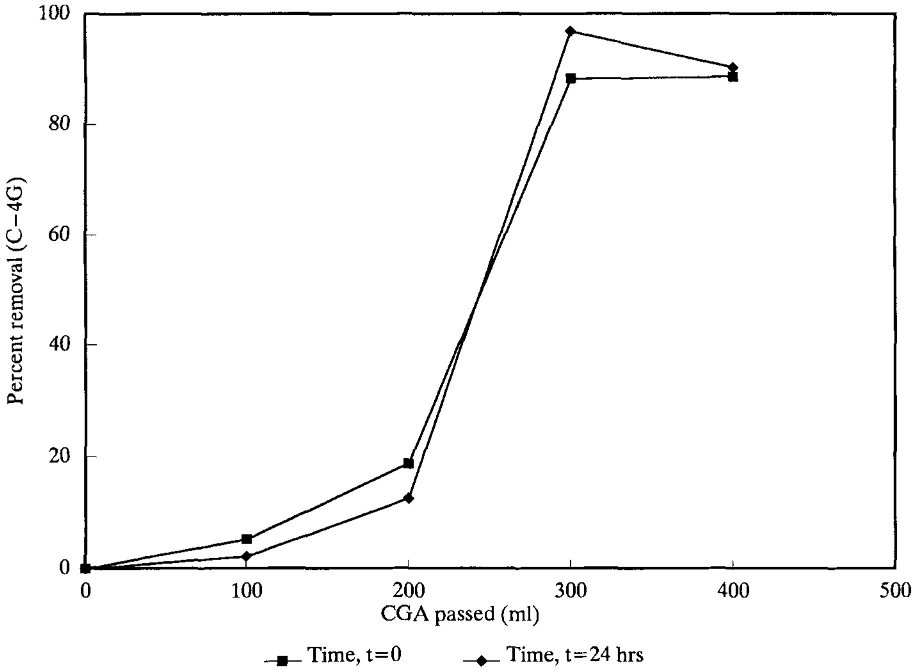

FIG. 11. Percent removal of Cibacron-4G using HTAB CGAs after flotation (samples designated t = 0 h) and subsequent settling (samples designated t = 24 h) of the suspended colloids.

subsequent to flotation of the wastewater. CGA suspensions also contain monomeric surfactants in the aqueous phase which can adsorb on the colloids, leading to a charge neutralization of the colloids which allows them to settle out of the aqueous phase. Dye molecules that are adsorbed on these colloids will also settle out with them. The process of colloid settling may take hours or even days since the process is kinetically controlled and depends both on the amount of surfactant present in the aqueous phase and on the amount of other ions present. In this regard, further experiments with CGAs are necessary to support this hypothesis.

CONCLUSIONS

Based on the results of this research on the separation of organic dyes from industrial wastes by using colloidal gas aphrons, the following specific conclusions can be drawn:

1. CGA treatment can be an effective method for the separation of synthetic organic dyes from industrial wastes.

2. Using HTAB, a cationic surfactant, CGA suspensions were capable of removing approximately 96% of the dyes from water containing methyl orange, Cibacron-6B, and Cibacron-4G dyes. CGA suspension using an anionic surfactant, NaDBS, was able to remove more than 95% of methylene blue. The types of surfactants used to generate CGA suspensions should be carefully selected so that they are compatible with the type of dye waste to be treated since ion flotation is inferred to be the mechanism of removal.
3. The flow rate of CGA suspensions into the column can affect the process of removal. There appears to be an optimum amount of CGAs required for effective removal of Cibacron-6B and Cibacron-4G dyes. A process of flotation of CGAs followed by settling of the colloid suspension appears to be an effective method of treatment of wastewaters containing dyes.

Acknowledgments

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