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Separation of Algal Cells from Water by Column Flotation

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ABSTRACT

The dispersed air flotation (DiAF) process was utilized to separate algal cells (*Chlorella* sp.) from water. Two types of collector, cationic *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide (CTAB) and anionic sodium dodecylsulfate (SDS), were used. It was observed that 20% of cell removal was achieved in the presence of 40 mg/L of SDS, and ca. 86% of the cells were removed at 40 mg/L of CTAB. Upon the addition of 10 mg/L of chitosan, over 90% of the cells were removed when SDS (20 mg/L) was used as the collector. Air flow rate affected cell flotation slightly. Optimum pH values for cell flotation were from 4.0 to 5.0. Flotation efficiency decreased at high ionic strength. The electrostatic interaction between collector and cell surface plays a critical role in the separation processes.

Key Words. Algae; Chitosan; Collector; Dispersed air flotation (DiAF); Electrostatic interaction; pH

INTRODUCTION

Flotation, a separation process originating from the mineral industry, is finding its way as an effective process for both concentration and separation purposes in dilute aqueous solutions (1). The flotation technique possesses some distinctive advantages: rapid operation, low space requirements, flexibility of application, and moderate cost (2). The flotation of microorganisms

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from aqueous solution has been explored from both pollution control and aquaculture viewpoints. The microbial enrichment in foams with and without the use of collectors has been investigated for yeast cells (3, 4) and protozoa (5). As for algae harvesting, flotation is generally considered more advantageous than sedimentation due to the relatively high overflow rate (6). In addition, flotation has emerged as a favorite technique for the removal of algae in water treatment plants (7). In dissolved air flotation (DAF), an inorganic coagulant is usually added. It has been indicated that both alum and $FeCl_3$ are effective in removing algae from water (8, 9). Similarly, alum has been successfully applied in the removal of *Microcystis aeruginosa* and *Chlorella vulgaris* (10). Compared with the well-studied DAF, only limited published works are available on the dispersed air flotation (DiAF) of microorganisms. It has been shown that *Chlorella vulgaris* can be effectively removed from water by using either alum in combination with SDS or dodecylamine alone as the collector (11). Nonionic surfactant has been shown to concentrate yeast cell, *Saccharomyces cerevisiae*, to a enrichment factor of 7 in a DiAF column (3).

Surface water accounts for 80% of the water source for public water supply in Taiwan. Some forty reservoirs are therefore critical in national water resource management. However, a large portion of the major reservoirs are eutrophicated, mainly caused by poor watershed protection and lack of sewer systems (10). Many water treatment plants have been troubled by excessive amounts of algae in the raw water. Common problems, similar to foreign experiences, are risk of disinfection by-products (DBP), shortened filtration cycle, taste and odor, and high organic content in raw water (7, 8). The removal of algae from water has been under intensive study recently. In this work the separation behaviors of a commonly found species of algae in local reservoirs, *Chlorella* sp., are investigated. Two types of surfactant were used as collectors in the DiAF experiments. Through better understanding of the reactions at cell/water interfaces, this study is believed to be beneficial to the development of control technologies for algae removal in water treatment plants, and also to the harvesting of algae cultivation.

METHODS AND MATERIALS

Cultivation of Algae

Cells of algae, *Chlorella* sp., were obtained from Academia Sinica. An NC medium was used in cultivation. It contained, per liter: 10 mL KNO_3 (1 M), 4 mL $NaH_2PO_4 \cdot 2H_2O$ (0.2 M), 1 mL $Na_2HPO_4 \cdot 12H_2O$ (0.2 M), 5 mL $MgSO_4 \cdot 7H_2O$ (0.2 M), 5 mL $CaCl_2 \cdot 2H_2O$ (0.02 M), 1 mL trace elements solution, and 1 mL Fe-EDTA solution. The trace elements solution contained, per 500 mL: 1.438 g $ZnSO_4 \cdot 7H_2O$, 0.85 g $MnSO_4 \cdot H_2O$, 0.31 g H_3BO_3, 1.19

g $CoCl_2 \cdot 6H_2O$, 0.12 g $Na_2MoO_4 \cdot 2H_2O$, and $CuSO_4 \cdot 5H_2O$. The Fe-EDTA solution was prepared by mixing 2.33 g of EDTA and 1.74 g of $FeSO_4 \cdot 7H_2O$ in 500 mL. First, 350 mL of NC medium was added to each 500-mL Erlenmeyer flask equipped with a gauze stopper and autoclaved. The flasks were then irradiated with UV light for 1 hour before the cells were added. The Erlenmeyer flasks were placed on a thermostat shaker (Firstek, B603). The temperature was controlled to 25°C, and the speed of shaker was set at 75 rpm. Cultivating flasks were shaken for 20 days, with solar light illumination (National EFG 16DX) for 14 hours each day. Cells were vacuum dried for further experiments.

Characterization of Cells

Figure 1 shows the scanning electron microscopic (Cambridge, S300) photograph of *Chlorella* sp. Each cell is spherical with a diameter of 3.5 μm. To analyze the surface functional groups, a Fourier transformation infrared spectroscope (Digilab, FTS-40) was applied. Figure 2 demonstrates the existence of —N—H, —C═O, and —C—H. This is in agreement with reported surface functional groups of $—NH_2$, and —COOH on algal cells (12). The ζ-potential was analyzed by a zeta meter (Photo ELS-600). The experimental procedures

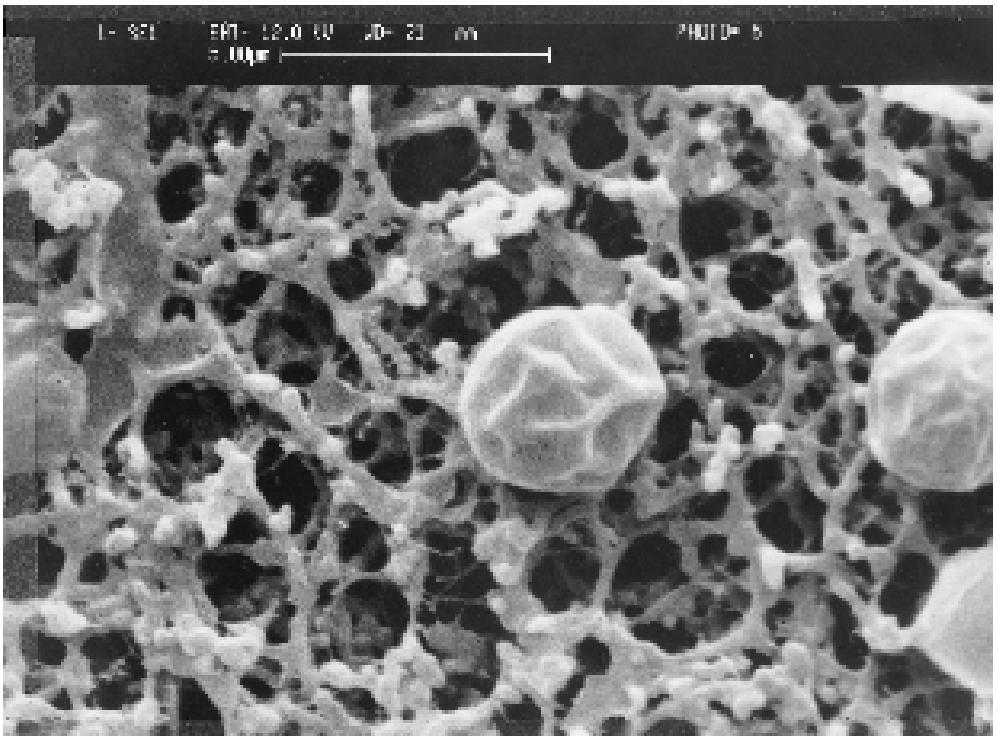

FIG. 1 The SEM picture of *Chlorella* sp.

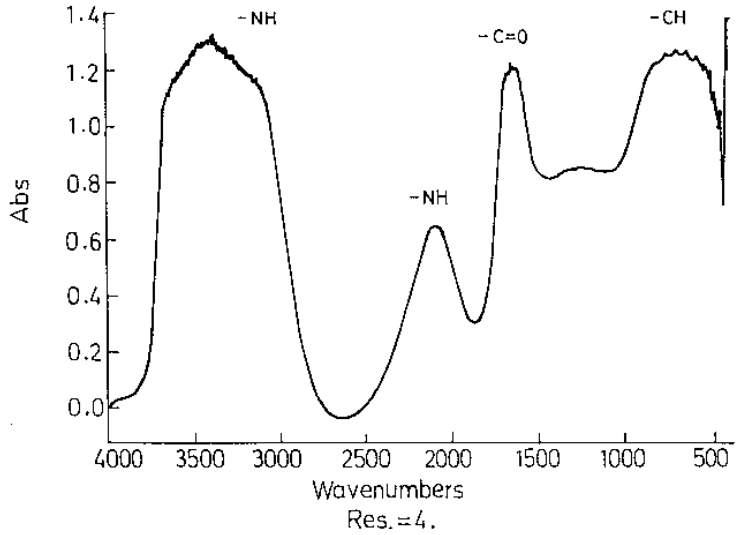

FIG. 2 FTIR spectrum of *Chlorella* sp.

used were the same as described in our previous work (13). In numbering cells, a calibration curve was first established by using a known concentration of algal cells as determined by a particle counter (Coulter, Channelzer 256). The correlation between particle number and optical density measured by a UV Spectrophotometer (Shimadzu, UV-160A) was then constructed. Another calibration curve was established between algal cell concentration and optical density. It was then utilized to determine cell concentration. The removal percentage of algal cells was determined as the difference between the initial and the final algal concentrations divided by the initial concentration.

Jar Tests

Jar tests were run to determine optimum conditions for the separation of algae from water through coagulation–flocculation. Tests were conducted using 200 mL suspensions of algal cells in each of the six 500 mL jar-paddle stirrer beakers. The suspension was rapidly mixed at 100 rpm for 2 minutes, then at 25 rpm for 20 minutes, and left to settle for 30 minutes. NaOH was used for pH adjustment. Alum and polyaluminum chloride (PAC) were used as coagulants.

Dispersed Air Flotation Experiments

The flotation column was made of acrylic with an inner diameter of 3 cm and a height of 40 cm. The detailed experimental apparatus for the flotation system is similar to that described earlier (14). A lipped side arm at 5 cm from the top of the column serves as the foam discharge port. There is a gas sparger

(pore size 10–16 μm, Merck) at the bottom of the column, and a side arm with a stopcock for sampling. Nitrogen gas passes through a pressure regulator (Norgren), a flowmeter (J & W), and a humidifier (Merck) before it flows into the column.

CTAB and SDS were used as the frother and collector, respectively. Measured amounts of stock solutions of collector and algal cells were added to a 500-mL volumetric flask placed on a stirrer (Corning). The pH was adjusted with 0.5 N NaOH and 0.5 N HNO_3. A steady flow rate of air was adjusted before 200 mL of suspension was transferred to the flotation column. The duration of flotation was 20 minutes for all runs. Samples was taken at certain time intervals and the algae concentrations were measured.

RESULTS AND DISCUSSION

Coagulation–Flocculation

Coagulation–flocculation processes are widely utilized in the separation of algae from aqueous solutions. Oxidation has proved to be an effective pretreatment (15, 16, 19). Among other chemicals, chitosan has been utilized as either a coagulant or a coagulant aid in chemical flocculation for harvesting microalgae (17, 18). Figures 3 and 4 summarize results of coagulation–

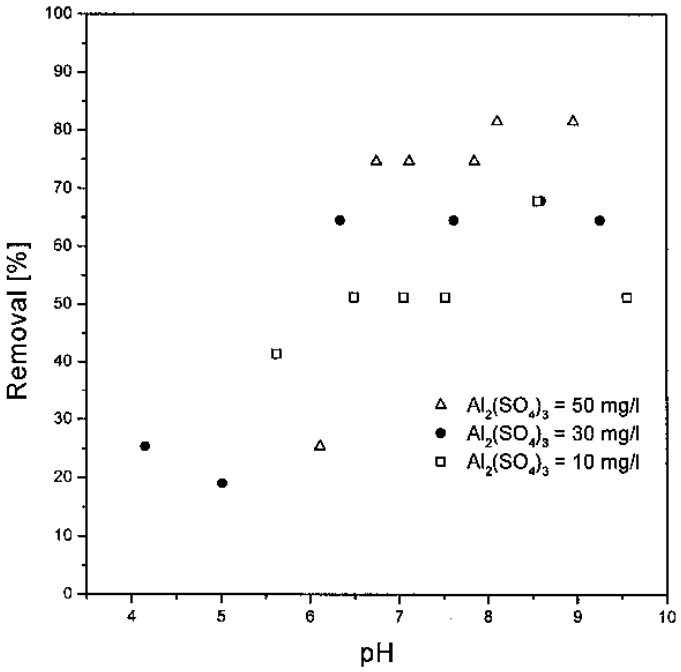

FIG. 3 Removal of *Chlorella* sp. when alum was used as the coagulant. $I = 0.05$ M $NaNO_3$, initial cell concentration (C_0) = 6.8×10^5 cells/mL.

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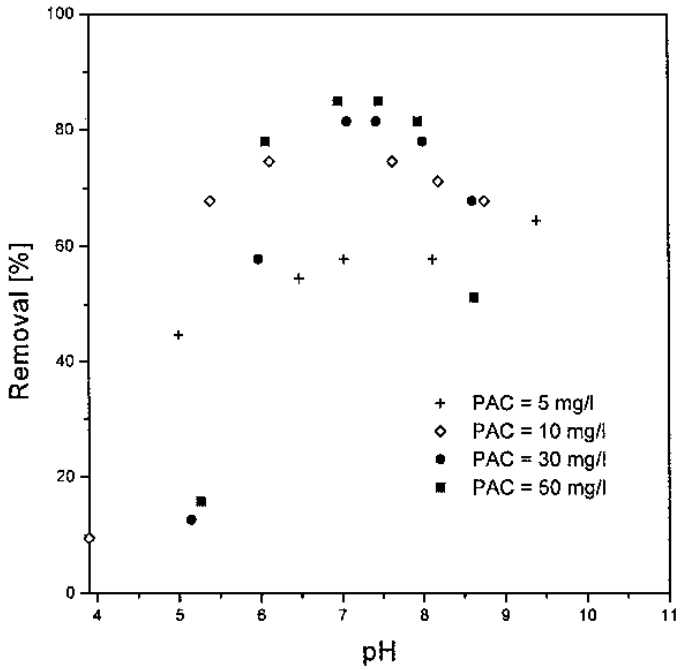

FIG. 4 Removal of *Chlorella* sp. when PAC was used as the coagulant. $I = 0.05$ M $NaNO_3$, initial cell concentration (C_0) $= 6.8 \times 10^5$ cells/mL.

flocculation. The optimum pH for algae separation was in the neutral to slightly alkaline range when alum was used as the coagulant (Fig. 3). Algal removal efficiency increased with increasing alum dose, and up to ca. 80% removal could be achieved at an alum concentration of 50 mg/L. Neutral pH was favorable for algal removal when PAC was used as the coagulant (Fig. 4). PAC produced better coagulation–flocculation efficiency than alum. This agrees with previous findings (17).

Effects of Collector

Figure 5 shows that poor cell removal (<8%) was achieved when 10 mg/L of anionic SDS was used as the collector at pH 8.0. The removal efficiency increased to 20% when SDS concentration was increased to 40 mg/L. When 10 mg/L of cationic CTAB was used, ca. 40% of algal cells was removed (Fig. 6). The removal percentage increased with increasing CTAB concentration, and reached 86% at a CTAB concentration of 40 mg/L. It has been proposed that the collector ions at the air–liquid interface may become adsorbed on the solid surface and thereby increase the hydrophobicity of the solid particles, and may provide electrical interactions between gas bubbles and solid particles (20). It is speculated that the electrostatic interaction between collector and cell surfaces plays a key role in the separation process. It was observed in

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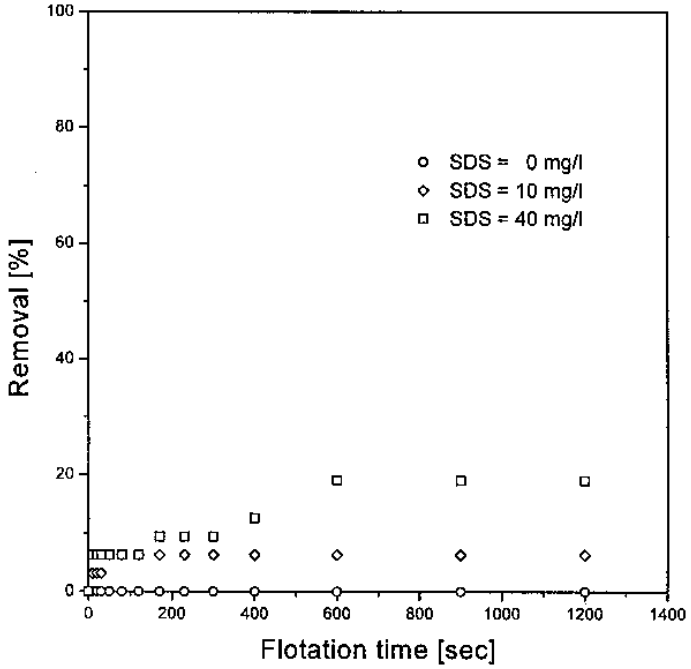

FIG. 5 Removal of *Chlorella* sp. when SDS was used as the collector. $I = 0.05$ M $NaNO_3$, initial cell concentration (C_0) $= 6.8 \times 10^5$ cells/mL, pH 8.0 $\pm$ 0.1, air flow rate = 114 mL/min.

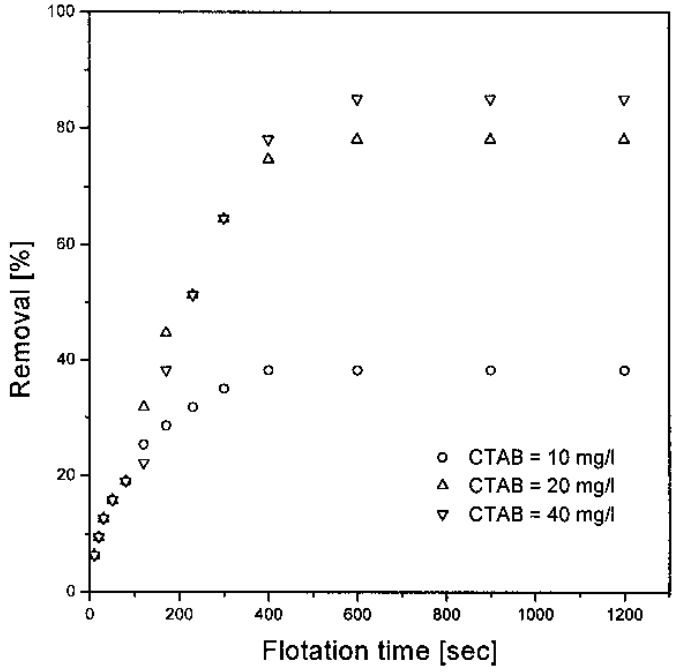

FIG. 6 Removal of *Chlorella* sp. when CTAB was used as the collector. $I = 0.05$ M $NaNO_3$, initial cell concentration (C_0) $= 6.8 \times 10^5$ cells/mL, pH 8.0 $\pm$ 0.1, air flow rate = 114 mL/min.

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the current work that both CTAB and SDS are good frothers; fine and stable air bubbles were generated. Nevertheless, the adsorption of collector ions onto cell surfaces was a prerequisite to effective separation. Contrary to SDS, CTAB was favorably adsorbed onto the cell surfaces through electrostatic interaction under neutral to slightly alkaline pH conditions. Cell surfaces then became more hydrophobic and were easier to separate from water. Similar behaviors have been reported for the flotation of *Chlorella vulgaris* where SDS is a poor collector while cationic dodecylamine is an effective one (11). The properties of the cell/water interface change as pH changes. It is noted that collectors might differ in effectiveness under different pH conditions, as evidenced by ζ-potential data that will be shown in the following paragraph.

Effects of Chitosan

In order to verify that electrostatic interaction between collector and cells is critical, chitosan was used in modifying the electrical properties of cell surfaces. Figure 7 indicates that cell removal increased to 62% on the addition of 5 mg/L of chitosan when using 20 mg/L SDS as the collector. Removal efficiency of algal cells increased with increasing concentration of chitosan, and reached 90% at 10 mg/chitosan. On the contrary, the addition of chitosan had negative effects on the separation of algal cells from water when CTAB was

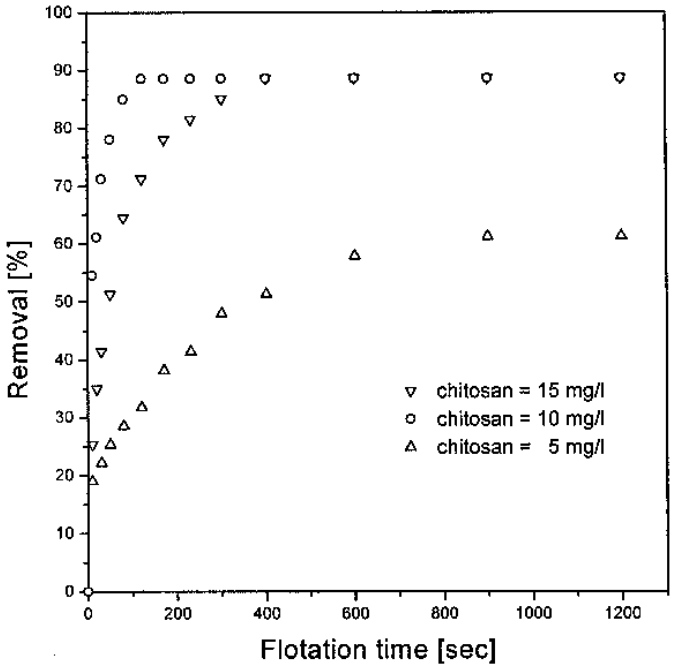

FIG. 7 Removal of *Chlorella* sp. on the addition of chitosan when SDS was used as the collector. [SDS] = 20 mg/L, I = 0.05 M $NaNO_3$, initial cell concentration (C_0) = 6.8×10^5 cells/mL, pH 8.0 ± 0.1, air flow rate = 114 mL/min.

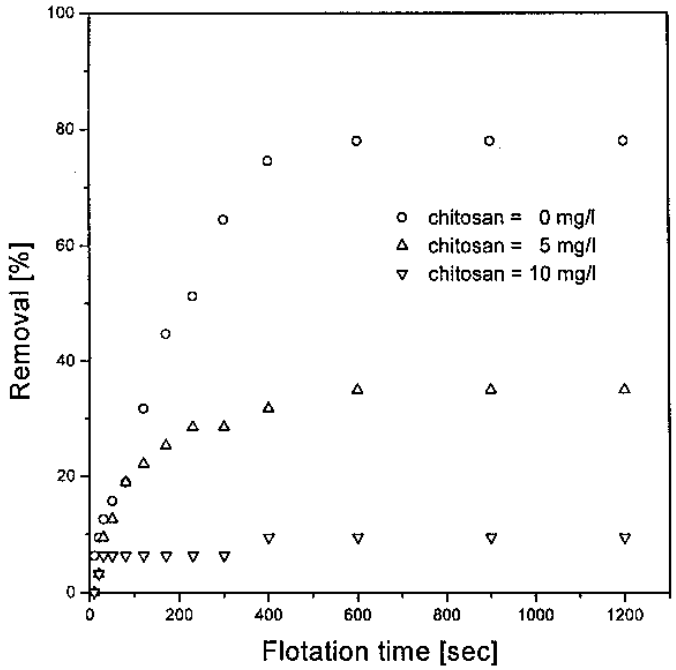

FIG. 8 Removal of *Chlorella* sp. on the addition of chitosan when CTAB was used as the collector. [CTAB] = 20 mg/L, I = 0.05 M $NaNO_3$, initial cell concentration (C_0) = 6.8×10^5 cells/mL, pH 8.0 ± 0.1, air flow rate = 114 mL/min.

used as the collector (Fig. 8). The removal efficiency was poor (36%) and even worse (10%) when chitosan concentrations were 5 and 10 mg/L, respectively. From ζ-potential data the isoelectric point (IEP) of algal cells was 3.0 in both pure water and 0.05 M $NaNO_3$ (Fig. 9). However, the IEP shifted to 7.6 upon the addition of 10 mg/L chitosan. It is proposed that the deprotonation of surface functional groups renders the cell negatively charged in the neutral natural water systems (12). Since chitosan is positively charged (21), the adsorption of chitosan onto algal cells caused the shift of IEP. The cells were thus positively charged when pH was lower than 7.6. The adsorption of SDS onto cell surfaces through electrostatic interaction was therefore made possible. Consequently, the separation of algal cells became more effective. As a natural cationic polyelectrolyte, chitosan acts as an activator in the flotation process, similar to alternative activators such as Al(III) and Pb(II) (2, 11). In the meantime, chitosan could also be regarded as a coagulant that enhanced the flotation performance (9). On the other hand, the addition of chitosan hindered the flotation separation of algal cells when CTAB was the collector. It can be reasoned that the direct competition of chitosan and CTAB for adsorption sites on cell surfaces resulted in decreased adsorption of CTAB. It is also probable that the electrostatic interaction between cell surfaces and CTAB de-

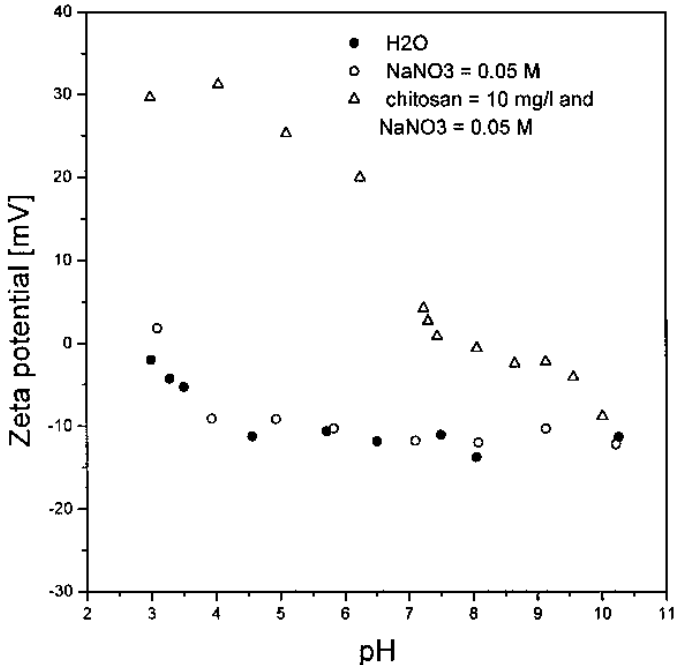

FIG. 9 ζ-Potential of *Chlorella* sp. cells as a function of pH.

creased in the presence of chitosan. Both made flotation efficiency poor. It is therefore concluded that electrostatic interaction between collector and cell surfaces is crucial in the separation processes.

Effects of Air Flow Rate

In the flotation process the gas flow rate affects the bubble size and flow pattern in the column, therefore, neither too fast nor too slow a flow rate is advised (2). In the current work the effect of air flow rate was examined. Results are shown in Table 1. The cell removal percentage remained fairly constant when the air flow rate was changed from 68 to 206 mL/min. Similar phenomena have been shown in the flotation of As(V) and Zn(II) (1, 14).

Effects of pH

It has been pointed out that pH is one of the most important parameters in flotation processes. Interfacial properties and reaction mechanisms depend on pH (1, 2). Optimum pH values for *Chlorella vulgaris* flotation were not the same when different types of collectors were used (11). The effects of pH on the flotation of algal cells when SDS was used as the collector in the presence of chitosan are illustrated in Fig. 10. It was observed that in the 5.0 to 8.0 range, pH had a negligible effect on separation efficiency. Good removal of

TABLE 1
Effect of Air Flow Rate on the Removal of *Chlorella* sp. ($C_0 = 7.4 \times 10^4$ cells/mL) at pH 8.0 ± 0.1, [Chitosan] = 10 mg/mL, [SDS] = 20 mg/mL

Air flow rate (mL/min)	Removal (%)
68	88.0
114	88.0
206	92.0

algal cells (85–90%) was found. As evidenced by the ζ-potential of cell surfaces, it was reasoned that the electrostatic interaction was the major driving force for the adsorption of anionic collector ions onto the positively charged cells (pH < 7.6). The flotation was thus facilitated. However, the affinity of SDS to the algal surfaces no longer existed when the pH was higher than 8.5. The is the reason for decreased separation efficiency (42%) at pH 8.5, and very poor separation efficiencies (<5%) were observed at pH 9.0 and 9.5.

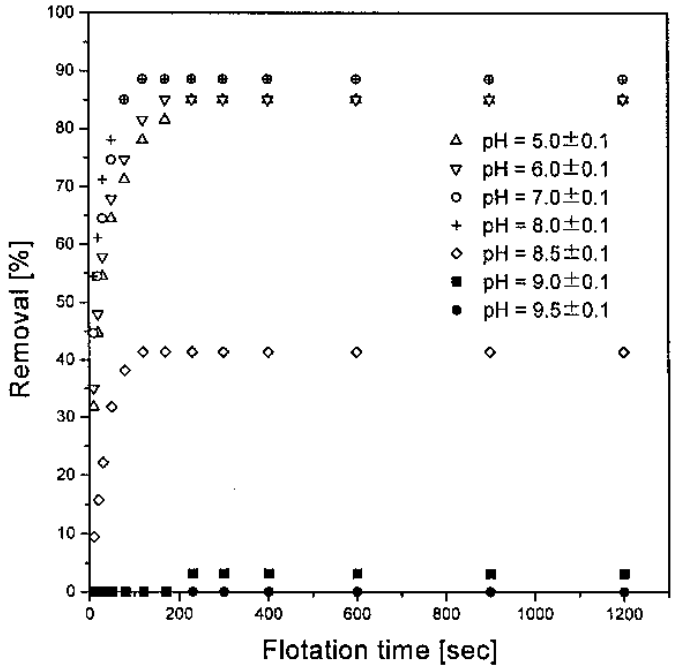

FIG. 10 Effects of pH on the removal of *Chlorella* sp. when SDS was used as the collector. [Chitosan] = 10 mg/L, [SDS] = 20 mg/L, $I = 0.05$ M $NaNO_3$, initial cell concentration (C_0) = 6.8×10^5 cells/mL, air flow rate = 114 mL/min.

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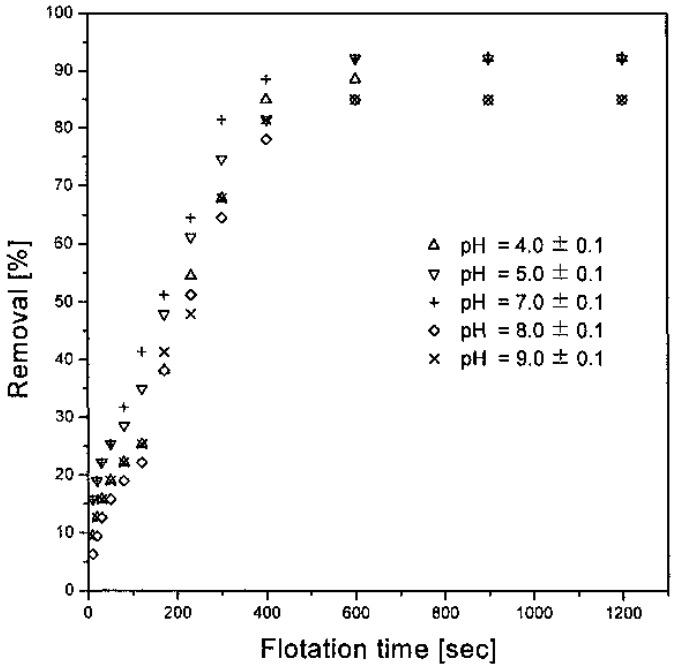

FIG. 11 Effects of pH on the removal of *Chlorella* sp. when CTAB was used as the collector. [CTAB] = 40 mg/L, I = 0.05 M $NaNO_3$, initial cell concentration (C_0) = 6.8×10^5 cells/mL, air flow rate = 114 mL/min.

Similarly, it is the electrostatic attraction between cationic CTAB and negatively charged algal cells (pH > 3.0) that made the removal of cells possible, regardless of changes in pH values (Fig. 11). Satisfactory flotation efficiency (85 to 92%) was observed in the 4.0 to 9.0 pH range.

Effects of Ionic Strength

The effects of ionic strength on flotation at pH 8.0 ± 0.1 were investigated. The results are shown in Fig. 12. It was found that flotation was significantly affected by ionic strength. Good (90–92%) removal of algal cells was found in dilute aqueous solutions of $NaNO_3$ ($\leq$0.1 M). However, as the ionic strength was increased to 0.2 M, the removal efficiency decreased to 32%. It has been indicated that flotation efficiency decreases with an increasing concentration of inert salt in solution (1, 2). This is due to the decrease in ζ-potential and the weakened electrostatic interaction between collector ions and solid surfaces. We also observed during experiments that, under high ionic strength, gas bubbles were larger and tended to rupture more easily as they flowed upward to the air–water interface. The flotation efficiency under such conditions can be improved by increasing the collector concentration or by lowering the pH (1, 2).

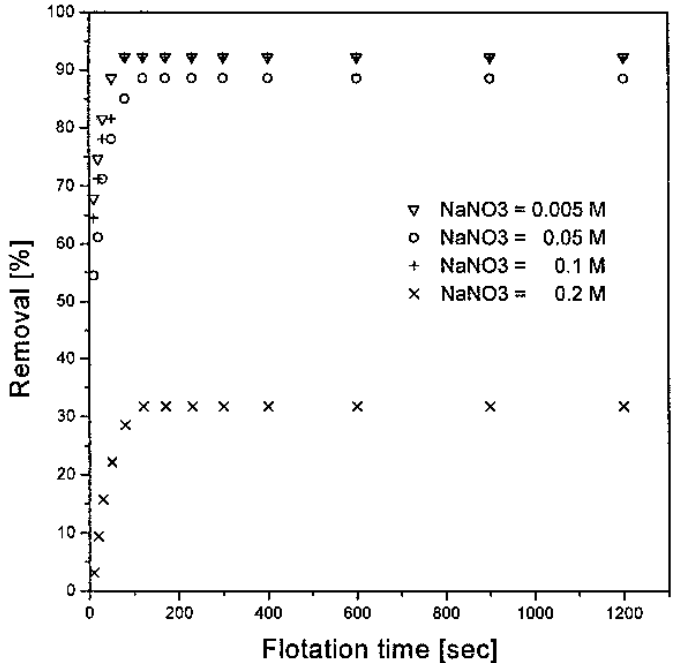

FIG. 12 Effects of ionic strength on the removal of *Chlorella* sp. when SDS was used as the collector. [Chitosan] = 10 mg/L, [SDS] = 20 mg/L, pH 8.0 ± 0.1, I = 0.05 M $NaNO_3$, initial cell concentration (C_0) = 6.8×10^5 cells/mL, air flow rate = 114 mL/min.

Comparison of DiAF with Coagulation-Flocculation

Flotation techniques have been shown to possess certain advantages over conventional processes in the separation of algal cells (13). While some reaction parameters were different in DiAF and coagulation–flocculation processes of the current work, it is difficult to conduct an in-depth comparison. In addition, that was not the major objective of our work. However, the results indicated that DiAF could achieve comparable algal cell separation efficiency with a similar chemical dose. It is suggested that experiments can be carried out in future work to compare the two processes.

CONCLUSION

This study demonstrates that *Chlorella* sp. can be effectively removed from water through the dispersed air flotation technique. The cationic collector CTAB is more effective than the anionic SDS. However, upon the addition of chitosan, the performance of SDS as the collector is significantly improved. Flotation efficiency is satisfactory in the 5.0 to 8.0 pH range. The electrostatic interactions between collector and cell surfaces play a key role in determining

the flotation efficiency. Some important parameters affecting the flotation process, such as pH values, ionic strength, and air flow rate, were also investigated.

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