

Comparison between the removal of live and dead algae using froth flotation

W. Phoochinda, D. A. White[†] and B. J. Briscoe

ABSTRACT

Froth flotation separation was used to remove *Scenedesmus quadricauda*, an algae species which is commonly found in lakes and reservoirs, from an aqueous suspension as a function of several variables. The removal efficiencies of both live and dead algae (thermally terminated) using the froth flotation method as a function of the introduction of two types of surfactant, aeration rates, pH and temperature of operation are compared. The characteristics of the algal suspension such as the zeta potential of the algae and the surface tension measurements are also reported. Cetyltrimethylammonium bromide (CTAB), a cationic surfactant species, gave a comparatively good algal removal efficiency while sodium dodecylsulphate (SDS), an anionic surfactant species, gave, in comparison, a relatively poor removal efficiency. By decreasing the ambient pH values of the algal suspensions, the SDS gave an increasingly better extent of separation. As the aeration rates were increased, the removal efficiencies of both the live and the dead algae were increased slightly whereas when the temperature increased from 20 to 40°C, the removal rates were, more or less, unchanged. In most cases, the removal of the dead algae was greater than that of the live algae. The surface tension of the dead algal suspensions with CTAB was slightly lower than that of the live algal suspensions with CTAB at comparable concentrations, which may facilitate the removal of the dead algae.

Key words | algae, froth flotation, surfactants, water treatment, zeta potential

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INTRODUCTION

Planktonic algae are small plant organisms that range in form from small single and circular shapes to large colonies. Some of them have physical spines to resist sedimentation. Some of them can also 'swim' actively using flagella. The eutrophication of lakes and rivers by nutrient wastes may result in the formation of massive algal blooms. The presence of such algal blooms may cause a significant shortening of effective filtration cycles and an increase in the amounts of coagulants that are required, which in turn increases the volume of sludge to be disposed. A range of methods has been devised in order to reduce the presence of such algae. In water treatment, flocculation, filtration and sedimentation have long been used to remove such algae.

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Coagulation and flocculation processes have long been applied to remove colloidal particles from water. Colloidal particles in water are usually negatively charged and so there are net repulsive forces between each particle. Chemical coagulants are usually applied to destabilize these particles causing the formation of aggregates which can then be easily separated from water. Coagulation and flocculation were also investigated to remove the algae *Scenedesmus quadricauda* from water. The commercial cationic polyelectrolytes and ferric salts were used separately as a coagulant to produce the algal flocs and as a consequence the algal cells were removed from water. The effectiveness of the coagulants was compared. One mg l⁻¹ of the commercial cationic polyelectrolyte was chosen as the optimum because it gave the highest turbidity removal and

produced less sludge compared with the ferric salts and the other polyelectrolytes (Phoochinda & White 2003).

Coagulation and flocculation of algae species may differ from that of other colloids and suspended matters as algae are living organisms. Their size and shape change during their growth. Photosynthesis and respiration can also affect the coagulation and flocculation processes. In addition, some types of algae such as *S. quadricauda* have spines which could influence flocculation efficiency. After the coagulation and flocculation processes, a further process is sometimes required to separate the flocs from water and therefore results in an additional cost. Other processes such as flotation and filtration have been studied to remove algae from water. These processes can be usually used on their own to remove the algae, and commonly give high removal efficiency; therefore further removal processes are not required. In this current study, froth flotation was therefore of particular interest.

Flotation is a promising process in water treatment as a removal efficiency of up to 90% can be obtained. The process has been extensively applied in mineral separation over many years. It has also been used in many applications such as oil/water separation and removal of microorganisms (Kitchener 1984). The flotation process can be classified into three distinct types, with respect to the different methods of producing the air bubbles: dispersed air flotation, dissolved air flotation and electrolytic flotation (Zabel 1984); the central mechanism of attachment is however the same. Dispersed air flotation tends to produce large bubbles (greater than 1 mm), and surfactants are therefore commonly added to decrease the size and the coalescence of these bubbles. This process is also called froth flotation. In dissolved air flotation, air is dissolved in water at a high pressure and then bubbles are produced by the reduction of the pressure of a water stream saturated with air. The size of the bubbles is generally smaller than 0.1 mm. Electrolytic flotation involves applying a current to split water molecules. Bubbles of H₂ are formed at the cathode and bubbles of O₂ are formed at the anode. The bubble diameters usually range from 22 to 50 µm.

There are two generally adopted methods to disinfect microorganisms: 1) using chemical agents such as ozone, chlorine and chlorine dioxide and 2) using non-chemical agents (energy-related) such as ultraviolet radiation and

gamma radiation (Montgomery 1985). In many conventional water treatment processes, ozonation and chlorination are frequently applied prior to conventional processes such as sedimentation, filtration and flotation. This is because ozone and chlorine have not only an ability to disinfect or kill microorganisms like bacteria and algae but they can also enhance the performances of the conventional processes used for the removal of algae. Ozone and chlorine act as an oxidant of constituent elements of cell walls before penetrating inside microorganisms and oxidizing certain essential components (e.g. enzymes, proteins, DNA and RNA; Legeron 1984). As a result the microorganisms are disrupted and inactivated and reproduction ceases. The oxidation potential of ozone is higher than chlorine but chlorine can persist in a water distribution system for a longer time (Montgomery 1985).

Johnson *et al.* (1995) investigated a dissolved air flotation (DAF) method for treating a Boston low-turbidity surface water supply and the occasional algal blooms of *Synura* spp. They compared its performance with that of inline filtration, direct filtration and contact adsorption clarification. The performance of all these processes was improved when ozonation was applied. Moreover, the DAF method performed much better in reducing the particle population especially when used in conjunction with ozone treatment. Montiel & Welte (1998) investigated the removal of algae (diatoms and green algae) using a preozonation step coupled with subsequent flotation and filtration. A simple treatment with a low dose of ferric chloride allowed 75% of the green algae to be removed by filtration, whereas the addition of an ozone pretreatment allowed 95% to be removed. This implies that dead algae are more easily removed than live species by this procedure.

Schofield (2001) studied the use of DAF for drinking water production and found that the DAF method was more efficient in removing the algae than other conventional processes at the higher values of hydraulic loading. An algal removal of 50–80% was normally achieved, depending upon the size and the density of the algae; the relative density of the current algae is close to unity. An addition of ozone, or chlorine, as a pretreatment prior to flotation was found to assist the removal of some algal species, which were otherwise difficult to remove. Ferguson *et al.* (1995) compared the direct filtration (with and without

pre-ozonation) with the direct filtration and DAF methods for the production of low turbidity water and the control of algae. They found that, when using ozone prior to direct filtration, the rate of clear water production was approximately double that without an ozone treatment and that the filters could be used for longer periods. They also found that the use of a DAF method as a pretreatment, prior to filtration, gave many advantages such as allowing a higher filtration rate, greater water production and the creation of lower volumes of sludge.

The removal of algae using dispersed air flotation (froth flotation) has also been investigated. Surfactants usually play a key role in the removal efficiencies. [Chen *et al.* \(1998\)](#) and [Liu *et al.* \(1999\)](#) found that CTAB (cetyltrimethylammonium bromide, a cationic surfactant) was an effective collector to remove algae (*Scenedesmus quadricauda* and *Chlorella* sp.) from water whereas SDS (sodium dodecylsulphate, an anionic surfactant) gave, by comparison, very poor algal removal. Chitosan, a positively charged coagulant, was used to modify the electrical properties of the algal surfaces rendering them positively charged and thus making possible the adsorption of SDS onto the cell surfaces.

[Phoochinda & White \(2003\)](#) studied the removal of live algae as a function of the surfactant type, the aeration rate, the pH and the temperature of operation using froth flotation. The degree of the water loss in the sludge using one-stage froth flotation and that using a two-stage froth flotation method were investigated. It was found that the amount of water removed with the algal phase (sludge) was significantly reduced by using the two-stage flotation method. In addition, it was shown that the introduction of CTAB promoted a good algal removal rate while the addition of SDS gave, in comparison, a relatively poor removal efficiency. By decreasing the ambient pH, the SDS gave a relatively better removal performance.

In a typical algal colony, there will invariably be a mixture of both 'live' and 'dead' algae especially in winter months, owing to lower temperatures and levels of sunlight which provide lower levels of photosynthesis. Live and dead algae appear to have rather different surface characteristics, which will naturally lead to different removal efficiencies, particularly in froth flotation methods where the hydrophobicity of the particle is a key influence in the efficiency of the air bubble/particle attachment process. This current

paper focuses mainly on a comparison of the removal efficiencies between the live and dead algae species, recognizing that they have rather different surface chemical features such as the natural charges on their surfaces. The froth flotation process was used, with an addition of two surfactants separately, CTAB and SDS, to effect the separation. The associated variables such as the type of surfactant, the ambient pH of the algal suspension, the aeration rates and the temperature were also considered.

The algae *S. quadricauda* was chosen since it is generally found in natural water such as lakes and reservoirs and it is one of the 20 most frequently observed algal species in Thames Water ([Ta & Woodward 1995](#)). In addition, this species is easily cultivated and its biology is rather well understood. It has been suggested by [Nurdoğan & Oswald \(1996\)](#) that flotation, one of the alternative low-cost separation processes, could be used to effectively remove this algal type. The current paper also describes the use of froth flotation to separate both live and dead algae from water. In order to convey the necessary surface hydrophobicity to the algae, this process invariably requires the addition of relatively low concentrations of surfactants into the influent stream. These surfactants will naturally have some residual effects if used in potable water treatment and are currently limited to a maximum admissible concentration. An acceptable level of a foaming agent or surfactant in potable water is 0.5 mg l^{-1} ([Kawamura 2000](#)). Nevertheless, it has been shown that froth flotation using surfactants is usefully applicable to the treatment of wastewater for both industrial and agricultural use.

Images of the current live and dead algae are shown in [Figure 1](#). Usually, aggressive chemicals like ozone and chlorine are added to disinfect such microorganisms. In this work, these chemicals could not be used as they would also extensively oxidize the ambient surfactants, which were used to promote the froth flotation. The dead algae species were thus obtained by boiling the live algae in water for circa 20 min. This is certainly not a practical method of sterilizing large quantities of water. However it was used in this case as it killed the algae without the addition of potentially disruptive chemicals. It is thought that ozone and chlorine have broadly similar effects to heat (thermally induced) since they all increase the permeability of, and perhaps disrupt, the cell membrane. These make the algal

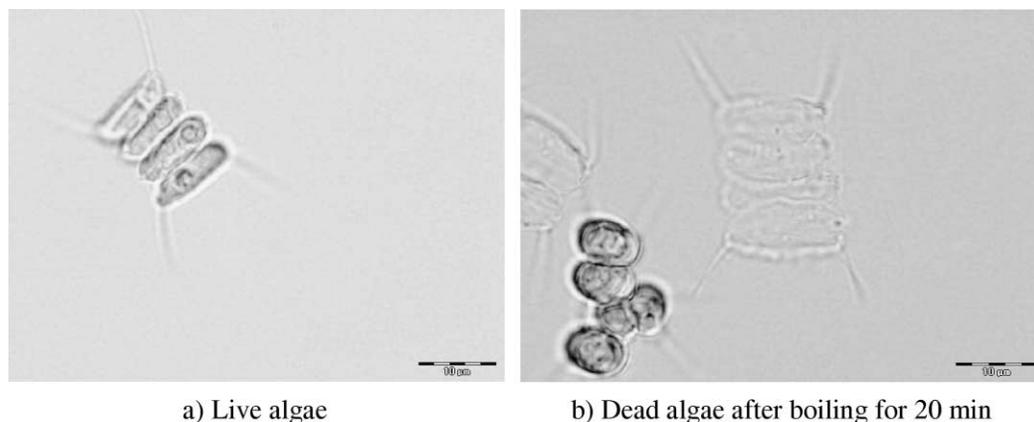


Figure 1 | Comparison between the appearance of the live and dead algae of *Scenedesmus quadricauda* obtained using a light microscope.

cells release some of their cell contents. It was found that after boiling for about 20 min, most of the algae were dead and their primary structures were irreversibly damaged as is illustrated in [Figure 1](#). There was invariably a mix of the algae that were completely damaged and some algae that were just partially broken and their green pigments remained, as is shown in [Figure 1\(b\)](#).

The 'living' algal cells are naturally negatively charged (-24.7 mV) in neutral aqueous media and their mean diameter and specific surface area are approximately $14\ \mu\text{m}$ and $0.5\text{ m}^2\text{ g}^{-1}$, respectively, as characterized by the zeta potential and the particle size measurements.

THE SUGGESTED MECHANISM OF ALGAL REMOVAL

The principle of the method is that the cationic (positively charged) surfactant molecules strongly adsorb onto the negatively charged algal surfaces by means of a charge neutralization process. This imparts a hydrophobicity to the algae surfaces and thus allows the air bubbles which are subsequently blown through the suspension to attach to the surface of the cells and thus carry the cells to the surface. There they form a froth zone that can be readily removed; the process is shown schematically in [Figure 2](#). Zeta potential measurements are described below as a function of the pH of the algae solution. It is possible, using these data and adopting some simplifying assumptions, to compute the extent of the coverage of the surfactant on the algae surface and to estimate the apparent interfacial

orientation of the molecules. These calculations indicate a close packed coverage with a normal orientation of the surfactant molecule with respect to the alga surface; [Figure 2\(c\)](#) shows a pictorial view and the estimated surfactant concentration of $c. 1.6 \times 10^9$ molecules per cell.

In order to separate the algae from water, the froth flotation process requires a finite contact angle (between the algal surface and the air bubble as is shown in [Figure 2\(d\)](#)) by means of which algae become attached to air bubbles and so are carried up into the froth layer by the forces of surface tension and gravity ([Kitchener 1984](#)).

MATERIALS, APPARATUS AND METHOD

The chemicals used in this study were SDS with 99% purity, supplied by BDH (UK) and CTAB with 99.5% purity obtained from Sigma-Aldrich (UK). A froth flotation process was carried out, in a batch mode, using the two types of surfactants: SDS (anionic) and CTAB (cationic) at concentrations ranging from 25 to 150 mg l^{-1} in aqueous solution. The pH of the system was adjusted using 1 M HCl and NaOH and measured using a pH meter (Corning 240, UK). A bench-scale flotation column was constructed from glass with an inner diameter of 40 mm and a height of 300 mm. Air was supplied using an air cylinder and the flow rate of air was measured using a rotameter. The air was passed through a sintered disc with a pore size number of 4 ($11\text{--}16\ \mu\text{m}$) at the bottom of the column ([Figure 3](#)).

To obtain the algal concentration of $10^5\text{ cells ml}^{-1}$, algal cells (*S. quadricauda*) and algal enrichment media (K10)

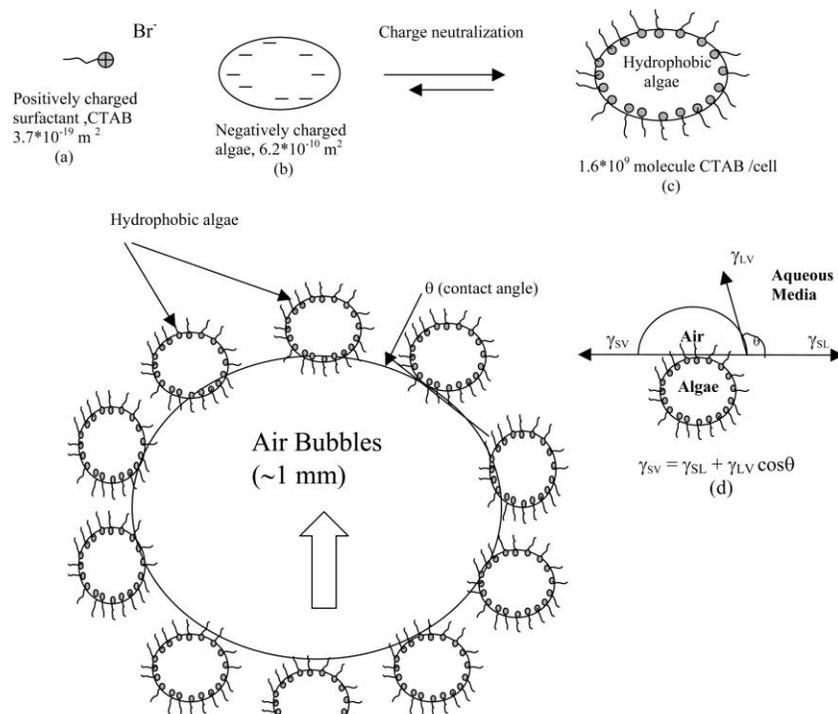


Figure 2 | Schematic diagram of the suggested mechanism of froth flotation (not to scale). (a) The head group area of the CTAB molecule is about $3.7 \times 10^{-19} \text{ m}^2$ (Fan *et al.* 1997); (b) the surface area of the algal cell is $6.2 \times 10^{-10} \text{ m}^2$; (c) adsorption of 1.6×10^9 CTAB molecules per cell of algae (a close packed coverage); (d) schematic diagram of contact angle.

were obtained from Sciento (Manchester, UK). The algal cells were mixed with the media and cultivated in Erlenmeyer flask under fluorescent light at approximately 25°C for 18 h each day for 2 weeks. A calibration curve between the number of algal cells and the absorbance was derived using a haemocytometer (Improved Neubauer, 0.1 mm depth) and a UV/VIS spectrophotometer (Jenway 6300 spectrophotometer), respectively. The spectrophotometer was used to measure the absorbance from the

amount of light at a specified wavelength (500 nm) passing through the algal suspension. The calibration curve was frequently checked. To determine the extent of the algal removal the absorbance measurement was undertaken for the treated water and the collected sample. The number of the algal cells removed was then calculated.

A concentration of approximately $10^5 \text{ cells ml}^{-1}$ of the algae was used in all experiments to be described. Firstly, the flow rate of air was adjusted to the required value and then 200 ml of the algae suspended in either SDS or CTAB solution was transferred into the column. Samples were then collected at time intervals of 3, 5, 10, 15 and 20 min. The period of time required, in each experiment, to remove this initial quantity of the algae was approximately 20 min. In order to study the effects of temperature, the algal suspension was mixed with an aqueous CTAB concentration of 100 mg l^{-1} . The mix was then placed in an icebox or a water bath until it reached the desired temperature. After that it was transferred into the flotation column. The temperature of the algal suspension was reasonably constant and varied by only 1°C during the experimental period.

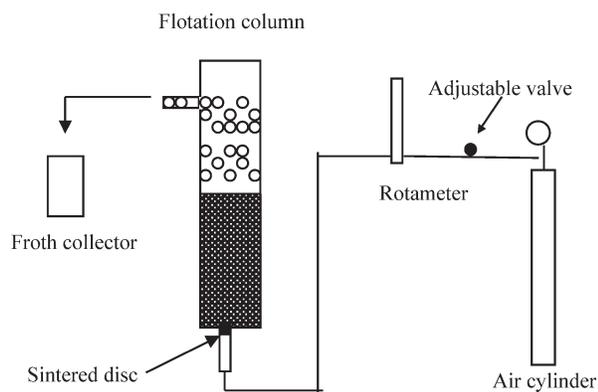


Figure 3 | Schematic diagram of the apparatus.

The zeta potential, which is the electrical potential at the location of the shear plane between a moving particle and the surrounding liquid, was used to measure the net charge on the particle surfaces. A Zeta Master (Malvern Instruments, UK) was used in this study. The sample under investigation was injected into an electrophoresis cell and a known field gradient was applied. The algal sample was then illuminated by cross-focused laser beams. The zeta potential of the systems of the live and dead algae in distilled water, the live algae in 100 mg l^{-1} of CTAB and 100 mg l^{-1} of SDS separately as a function of pH were monitored.

The surface tension of the algae suspended in CTAB solutions was also investigated using Tensiometer K10 (KRÜSS, Germany). The Wilhelmy Plate (Myers 1999) was used in this experiment. The size of the algal cells was measured using a light scattering unit, Mastersizer 2000 (Malvern Instruments, UK).

RESULTS AND DISCUSSION

Solution and algal characterizations

Zeta potential measurements

The results, shown in Figure 4, indicate that the zeta potentials of both the live and the dead algae change significantly with the change in the ambient pH. As the pH values are increased, the zeta potential decreases due to the increase in the OH^- activity and the corresponding adsorption of the OH^- groups onto the algal cells. The zeta potential reached a value of zero at a pH of

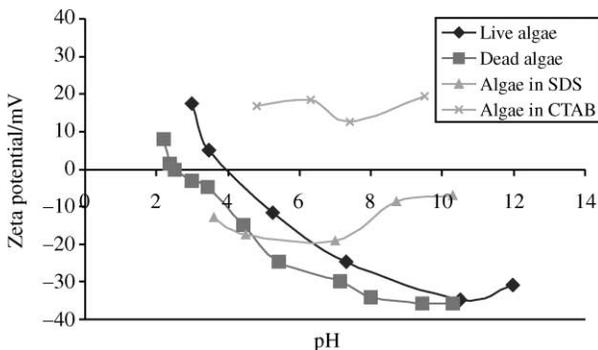


Figure 4 | The zeta potential of the algae as a function of different pH values for four systems: the live and dead algae in distilled water, the live algae in 100 mg l^{-1} of CTAB and 100 mg l^{-1} of SDS separately.

approximately 4 for the ‘live’ algae and a pH of approximately 2.5 for the thermally induced ‘dead’ algae. The results, given in Figure 4, show that the dead algal cells have a greater propensity to acquire a negative surface charge than the live cells. This observation is consistent with the lower point of zero charge (pzc) of the dead algae compared with that of the corresponding live algae.

The more positive value of the surface potential of the living cells, compared with that of the non living cells, is probably due to the fact that living plant cells actively secrete hydrogen ions and, as a result, their surfaces are thus more relatively positive. Most plant cells have a membrane potential of at least -120 mV (Purves *et al.* 1998). Due to the difference in electric potential, cations such as K^+ are thus drawn in passively along the voltage gradient via selective ion channels, whereas anions such as Cl^- enter by co-transport with the protons. The transmembrane potential collapses when the cells are killed, leading to more negative values of the surface charges. The zeta potential of the live algae in the CTAB and SDS systems was also investigated and the results show that the zeta potential of the algae in the CTAB system was positive whereas that in SDS system was negative at all the pH values investigated. This suggests that the CTAB and SDS molecules adsorbed directly onto the surface of the algal cells; it was mentioned above that the current data suggest a ‘closed packed’ normal coverage of the CTAB molecules on the algae at the range of aqueous concentrations investigated.

Surface tension

The surface tension of the live algal suspension ($10^5 \text{ cells ml}^{-1}$) and the dead algal suspension in a CTAB solution were also compared. A CTAB concentration of 100 mg l^{-1} , ambient pH of 7.8 and temperature of 25°C were used. The results reported in Figure 5 show that the variables of the surface tension of the live and dead suspension as a function of CTAB concentrations were almost the same. Those of the dead suspensions were slightly lower, perhaps because when the cells were killed their membranes were damaged and surface-active cell contents such as phospholipids are released. As a result it may then be marginally easier for the air bubbles to attach to the dead algae and carry them to the surface.

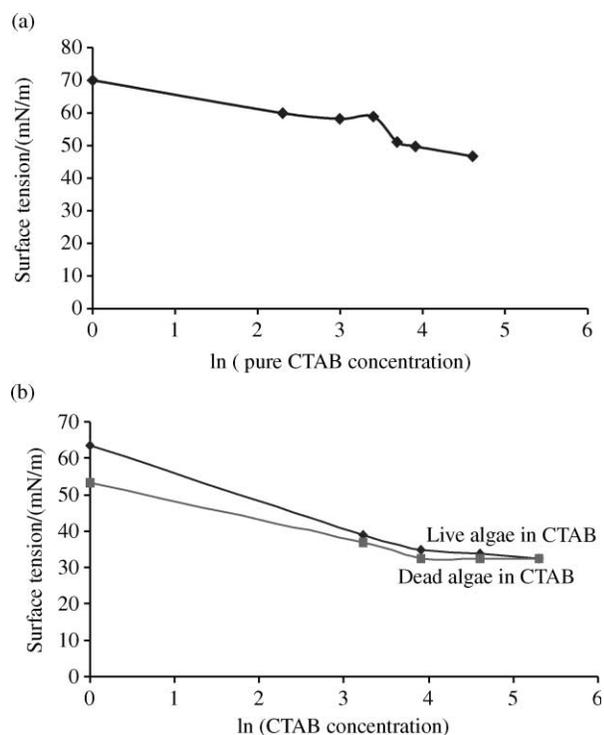


Figure 5 | The comparison of the surface tension of live and non-living algae as a function of the aqueous CTAB concentration, at 25°C and with an algal concentration of 10^5 cells ml^{-1} .

The critical micelle concentration (CMC) of pure CTAB is $9.2 \times 10^{-4} \text{ mol l}^{-1}$ (335.5 mg l^{-1} ; Mw of CTAB is 364.5) and the surface tension at CMC is 32 mN m^{-1} (Myers 1999). The surface tension for the algal systems remained constant at above the CMC. This might be because algae themselves might also release some surface active cell contents as is evident from the surface tension of the pure living and non living algal suspensions (without CTAB) of 64 mN m^{-1} and 53 mN m^{-1} , respectively. Moreover, the surface tension of the non-living algae was notably lower than that of the living one because when the cell membrane was disrupted, more surface active substances were released. In addition, the algal enrichment media composed of salts such as NaNO_3 might not have been consumed completely by the algae and therefore these remaining salts probably lower CMC value. For instance, an addition of 0.1 M NaCl to a system of ionic surfactant can cause a reduction of the surface tension and the CMC from approximately 10^{-2} to $10^{-3} \text{ mole l}^{-1}$ (Clint 1992). Figure 5(a) shows the surface tension of an aqueous pure CTAB solution as a function of the concentration obtained from this study.

Flotation studies

Effects of CTAB and SDS concentrations on the extent of the algal removal

The extent of the removal of the live and dead algae was significantly improved as the CTAB concentrations were increased from 25 to 100 mg l^{-1} as is shown in Figure 6. The results indicate that up to 93% removal of the dead algae was achieved compared with 85% for the live algae when using a 100 mg l^{-1} CTAB suspension medium. This may arise because the surface charges on the dead algae are relatively more negative, compared with the live species, which results in a relatively higher extent of adsorption of the CTAB species onto the algal surfaces. When the CTAB concentration was increased above 100 mg l^{-1} the removal efficiencies clearly decreased. This may occur because there were excess amounts of CTAB introduced into the system resulting in a decrease in the contact angle; Fan *et al.* (1997) described a process where reverse orientation and bilayer coverage may occur at high surfactant concentrations. As a consequence, the algal cells become hydrophilic and are not attached to the air bubbles.

The removal efficiencies of the live and dead algae, using SDS solutions, are shown in Figure 6. Compared with CTAB solutions, the SDS solutions generally gave rather low algal removal efficiencies, regardless of whether the cells were alive or dead. It is likely that the SDS gave a relatively poor removal efficiency as the surfactant was negatively charged and thus did not effectively adsorb onto the negatively charged cell surfaces. However, the SDS may

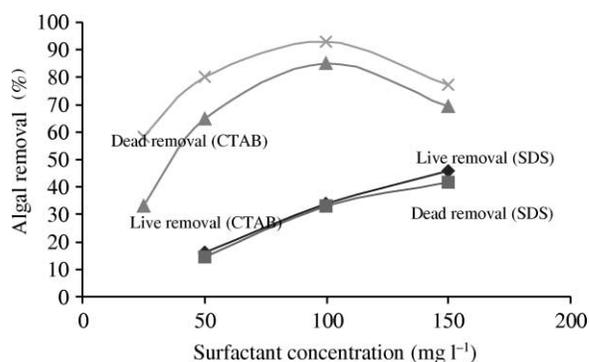


Figure 6 | The extent of algae removal (as a percentage) from an initial algal suspension of 10^5 cells ml^{-1} as a function of different concentrations of CTAB and SDS, a pH of 7.8 and an aeration rate of $0.05 \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$.

still have some other beneficial effects since charge neutralization and the associated hydrophobic action may not be the only factor enhancing the algal removal process. There might also be a change in the surface hydrophobicity of the cells since the SDS may damage the cell membranes. The algae may then release some of the hydrophobic cell contents into the cell walls and so facilitate the attachment of the flotation bubbles. Furthermore, SDS will lower the surface tension of the whole system and this would decrease the size of air bubbles and also improve the stability of the froth and so might enhance flotation.

Effects of aeration rates

The rate of the removal of the live and dead algae naturally increased as the aeration rates were increased from 2 to $9 \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ and then the extent of the removal was more or less constant (Figure 7). This was probably due to the fact that an increase of the aeration rates simply causes an increase in the particle–air bubble attachment rates; eventually there is an excess of air bubbles to attach the fixed particle population resulting in a constant removal rate. Again, the removal extents of the dead algae were distinctly higher than those of the corresponding live algae.

Effects of the pH variation

The pH of the algal suspension was adjusted in order to alter the net surface charge on the algal surfaces and thus alter the extent of the surfactant adsorption onto the algal cells and the consequent extent of their hydrophobic and

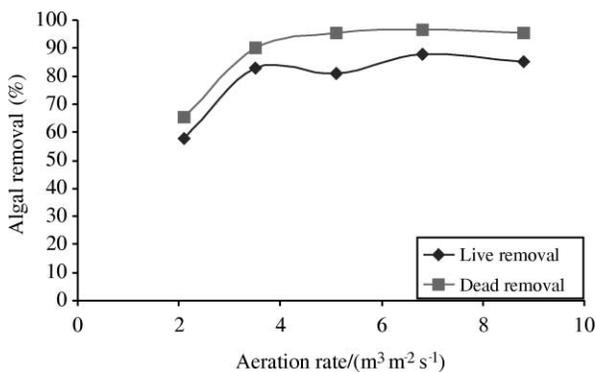


Figure 7 | The extent of algae removal (as a percentage) from an initial algae suspension of $10^5 \text{ cells ml}^{-1}$ as a function of different aeration rates, a CTAB concentration of 100 mg l^{-1} , a pH of 7.8 and temperature of 20°C .

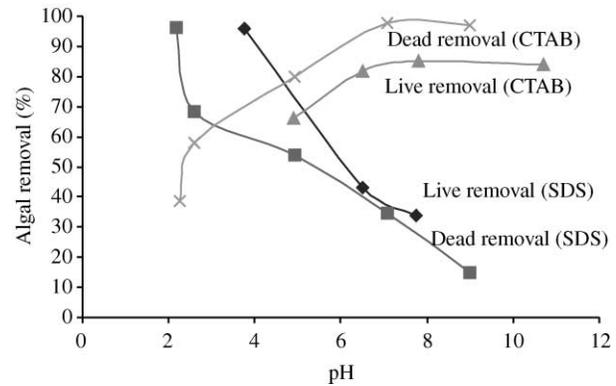


Figure 8 | The extent of algae removal (as a percentage) from an initial algae suspension of $10^5 \text{ cells ml}^{-1}$ as a function of different pH values, with CTAB and SDS concentration of 100 mg l^{-1} ; an aeration rate of $0.05 \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ and temperature of 20°C .

thus the ultimate wetting behaviour. Figure 8 shows the comparison of the removal of the live and dead algae using both the CTAB and SDS surfactant solutions at different pH conditions. The results for the CTAB solutions show that the highest removal rates of the live and dead algae were achieved at a pH of approximately 7.8, near to the natural pH of the suspension. When the pH of the algal suspension was reduced, the extent of the algal removal decreased. As the pH of the algal suspension was now below the pzc (point of zero charge), the algal cells were more positively charged under these conditions. A repulsive force, between CTAB molecules and the algal cells, was produced resulting in a lower level of net surfactant adsorption and confirmed hydrophobicity and thus a relatively lower level of cell removal. A large increase in the extent of dead algal removal was obtained as the pH of the algal suspension was increased above the value corresponding to the pzc. However, the removal levels of the live and dead algae at the basic pH range were seen to be little different. Better removal efficiencies were again generally obtained for the dead algae species.

In contrast to the results for the CTAB solution, a change of ambient pH significantly affected the removal of the algae when SDS was used as a surfactant. As the algal surface charges were invariably negative, a reduction of pH below the pzc renders the charges of the algal surface positive. It therefore can be seen from Figure 8 that at a pH of the algal suspension below the pzc (pH of 4 for the live algae and pH of 2.5 for the dead algae), the removal levels of the algae were markedly improved for the anionic surfac-

tant (SDS). On the other hand, at a pH value above the pzc, the removal levels were comparatively poor due to the generation of repulsive forces between the negatively charged algae and the anionic SDS leading to a poor degree of adsorption and conferred hydrophobicity. The extent of the removal further decreased with the further increased in pH as is shown in Figure 8. In this study, better removal efficiencies using the live algae were observed compared with those of the dead algae as a result of the smaller negative charges of the live algae. This resulted in a lower repulsive force and hence a greater degree of adsorption and corresponding conferred particle hydrophobicity.

Effects of temperature on the flotation process

The current results may be interpreted based on the contributions from two specific processes. Firstly, the rate of particle–surfactant–bubble collisions and the rising velocity of the bubbles carrying the particles play important roles that cause the algae removal at 5°C to be lower than those at the higher temperatures: both are decreased as the temperature decreases roughly in proportion to the change in the density and viscosity. Secondly, the effects of temperatures on the system will shift of the pzc and thus might cause a reduction in the level of the surface charge as the temperature increased resulting in a decrease in adsorption (Fuerstenau & Ronald 1991). It can be seen that the extent of algae removal at 20°C was slightly higher than that obtained at 30 and 40°C for both types of algae (Figure 9).

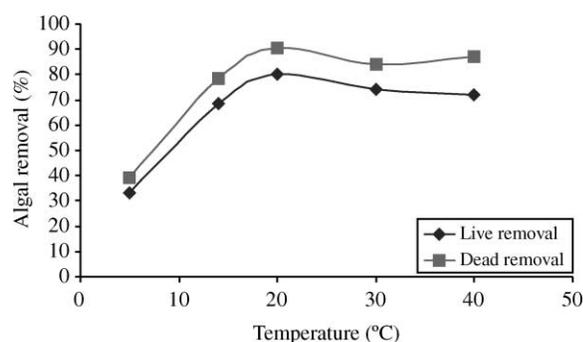


Figure 9 | The extent of algae removal (as a percentage) from an initial algae suspension of 10^5 cells ml^{-1} as a function of temperature, CTAB concentration of 100 mg l^{-1} , a pH of 7.8 and aeration rate of $0.05 \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$.

Residue of CTAB

The quantities of CTAB remaining in the treated water were also determined using a total organic carbon analyser (TOC 5000, Shimadzu Scientific Instruments). The liquid sample was injected into a furnace where the water was evaporated and the organic carbons catalytically burnt to produce carbon dioxide. The carbon dioxide was then carried by the stream of oxygen and was detected and quantified by an infrared analyser.

The corresponding amounts of CTAB in the treated water were determined and are shown in Table 1. The results show that there was no detection level of CTAB remaining in the treated water when concentrations of CTAB of $25\text{--}100 \text{ mg l}^{-1}$ were used in the flotation process while approximately 40 mg l^{-1} of CTAB remained in the treated water when a CTAB concentration of 150 mg l^{-1} was used. As mentioned above, an acceptable level of a foaming agent or surfactant in potable water is 0.5 mg l^{-1} (Kawamura 2000). This implies that when CTAB concentrations of $25\text{--}100 \text{ mg l}^{-1}$ were used the treated water could be safely used for any purpose.

CONCLUSIONS

A comparison of the extent of removal of both live and dead algae by a froth flotation method has been examined using *S. quadricauda* (a four-celled green alga). The key factor is the extent of the attachment between air bubbles and algae, which is induced by a natural hydrophobic interaction. The removal process invariably requires the addition of surfactants to the influent stream. An excess of these surfactants usually remains in the water stream and thus needs to be biologically degraded before the treated water is suitable for

Table 1 | The quantities of CTAB remaining in the treated water

Initial CTAB (mg l^{-1})	Residue organic carbon (mg l^{-1})	Residue CTAB (mg l^{-1})
25	0	0
50	0	0
100	0	0
150	25.2	40

potable use; the excess may also reduce the efficiency of the process. The surface charges of the algal cells significantly affect their removal efficiencies. The dead algae (produced here by thermal degradation) have a more net negative surface charge compared with the corresponding live species, and as a result they adsorb cationic (positive) surfactant molecules more easily and are thus removed more effectively than the live algae by froth flotation.

The behaviours of two generic types of surfactants were examined: the positively charged cetyltrimethylammonium bromide (CTAB) and the negatively charged sodium dodecylsulphate (SDS) surface active species. The removal of both live and dead algae was greater with the CTAB solution and also took less time than with the corresponding SDS solution. This was presumably due to the greater electrostatic attraction between the algal surfaces and the oppositely charged CTAB molecules. Increasing the CTAB concentrations also aided algal removal by preventing the coalescence of air bubbles so that more suitably sized bubbles were available for the froth flotation action; it lowers the surface tension. When using CTAB, the removal efficiencies of the dead algae were higher than those of the live algae, possible because the more negatively charged dead cells adsorbed the oppositely charged surfactant more extensively. When a SDS solution (which normally has an adsorbing species charge of a similar sign to that of the cells) was used, the removal efficiencies of the live and dead algae were almost the same. However, reducing the pH of the algal suspension, below the pzc (point of zero charge) now made the cell surfaces positively charged. This resulted in a distinct improvement in algal removal when using SDS as the surfactant, since it was now oppositely charged to the cells and hence bound more readily. By contrast, a similar change of pH of the algal suspension from the natural pH of 7.8 did not improve the algal removal when a CTAB addition was used.

Therefore, the removal efficiencies are critically dependent on the charge densities (and potential) of the algal surfaces (which in turn depends on the pH of the algal suspension) and also on the nature of the surfactant. We may conclude that, when using the CTAB species as the surfactant, the species is naturally much more effective in facilitating the removal of both live and dead algae than the SDS solution at their natural pH values. The SDS

solution only functioned well if there was a correspondingly large reduction of the ambient pH to below the pzc, which was in an extremely acidic condition. Thus the general use of the SDS system cannot be viable since it is quite unrealistic, in water treatment, to release such acidic water into the environment. A further treatment to increase the pH of the water would therefore be required, which would add to the complexity and expense of the process.

An increase of the temperature of the algal suspension from room temperature (20°C) did not increase the algal removal (as might be expected from a reduction in surface charges with increasing temperature) although algal removal did decrease below 20°C because of reduced interaction between the algae and the air bubbles.

In summary, it may be concluded that the use of froth flotation for the separation of algae solutions is a practical method, the basis for which may be rationalised using established principles of colloid science and flotation separation technology. The surface modification or engineering of the algae for flotation purposes naturally necessitates rather different requirements from those for optimal coagulation.

The use of surfactants in froth flotation will naturally have some residual effects if used in potable water treatment and surfactants are currently limited to a maximum admissible concentration of 0.5 mg l⁻¹. Nevertheless, it has been shown that the froth flotation method with the aid of surfactants is usefully applicable to the treatment of wastewater for both industrial and agricultural use. The concentration of CTAB remaining in the treated water was less than 0.5 mg l⁻¹ when the initial CTAB concentrations of 25–100 mg l⁻¹ were used. This showed that the treated water could possibly be used for any purpose.

Although coagulation and flocculation have been widely employed in water treatment and used to remove colloidal particles such as algae, in this context, froth flotation with the aid of surfactants was proved to be the viable method to remove the algae, *S. quadricauda*.

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