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Removal of Emulsified Oil from Water by Coagulation and Foam Separation

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Abstract: A new method of emulsified oil separation for oily wastewater incorporating simple operation and shortened treatment time is necessary for improved wastewater treatment in some manufacturing plants. In the present study, the removal of emulsified oil from water by coagulation and foam separation using poly aluminum chloride (PAC) and milk casein was examined. By adding casein before the foam separation process, the oil removal was dramatically improved. By using surfactant (LAS) as a frother, the dosage of casein was drastically reduced. Furthermore, for processing actual oily water, LAS was unnecessary because a sufficient amount of surfactants for foaming was included in the wastewater. For treatment of the actual oily wastewater collected from a steel manufacturing plant, the optimum condition for PAC and casein was 30 mg-Al/L and 10 mg/L, respectively, and the oil concentration decreased from 170 mg/L to 2.2 mg/L. After examining several types of oily wastewater, 96–99% of oil removal efficiency was obtained by adjusting the dosages of PAC and casein. Coagulation and foam separation using casein has shown a high potential as an alternative method to dissolved air flotation (DAF) for processing emulsified oil water.

Keywords: Casein, coagulation, collector, emulsified oil, foam separation, frother

INTRODUCTION

A large amount of oily wastewater is generated by various industries such as petroleum refining, steel manufacturing, vehicle repair, and other manufacturing plants. Oily wastewater discharged into an aquatic environment causes

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serious pollution problems. Furthermore, the biodegradability of oil in wastewater is very low, and oily wastewater hinders biological processing at sewage treatment plants. Therefore, the discharge of oily wastewater to public water bodies and sewage systems must be controlled by laws or regulations. In Japan, both the Basic Environmental Law and Sewage Works Regulations show the same regulated standard for mineral oil contained in discharged water, less than 5 mg/L. To remove oil from wastewater, the wastewater is normally introduced to a gravity oil/water separator, such as an American Petroleum Institute (API) or a Parallel Plate Interceptor (PPI) type. In a separator, with time and quiescence, most free oil droplets rise to the surface where they are skimmed off, while emulsified oil remains in the effluent. The residual oil concentration in the effluent, which then passes through a gravity oil/water separator, was approximately 50 mg/L (ranging from 10 to 100 mg/L) (1). The removal of emulsified oil from water is an essential process for the oily wastewater treatment.

Currently, dissolved air flotation (DAF) with flocculation developed in the 1970's (2) has been widely adopted for the removal of emulsified oil. Generally, the DAF process is performed as follows: flocculation of oil droplets with a coagulant such as alum or ferric chloride and a polymer; the introduction of fine air bubbles into the wastewater; attachment of the fine bubbles onto the surface of the floc structure; the upward rise of flocs in a sweeping action; and, the skimming of accumulated flocs off the water surface layer. Flotation using air bubbles is unnecessary for the exchange of membranes or adsorbents, but is suitable for processing unsettleable matter such as emulsified oil. However, DAF requires a high-pressure condition to create a sufficient amount of dissolved air water for the introduction of fine bubbles. As larger DAF systems are utilized, additional labor is needed to maintain the high-pressure equipment. In addition, good flocculation and the effective recovery of scum are also required. Presently, DAF must be utilized by an oily wastewater treatment plant to meet the effluent standard for emulsified oil. At present, many types of technology applying DAF are developed for removing emulsified oil (3–5). A new process, which could combine the efficient removal emulsified oil with easy maintenance, is still needed.

In air flotation methods other than DAF, foam separation is used to disperse air bubbles. Ores flotation, a foam separation method, has been used for many years in the mineral processing industries for the purpose of solid-liquid separation. Generally, ores flotation follows these steps: changing the solid interface condition from a hydrophilic site to hydrophobic site using a collector; introducing dispersed bubbles into a solid suspension; adsorption of solids to the bubble surface; flotation of solids with bubbles; foam generation with a frother; separation of solids with foam. In the past, large numbers of studies evaluated wastewater processing using the foam separation method (6–8). However, while this method was very effective in removing detergents such as alkylbenzene sulfonic acid, it was ineffective in removing suspended solids (6). To date, a foam separation method has not successfully removed suspended solids from wastewater.

To apply the principle of suspended matters concentrated in sea foam (9) or fish-rearing foam, we developed a coagulation and foam separation method using milk casein as the active chemical (10). This method showed extremely high removal efficiency (above 98%) of suspended solids from sewage (11). Casein functions as an excellent collector, creating the floc interface hydrophobic site. Casein also has a high foaming capacity as a frother. The "coagulation and foam separation" (CFS) process described in this study, differs from DAF in terms of bubbling, the adsorbed pattern of suspended substances on the bubble surface, and the method of recovering floating substances. Dispersed air flotation has the advantages of rapid separation and easy maintenance.

For suspended substances such as fine oil droplets, coagulation is possible using a coagulant such as poly aluminum chloride. Therefore, CFS was considered to have a high potential for removing emulsified oil from water, as an alternative to conventional DAF. The present study examined the removal of emulsified oil from wastewater by foam separation using poly aluminum chloride and casein.

MATERIALS AND METHODS

Preparation of Emulsified Oil Water

In the basic experiment, semi-synthetic motor oil (Shell Co., HELIX Premium 5W-30) was used as a sample oil. An adequate amount of oil was added to 200 mL of tap water, which was then emulsified by an ultra-high intensity disperser (Kinematica Co., POLYTORON PCU11). The dispersed-oil condition mixed for 3 minutes under middle-range intensity at room temperature. Emulsified oil droplet particle size was measured by photomicrography (Nikon Co., TMD300 model). The average diameter of the oil droplet was $3.1 \pm 0.3\,\mu m$ ($n = 200$), which confirmed that the oil droplets were almost perfectly dispersed at $5\,\mu m$ or less. By diluting this dispersed oil water with tap water, approximately 90 mg/L of emulsified oil was made for the experiment.

Sampling

Samples of the actual oily wastewater were collected from the effluent of a gravity oil/water separator at the wastewater treatment plants of a steel manufacturing. The wastewater, which showed a darkly gray color, was miscible with emulsified oil, suspended solids and some undefined surfactants. In the monitoring of the water quality for 2 months, the oil concentration and the turbidity fluctuated from 72 mg/L to 233 mg/L (mean ± SD;

145 ± 59 mg/L, n = 6) and from 83 turbidity units (TU) to 561 TU (240 ± 142 TU, n = 15), respectively. In addition, the actual wastewater samples collected at a vehicle repair facility were also investigated.

Reagents

The tested coagulant was poly aluminum chloride (PAC) (Taki Chemical Co., PAC250A). The stock solution of milk casein (Reagent grade, Wako Chemical Co.) was dissolved in 0.01 M NaOH resulting in a concentration of 10,000 mg/L. Linear dodecyl benzene sulfonic acid sodium (LAS) (Kao Co., F-60) was used as a frother. LAS stock solution was made up in a concentration of 5,000 mg/L.

Jar Test Procedure

Experiments on 800 mL samples were performed using a jar test apparatus (Miyamoto Co., MJ-8). The standard jar test procedure consisted of rapid mixing at 150 rpm for 3 min after the addition of chemicals, followed by slow mixing at 40 rpm for 20 min. The floc was then allowed to settle for 60 min. After settling, the supernatant liquid was taken out, and oil concentration was measured.

Coagulation and Foam Separation (CFS)

An 800 mL sample was dosed with the coagulant and rapidly mixed (150 rpm) for 3 min. The pH was adjusted by addition of NaOH or HCl. After coagulation, casein was added to the sample and mixed for 1 min. Foam separation was carried out by transferring this suspension to the cylindrical column (height, 100 cm; diameter, 3.6 cm) of the batch flotation equipment (10). Dispersed air was supplied from the bottom of the column with a glass ball-filter (Kinoshita Rika Co., G-4 type). Foam generated on the water surface was drawn into a trap bottle by a vacuum pump. The recovered foam was de-foamed, called "foam water." The processing time for foam separation was 5 min. The air supply flow rate was 0.5 L-air/min. The treated water was sampled from the drain.

Analysis of Oil in Water

Oil in water was extracted in solvent (polychorotrifluoroetylene, Horiba Ltd., S-316) and oil concentration was measured by an oil analyzer (Horiba Ltd., OCMA-300), using an infrared absorption method.

RESULTS AND DISCUSSION

Optimum Condition for Coagulation and Sedimentation

The changes in the residual oil concentration as a function of pH at different dosages of PAC in coagulation and sedimentation are shown in Fig. 1. The residual oil concentration rose further than with PAC free at pH 7 and 3 mg-Al/L of PAC. Oil droplets flocculated, but the flocs surfaced in water surface without settling. It was assumed that although the electric charge of the oil droplet interface was neutralized by PAC addition, the foamed oil droplet flocs were easy to float. Therefore, the oil concentration of treated water was higher than that of raw water. The quantity of aluminum hydroxide was insufficient to settle the oil flocs at 3 mg-Al/L. When the PAC dosage was increased above 5 mg-Al/L at pH 7–10, the oil flocs settled to the bottom layer, but the PAC was still insufficient to achieve an effluent level of 5 mg/L, at 5 and 10 mg-Al/L of PAC. The settling flocs formed at pH ranging from 6 to 11, and at a concentration of 20 mg-Al/L of PAC, the residual oil concentration then became 5 mg/L or less. The residual oil concentration could not achieve the effluent standard by coagulation and sedimentation at 10 mg/L of PAC and 1 hour settling, despite well-formed floc.

Effect of pH and Casein Dosage for Coagulation and Foam Separation

The changes in the residual oil concentration as a function of pH at a different dosage of casein in CFS are shown in Fig. 2. The PAC dosage was fixed at

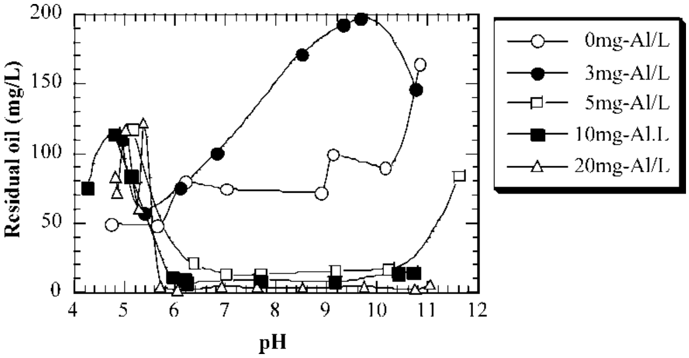

Figure 1. Changes in residual oil concentration as function of pH at different dosage of PAC in coagulation and sedimentation. Raw water oil concentration, 102.5 mg/L. Data plots are based on a single trial.

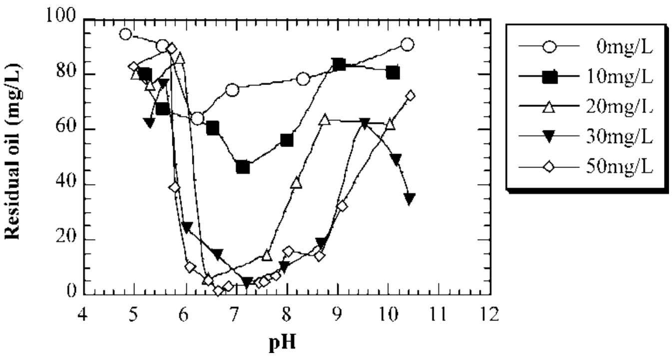

Figure 2. Changes in residual oil concentration as function of pH at different dosage of casein in CFS. Raw water oil concentration, 86.2 mg/L; PAC, 20 mg-Al/L. Data plots are based on a single trial.

20 mg-Al/L, the optimum dosage for coagulation and sedimentation. At pH 6 or less, the flocs did not separate even at 50 mg/L, the maximum casein dosage. Foam separation using casein was difficult in the pH region where flocs were not formed. Foam did not generate on the water surface with casein free and 10 mg/L casein. It was impossible to recover the flocs without generating the foam. However, at pH near 7 and 10 mg/L casein, foam did not generate on water surface, flocs accumulated on the water surface with bubbles. The casein molecules in the coagulation formed in the pH 6 to 10 region had a strong negative charge because the isoelectric point of casein occurs at pH 4.6–4.9. In contrast, a large number of positive charge sites exist at the aluminum hydroxide portion of the floc in the pH 6 to 8 range of the coagulation region (12). Therefore, the negative charge of the casein was adsorbed onto the positive electric charge of the floc in the pH 6 to 8 region. The floc interface was changed to a hydrophobic state with the casein addition. With a casein dosage of over 20 mg/L at pH 6.5–8.0, the foam which concentrated the flocs generated on the water surface, the flocs separated from water as foam. However, 20 mg/L was not a sufficient concentration of casein and foam generation stopped during the foam separation process and a portion of the flocs remained in the treated water. When the casein dosage was increased to 30 and 50 mg/L, the foam generation continued until the flocs were almost recovered. With a pH of 6.5–7.5 and a casein dosage of 50 mg/L, the residual oil concentration of the treated water was reduced to 5 mg/L or less. The residual casein concentration increased with casein dosage, elevating the availability of casein to generate foam used to recover hydrophobic flocs, which adsorbed the casein. Foam generation was the determining factor for recovering flocs in CFS. Under high alkali conditions above pH 9, although foam generation was sufficient, the flocs did not accumulate in foam and the residual oil concentration rose even in the flocculation pH region. The isoelectric point

of the aluminum hydroxide part of the floc is near pH 8.5 (12). The positive charge of the floc was neutralized with the rise in pH, and the number of adsorption sites for casein decreased, thus, the hydrophobicity of floc interface was lowered when the pH range above 9. The electrostatic reaction controlled casein adsorption onto the floc. The function of the hydrophilic floc converted to hydrophobic floc for processing of emulsified oil water was inactivated, because casein did not adsorb onto the flocs under high alkali conditions. The casein adsorbing onto the flocs acting as a collector and the casein remaining in the solution working as a frother were both necessary to obtain the high removal efficiency of oil. The characteristic of casein adsorption to the flocs was an important factor which controlled the treatability of CFS.

Relationship Between Coagulation and Casein

To allow the oil droplet flocs with a low specific gravity to settle by coagulation and sedimentation, the necessary optimum coagulant dosage was 20 mg-Al/L of PAC. However, the PAC dosage could be reduced in flotation using bubbles. The optimum casein dosage is also controlled by the coagulant dosage (10). The removal of emulsified oil was then examined by changing PAC and casein dosages. The effect of the coagulant and casein dosages on the removal of oil in CFS is shown in Fig. 3. As the appropriate pH condition for the foam separation process was obtained in Fig. 2, pH was fixed at 7. When the PAC dosage was insufficient, less than 1 mg-Al/L, emulsified oil was not removed despite the utilization of an excessive amount of casein. The aggregation of emulsified oil was incomplete

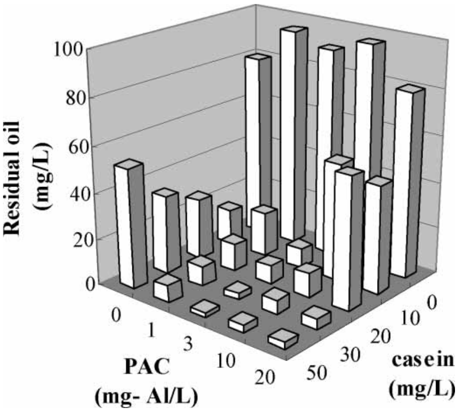

Figure 3. Effect of PAC and casein dosages on the residual oil concentration for emulsified oil water. Raw water oil concentration, 87.4 mg/L; pH, 7.

and the adsorption sites of aluminum hydroxide for casein were insufficient under the shortage of PAC dosage. With an increase in the coagulant, an increased casein dosage was also necessary to increase in order to remove the emulsified oil. Foam was generated at 20 mg/L or above of casein, and flocs were concentrated in the foam even with a small amount of PAC, 3 mg-Al/L. When increasing casein dosage, part of the added casein remained on the solution side and acted as the foaming agent. The optimum dosage for processing the emulsified oil was 3 mg-Al/L of coagulant and 30 mg/L of casein, resulting in a residual oil concentration of less than 3 mg/L. The PAC dosage of CFS was decreased further than by coagulation and sedimentation.

Utilization of LAS as a Frother

By adding the proper quantity of casein, it was possible to process oily water when using only casein as a collector and a frother. For emulsified oil water, despite a small PAC dosage, the appropriate casein dosage increased when compared with the processing conditions of polluted water such as sewage (Suzuki et al., 2002). Much casein was necessary for foam generation. Then, the utilization of LAS, because of its excellent foaming capacity was examined. The process flow follows: coagulation with PAC (3 min); casein addition (1 min); LAS addition (0.5 min); and, foam separation (5 min). The effect of casein and LAS dosage on the removal of oil in CFS is shown in Fig. 4. Figures 2 and 3 show the appropriate concentrations of PAC and pH for the foam separation process, PAC dosage and pH were fixed at 3 mg-Al/L and 7, respectively. In the case of LAS free, a high treatability of oil was obtained by increasing the casein dosage. However, with casein free, the residual oil concentration was high, despite the increased LAS dosage and excess foam generation. The removal of oil was difficult without using

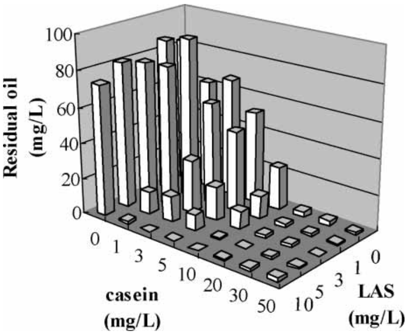

Figure 4. Effect of casein and LAS dosages on the residual oil concentration for emulsified oil water. Raw water oil concentration, 83.7 mg/L; PAC, 3 mg-Al/L; pH, 7.

casein, however, and the residual oil concentration decreased remarkably when LAS was jointly used with casein. By using LAS as a frother, the casein dosage was drastically reduced. In the present market, the cost of casein is approximately 4 times higher than that of LAS. Figure 4 shows the small casein dosages necessary for obtaining process efficiency, the optimum dosage concentrations were 3 mg/L of casein and 10 mg/L of LAS. Under these conditions, the residual oil concentration was less than 1 mg/L. In addition, the presence of high concentrations of emulsified oil was also examined. Under the same conditions (PAC 3 mg-Al/L, pH 7, casein 3 mg/L, LAS 10 mg/L), the oil concentration decreased from 445 mg/L to 6.7 mg/L by CFS. This indicated that the CFS process could also respond to drastic fluctuations in raw water oil concentration.

Treatment of Oily Water Containing Surfactant

By adding LAS before the foam separation process, it became clear that LAS could be utilized effectively as a frother. In many cases, however, the actual oily wastewater discharged from steel manufacturing, vehicle repairing, and other manufacturing industries contains many types of surfactants. It had been unclear whether the surfactants in oily wastewater improve or inhibit the CFS process. Therefore, the effect of surfactant in oily water on oil removal was examined using emulsified oil water containing LAS as a sample surfactant. The effect of casein dosages on the residual oil concentration is shown in Fig. 5. The residual oil concentration decreased with increasing casein, and the oil removal was efficiently achieved with a small amount of casein (3 mg/L). The surfactant previously contained in raw water had clearly functioned as a frother in the foam separation process.

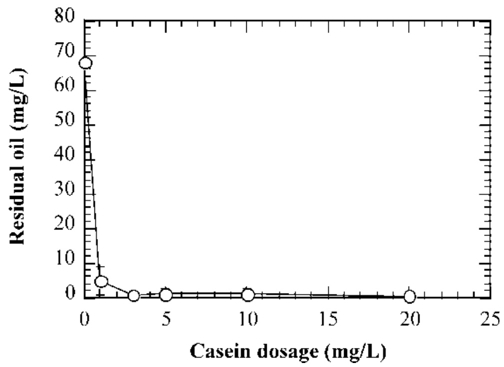

Figure 5. Effect of casein dosage on residual oil concentration for emulsified oil water containing LAS (10 mg/L). Raw water oil concentration, 83.1 mg/L; PAC, 3 mg-Al/L. Data pots are mean ± SD for three replicates.

Treatment of Actual Oily Wastewater

Processing, by CFS was examined for oily wastewater collected from a particular steel manufacturing plant. The foam generated on the wastewater surface by introducing dispersed bubbles that were LAS free, thus, LAS as a frother was not used. It could therefore be presumed that a sufficient amount of surfactants for foaming was included in the wastewater. The effects of PAC and casein dosages on the residual oil concentration are shown in Fig. 6. Under the good coagulating conditions of pH 7 and 30 mg-Al/L of PAC, the residual oil concentrations remarkably lowered with the increased casein dosages. The optimum conditions of PAC and casein were 30 mg-Al/L and 10 mg/L, respectively, and the oil concentration of treated water became 2.2 mg/L under these conditions. Simultaneously, suspended matters contained in the wastewater were also removed from liquid phase with foam generation, and the treated water became clear. The reagent dosages of actual wastewater increased in comparison with that of the emulsified oil water created in a laboratory. The suspended solids and dissolved matters that contaminated the emulsified oil in the actual wastewater required the increased use of coagulant. When the sufficient quantity of PAC was added, suspended solids was coagulated together with emulsified oil, and the aggregate formed the floc of aluminum hydroxide. The added casein was adsorbed onto the floc at the site of the positive electric charge of aluminum hydroxide, and then the floc interface changed to a hydrophobic state. The dosage of casein for making hydrophobic flocs also increased with the increased PAC dosage. The hydrophobic flocs adsorbed on the bubbles, and accumulated on the water surface. With generating foam derived from the surfactant in the wastewater, consequently, the flocs aggregated the emulsified oil and the suspended solids were separated from the water.

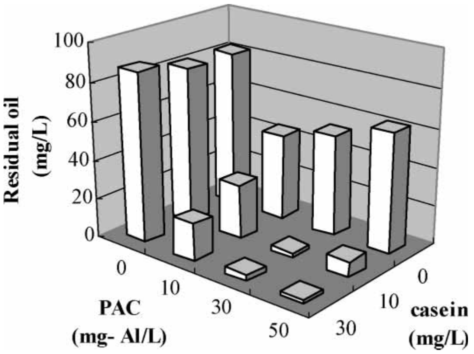

Figure 6. Effect of casein and LAS dosages on the residual oil concentration for the actual oily water collected from the steel manufacturing plant. Raw water oil concentration, 170 mg/L; pH, 7.

Table 1. Removal of oil from oily wastewater by CFS

Sample	Conditions			Oil concentration		
	pH	PAC (mg-Al/L)	Casein (mg/L)	Raw water (mg/L)	Treated water (mg/L)	Removal (%)
Steel manufacturing	7.0	30	10	170.0	2.2	98.7
	7.0	30	10	430.5	4.1	99.0
	7.0	50	30	143.2	2.8	98.0
Petroleum refining	8.2	20	100	1,900	58.8	96.9
Vehicles repairing	7.0	30	10	20.8	0.9	95.7

The surfactants, which are one of the processing object substances in the wastewater, is utilized as a foaming agent and is removed with foam, and hence addition of casein in excess or utilization of LAS was unnecessary for the actual wastewater treatment by CFS.

The results of each sample collected from wastewater treatment plants are summarized in Table 1. For each type of wastewater, CFS demonstrated a high treatability of oil by controlling both coagulation and foam separation processes by adjusting PAC and casein dosages. Sludge flocs in the foam water formed large firm flocs with an ionic polymer flocculant (Diafloc Co., AP-825B) at 10-30 mg/L. These firm flocs were easily separated into solid and liquid using a mesh screen (about 100 μm).

CONCLUSIONS

By adding casein before the foam separation process, the removal of oil was dramatically improved. The optimum pH region of the foam separation process was controlled by the pH region of coagulation. The PAC dosage of CFS was drastically lower than that of coagulation and sedimentation. The surfactant previously contained in raw water functioned as a frother in the foam separation process, thus the casein dosage for actual wastewater, containing surfactants, was less than that for the experimental wastewater without a surfactant. When controlling casein dosage under good coagulating conditions, 96–99% of oil removal was possible for the actual oily wastewater by CFS. At present, continuous treatment by a small pilot system, which consists of the coagulation process and the foam separation process, is being tested by a certain oily wastewater facility. It has been confirmed that residual oil in the treated water can achieve concentrations of less than 5 mg/L by varying the raw water quality. We believe that this method can be adopted as an emulsified oil process utilized after the gravity oil/water separation process for oily wastewater.

REFERENCES

1. Bennett, G.F. (1988) The removal oil from wastewater by air flotation: A review. *CRC Critical Reviews in Environmental Control*, 18 (3): 189–253.
2. Hyde, R.A., Miller, D.G., Packham, R.F., and Richards, W.N. (1977) Water clarification by flotation. *J. Am. Water Works Ass.*, July: 369–374.
3. Feris, L.A. and Rubio, J. (1999) Dissolved air flotation (DAF) performance at low saturation pressures. *Filtration & Separation*, November: 61–65.
4. Zouboulis, A.I. and Avranas, A. (2000) Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation. *Colloid. Surf. A: Phys. Eng. Asp.*, 172 (1–3): 153–161.
5. Al-Shamrani, A.A., James, A., and Xiao, H. (2002) Destabilization of oil-water emulsions and separation by dissolved air flotation. *Water Res.*, 36 (6): 1503–1512.
6. Rubin, E.R., Everett, J., Wenistock, J.J., and Schoen, H.M. (1963) Contaminant removal from sewage palnt effluents by foaming, No. 999-WP-5; U.S. Department of Health, Education, and Welfare, Public Health Service Publication: Cincinnati, Ohio, 1–45.
7. Grieves, R.B. and Schwartz, S.M. (1966) Continuous foam flotation for water clarification. *J. Am. Water Works Ass.*, September: 1129–1136.
8. Crandall, C.J. and Grieves, R.B. (1968) Foam separation behavior of aqueous suspensions of clays and/or iron. *Water Res.*, 2: 817–832.
9. Southward, A.J. (1953) Sea foam. *Nature*, 172 (4388): 1059–1060.
10. Suzuki, Y. and Maruyama, T. (2002) Removal of suspended solids by coagulation and foam separation using surface-active protein. *Water Res.*, 36 (9): 2195–2204.
11. Suzuki, Y., Maruyama, T., Tegane, H., and Goto, T. (2002) Removal of suspended substances by coagulation and foam separation from municipal wastewater. *Water Sci. Technol.*, 46 (11–12): 183–188.
12. Tambo, N. and Kamei, T. (1998) Coagulation and flocculation on water quality matrix. *Water Sci. Technol.*, 37 (10): 31–41.