SEPARATION OF ALGAE FROM GROWTH MEDIA BY CGA FLOTATION

by

Walter H. Lohse

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APPROVED:

Clifford W. Randall, Chairman

Gregory D. Boardman

Donald L. Michelsen

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(ABSTRACT)

The efficiency of colloidal gas aphron (CGA) flotation for separation of algae from growth media was investigated. Anionic, cationic and non-ionic surfactants were used to generate CGAs. Preliminary batch studies showed that two CGA flotation procedures could be successfully used for algae flotation. CGA flotation without pretreatment of algae was only successful using cationic surfactants. All three types of surfactants yielded promising results while combining CGA flotation with alum flocculation as a pretreatment step. Observed removal efficiencies were above ninty percent for batch applications.

"Pure CGA flotation" was studied in countercurrent continuous flow operations. Satisfactory removal of algae could be achieved even at substantially reduced volume ratios of CGAs to algae solution. However, TOC concentrations increased with higher volume ratios and higher flowrates due to carryover of CGA bubbles and diffusion of surfactant molecules into the bulk solution. The cationic surfactant Cetyl Pyrimidinium Chloride, present at very low concentrations in the raffinate and the froth algae mixture, exhibited biostatic and biocidal properties in the microbial activity test.

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1.0 INTRODUCTION

Algae are simple plants producing oxygen via photosynthesis. They inhabit freshwater, saltwater, barks, soil and rocks.[1] Algae are also a major link in the food chain in reservoirs and lakes. Their concentration is a valuable indicator of the trophic state of a water body, since their growth is mainly limited by the amount of nutrients available. The presence of algae in drinking water reservoirs can result in a number of problems: Production of endotoxins can cause Gastroenteritis in humans. Certain algae species are responsible for taste and odor problems, still others for clogging of filters.[2] Algal blooms are another seasonal phenomenon that can be observed in many lakes, ponds and reservoirs. The blooms are the result of rapid growth triggered by an excess of nutrients. Wastewaters and agricultural runoff, discharged into a water body, are the major sources for phosphates and nitrates, and hence responsible for the formation of algal blooms. Algal blooms can also create problems in shallow wastewater treatment lagoons. Their presence in the effluent increases the organic carbon level, thus reducing the efficiency of the treatment process.

The separation of algae from aqueous systems generally involves difficult and costly operations, but its potential for reclamation of water for reuse and harvesting algae for use as a valuable protein source attracts more and more attention. To operate economically, systems should be designed for combined waste diposal using algae as nutrient removers, reclamation of water and gen-

eration of feed protein.[3] Use and cost effectiveness of most separation processes are limited because of the small size of algae cells, their low specific gravity and the dilute suspensions of algae in their growth media.[4] Quality requirements for the reclaimed water and the feed proteins limit the use of chemicals in various processes.

The use of algae as a supply of protein was first discussed on a world-wide basis in an Algae Mass-Culture Symposium held at Stanford, California in 1952. Mass culture processing of algae and nutritional studies became issues of intensive research, since this method has the prospect to solve the problem of a rapidly increasing world-wide demand for food.[5]

The objective of this thesis was to determine the feasability of a process, called colloidal gas aphron (CGA) flotation to separate algae from their growth media. The project centered on the removal of algae using two flotation methods. An established technique (dissolved air flotation) serves as reference for the removal efficiency of CGA flotation during the initial batch test sequence. Different surfactants as well as different operating conditions were investigated. The results of the CGA flotation batch studies served as the basis for the construction of a continuous flow CGA flotation cell, suitable for scaling up. The continuous flow studies addressed questions like the loss of surfactant in the process effluent, harvesting efficiency, and residual surfactant in the harvested algae. Achieving an understanding of these issues is essential for determining economical applications of this technique.

2.0 LITERATURE REVIEW

2.1 Raw Water Reservoirs

The increasing demand for water requires more use of surface water in highly populated areas of the world. In many cases, raw water storage reservoirs were constructed to provide the necessary water source. The water is usually purified by a number of physical-chemical treatment processes to convert it into drinking water or to use it as groundwater recharge.[6] [7]

Seasonal algae blooms in nutrient-rich water create a number of problems and have occasionally resulted in the closure of sedimentation water treatment plants. Many unit processes, such as microscreening, rapid sand filtration, aeration or slow sand filtration fail to provide required water quality or cannot be operated economically. Addition of a pretreatment step in the form of flocculation and either sedimentation or flotation is obligatory under these cicumstances at present.[6] [7] [8]

2.2 *Oxidation Ponds*

The use of facultative oxidation ponds and lagoons have economic advantages over conventional biological treatment systems, wherever land is relatively inexpensive. These systems can be installed at low capital costs and have minimal operation and maintenance costs. They operate effectively in removing soluble organic matter from wastewater. However, most of these ponds and lagoons support the growth of algae as well. The carryover of algae can result in a significant oxygen demand on receiving waters. Most effluents of oxidation ponds contain up to 50 mg/l (dry weight) of algae and exceed the secondary treatment standards of 30 mg/l of either BOD_5 or Suspended Solids set by EPA.[9] Upgrading the effluent quality will either result in the replacement of existing low cost treatment systems with expensive conventional treatment systems or in the addition of an algae removing treatment step.[12]

2.3 *Algae Cultivation and Application*

Cultivation of microalgae has been a research topic for approximately forty years.[11 12] In these studies, maximum growth of algae is the goal, whereas growth of algae was never intended in the above described water supply cases and, hence, caused problems. The role of algae is similar in all three cases. Photothynthesizing algae grow on inorganic nutrients and carbon dioxide, and give off oxygen. Early studies of algal systems focused, therefore, on groth of algae on pure inorganic media.[13] High energy costs for aeration in conventional wastewater treatment plants and the increasing demand for animal protein are mainly responsible for the renewed interest in algal production technologies. Algal oxidation ponds and High Rate Algal Ponds (HRAP) for treatment of municipal and industrial wastewater were the first designs that made use of algae as the oxygen supplier. Heterotrophic bacteria utilize the oxygen while degrading soluble organic matter into in-

organic nutrients vital to the growth of algae.[14] Municipal, industrial and all kind of agricultural wastes can be treated by algal systems. High Rate Algal Ponds and shallow mixed ponds can yield up to 40 grams of algae per square meter per day under proper conditions. The productivity for a year round operation is reported to be 15 mg m^{-2} day^{-1} in Florida.[15] Similar yields are reported from Israel, Peru, Agypt, Bulgaria and Asia.[13 11 16 17 18] Algae can be used as food products for humans.[19] Algal powder is rich in protein, vitamins and minerals. It also has a good nutritional value for domestic animals.[11] Use of algae in perfumery, cosmetics and pharmaceutical industries is under investigation.[17] Other options are fermentation to methane, and pyrolysis to liquid fuel.[20]

2.4 Separation and Harvesting

The size of an individual algae cell varies from 3 to 15 μm. Algae generally have a slightly higher specific gravity than water and a negative surface charge. Photosynthetic production of oxygen leads to the attachement of minute bubbles on the cell suface and counteracts the gravitational forces on the cell.

A wide variety of physical and physical-chemical processes have been investigated to seperate algae from their growth media. Reliable, technically feasable processes have proven to be difficult and expensive. Consequently, expensive combinations of several concentration steps are typically used to harvest algae.

Two natural separation phenomena have been studied and applied for algae harvesting. Bioflocculation or autoflocculation can be observed in the absence of continuous agitation of the growth media. The separation of the supernatant and the settled algae is difficult and can only be achieved at very small flowrates.[9 21]

Autoflotation was first reported by Van Vuren and Van Duuren[22] in 1965. Autoflotation usually occures in the afternoon. Photothynthetic activity during the day results in the production of oxygen and the attachment of minute oxygen bubbles on the surface of the algal cell. The

buoyancy of the cell increases and the cells concentrate on the surface of the water. This process is not very reliable all by itself.[23] Either dissolved air flotation or electrolysis are generally used to support autoflotation.

A process for algae harvesting, called froth flotation, was reported in 1965. *Chlorella* were removed from their growth media by lowering the pH to 3 and aerating the suspension. No frothing agent was added and it was concluded that the algae cells produced a frothing agent, since a stable froth was observed. The process produced an algae concentration of 5.8% solids. However, the applications of this process are limited, since algal quality suffers at a low pH, unless the pH is rapidly adjusted to pH 7.[24]

Goluek and Oswald[25] studied filtration, flotation, centrifugation, precipitation, ion exchange, passage through a charged zone and ultrasonic vibration. Mohn[26] tested eighteen physical and physical-chemical methods for their applicability and costs with respect to algae harvesting. This investigation covered different types of centifuges, a hydrocyclone, sedimentation and ten different filter techniques. None of the various methods showed a clear superiority over the others. Algal size and quality requirements of the product limit the use of low cost filtration procedures.[26] The only reliable solution to date for large scale continuous applications is a combined process of flocculation, followed by either sedimentation or flotation.[15 23 27] Consequently, most systems use flocculation for primary concentration of algal biomass. Alum is the first choice as a coagulant, but ferrous and ferric sulfate, lime and various electrolytes have also been used with varying success. Lime treatment results in sludge that contains more lime than algae.[28] $FeCL_3$ leaves high residues of Fe^{3+} in the clarified effluent. Autoflotation in combination with flocculation removed 80 to 90% of algal cells and achieved more than 6% solids.[27] Dissolved air flotation and electroflotation also give satisfactory removal.[28] Electroflocculation using alum as flocculant showed promising results in lab scale experiments and is presently being investigated in Israel.[29]

A very different approach to harvesting algae are aquacultures. These systems use filterfeeding fish, shrimp or molusks to convert plant protein into animal protein. Harvested algae can also be fed to oysters during the depuration process. Several applications in China, Asia and the United States demonstrated that these culture systems are very effective and economically

attractive.[12 30] Expensive harvesting procedures are not required, because "live filters" collect algal biomass.

Practical applications of algae cultures are limited for various reasons. Complicated culture techniques, danger of infection and growth of other microorganisms, low yield, expensive harvesting and processing are mainly responsible for a still minor role in the worldwide protein production.[31] Several authors point out that a reliable low cost technique for separating algae from dilute solutions is the key to competitive marketing of algal products.[31 33] Flotation with colloidal gas aphrons has the potential to overcome the economic disadvantages, as initial studies by Honeycutt indicate.[34]

2.5 Colloidal Gas Aphron Flotation

Use of minute gas bubbles in dilute surfactant solutions for industrial applications was first proposed by Sebba in 1971. It was thought to be a gas emulsion system and thus called microfoams.[35] The name was later changed to colloidal gas aphrons (CGAs), when closer investigations showed it was in fact a dispersion of gas in liquid. Colloid refers to the minute bubble size, being sufficiently small to overcome gravitational forces by surface forces. "αφρον" is the Greek word for foam. Colloidal gas aphrons can be best described as very small soap bubbles wih a diameter between 25 and 100 microns. The elastic soap film entrapping the gas consists of several layers. As a result, collision of aphrons will not cause coalescence. Formation of bigger bubbles is based on gas diffusion from a smaller to a bigger bubble. The CGAs have a beaten-eggwhite-like appearance. However, they can be pumped since their viscosity is similar to the viscosity of water.[36]

2.6 CGA Generation and Stability

Generation of CGAs was a tedious and time consuming procedure before the spinning disk generator came into use. Initially, generation was based on a rapid flow of a dilute surfactant solution through a venturi throat with a narrow gas inlet. Gas was supplied with a slightly increased gas pressure.[34] This process required recycling and was not satisfactory for scaling up. The new spinning disk method can produce three liters of CGAs within twenty seconds. When generated with a disk rpm of 6000, CGAs are generally stable for 10 to 15 min. Creaming and disappearance of CGAs can be avoided by permanently agitating the surfactant solution with the spinning disk. The rotations can be reduced to about 3000 rpm for this purpose.[35]

2.7 Mechanism of Flotation

Conventional flotation is based on the successful collision of a particle and a gas filled hole. The particle penetrates the thin monolayer of the frothing agent, provided that the momentum is sufficient.[36] The particle remains attached to the hole and is buoyed to the surface, since energy is required to separate the particle-hole complex.

CGA flotation was investigated by Sebba[36] using a flowthrough cell. The observations showed that graphite particles did not pierce the soap bubble. They were attached to the outside of a single bubble. The precise flotation mechanism remains to be determined.

3.0 METHODS AND MATERIALS

3.1 Overview

This chapter outlines the methods and materials used in the experiments described below. The initial experiments were performed in batch reactors. These experiments were designed to screen different surfactants for their ability to separate algae from their growth media by flotation. Anionic, cationic and non-ionic surfactants were tested with and without pretreatment of the algae solution. The second set of experiments investigated the ability of CGA flotation as a continuous flow process. The final series of experiments focused on the effect of surfactant on the biological activity in the receiving water bodies and the biodegradation of the surfactant discharged.

3.2 *Algae Source and Cultivation*

The algae source for this study was a facultative wastewater treatment pond at Bryce Mountain Resort in Northern Virginia. 25 liters of algae containing water from the effluent of the aerated lagoon were collected on August 5th in a plastic carton and used to innoculate 100 liters of tap water. As algae were removed for experimental purposes an equal volume of media was replaced in each tank. Nutrients were added to provide the vital elements in the concentrations listed in Table 1. The algae were identified as a mixture of *Chlorococus*, *Ankistrodesmus closteriopsis* and *Tetraspora*, all very small green algae. The algae were grown in four aquaria at room temperature (24 $\pm$2 °C) with illumination provided 12 hrs daily by one 75 Watt Plant Grow and Show Lamp and one 20 Watt fluorescent (wide spectrum) lighter, both positioned approximately 30 cm above the top of the aquaria. Different algal concentrations were obtained by collecting settled algae from the bottom of the aquaria and mixing it with regular algae solution.

Table 1. Nutrient Concentrations for Algae Cultivation.

Compound	Concentration mg/l	Element	Resulting Concentration mg/l
		N	4.2
$NaNO_3$	25.5	Na	11.0
$NaHCO_3$	15.0	C	2.1
K_2HPO_4	1.04	K	0.5
		K	0.5
		P	0.2
$MgSO_4 \times 7H_2O$	14.7	S	1.9
$MgCl_2$	5.7	Mg	2.9
$CaCl_2 \times 2H_2O$	4.4	Ca	1.2

3.3 *Measurement of Algal Concentration*

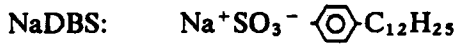
Various methods are used to determine algal concentrations. Cell counts, spectrophotometric and dry weight measurements are generally applied methods. In this study, total suspended solids, *Chlorophyll a* and total organic carbon (TOC) served as indicators of algal biomass. These parameters were quantified by established techniques described in Standard Methods.[38] In addition, pH was measured using a Corning pH meter 610 A. Temperature was monitored on a regular basis. Total suspended solids (TSS) were quantified by filtering 100 ml aliquots of water through preconditioned, preweighed Whatman glass microfibre filters (ø 5.5 cm), oven drying the filters at 103 °C for 12 hrs, then reweighing the filters on a Mettler Balance. For *Chlorophyll a* determinations, 100 ml aliquots were filtered through 2.1 cm glass fiber filters to concentrate cells. Filters were ground in 9 ml of 90% magnesium carbonate saturated, aquaeous acetone and extracted in the dark for 16 hrs. The extracts were filtered and absorbance was recorded at 664 and 750 nm using a Beckman model DU 6 spectrophotometer. *Chlorophyll a* values were corrected for the presence of *Pheophytin a* by acidifying the extracts and recording absorbance at 655 and 750 nm after a 90 sec delay.

For TOC analysis, 50 ml aliquots were blended at high speed for two minutes, 10 ml were then poured into a glass bottle which had a volume of 20 ml. One drop of Phosphoric acid was added and the sample was purged with oxygen for 5 min to remove inorganic carbon dioxide. Samples with high concentrations of surfactants showed a tendency to form a froth and overflow. This resulted in lower TOC values, since organic carbon was removed from the liquid. To prevent this, samples were intermittently purged for 30 sec and then stopped for 30 sec to allow the froth to collapse. The total time of purging was extended to 10 min. Purging was also used to provide a well-mixed sample, before the actual TOC tests were performed using a Dohrman DC-80 Automated Laboratory Total Organic Carbon Analyzer in the furnace mode. Three measurements were made on each sample. To be accepted, values could not differ by more than 1 mg/l. Two additional measurements were performed in case the difference was more than 1 mg/l. The pretreatment

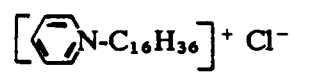
of the samples by blending increased the consistency of the obtained values. Maximum differences were 3 mg/l for values in the range of 15 to 40 mg/l and less then 1 mg/l for samples with less then 15 mg/l.

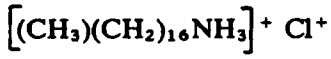
3.4 Surfactants

Anionic, cationic and nonionic surfactants were used to generate CGAs and to screen for their efficiency to remove algae from aqueous systems. Sodium dodecyl benzene sulfonate (NaDBS) represented the anionic group of surfactants. It was used at a concentration of 1.0 g/l to generate CGAs. Anionic surfactants usually contain either sulfonate, sulfate or carboxyl groups. Anionic detergents are commercially very important and represent the major fraction of surfactants produced today.

NaDBS: 

CGAs were also generated using the cationic surfactants Cetyl Pyrimidinium Chloride (CPCl) (0.7 g/l) and Arquad T-50 (2 ml/l). Cationic surfactant are mostly of interest because of their bactericidal and bacteriostatic properties. They are relatively expensive and show poor performance as detergents. Cationic surfactants are biodegradable at low concentrations despite their antibacterial effects.[39] CPCl is available as water soluble powder while Arquad T-50 is an alcohol based liquid.

CPCl: 

Arquad T-50: 

Tergitol 15-S-9 served as the representative of the nonionic group of surfactants. CGAs were generated using a concentration of 2 ml/l. About 25 percent of the surfactants in use are nonionic. They contain hydrophilic groups which do not ionize for the most part in aqueous solutions.[39]

Tergiol 15-S-9: $CH_3\text{-}(CH_2)n\text{-}CH(O\text{-}(CH_2CH_2CH_2O)_9H\ \dagger)\text{-}(CH_2)m\text{-}CH_3$

† where n + m + 3 represents the 15 hydrocarbon group of the hydrophobic head

3.5 CGA Generation

The CGA generator is depicted in Figure 1. A surfactant solution of 500 ml was made up each day using tap water with an average temperature of 22 ± 2 °C and a pH of 7.5. The surfactant solution was transferred into a four-liter metal container. The surface of the surfactant solution was adjusted to cover the spinning disk with 2 cm of liquid. The motor was started and the disk rotated at a speed of 6000 rpm. The resulting CGAs had a diameter of 25 to 100 microns.[37] Figure 2 is a microscopic picture of CGAs generated using the surfactant CPCl.

3.6 CGA Quality Control

Quality checks of the generated CGAs were performed daily, since some surfactants degrade rapidly and change their characteristics. CGA quality was quantified as percentage of air in the CGAs. The generated CGAs were pumped into a graduated cylinder holding 100 ml at a flowrate

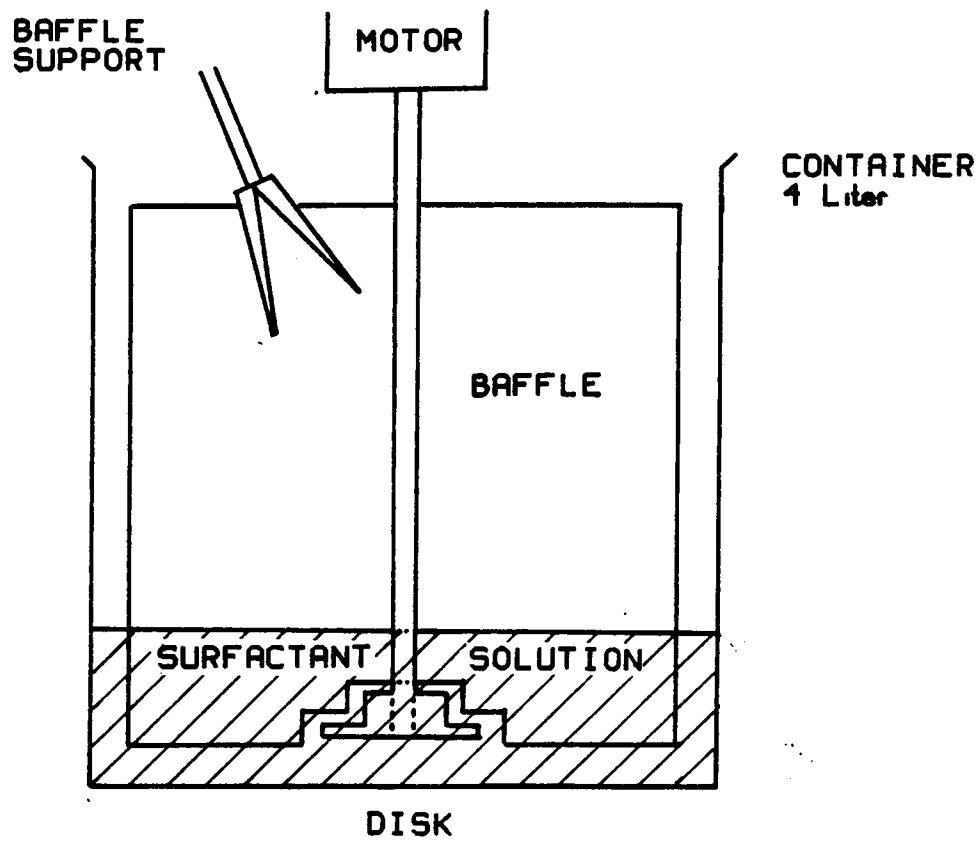


Figure 1. Spinning Disk CGA Generator (not in Operation).

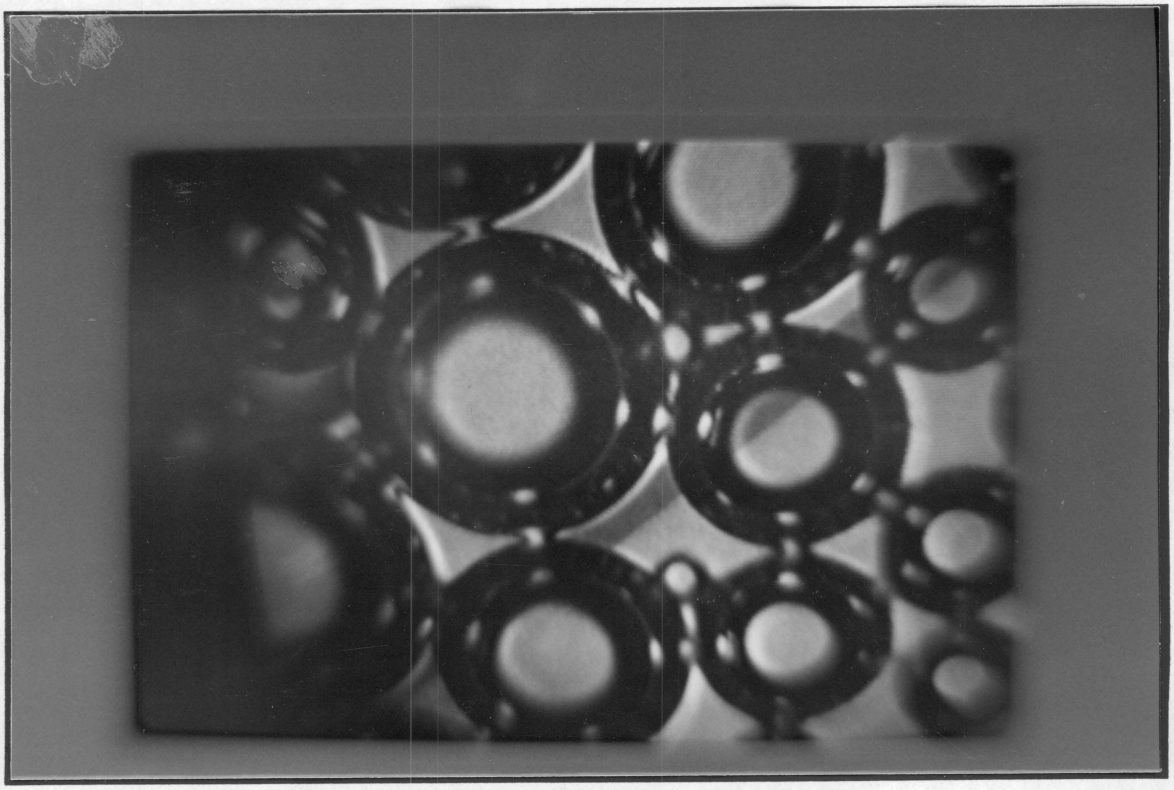


Figure 2. Microscopic Picture of CGAs.

of 100 ml/min. The CGAs were collapsed adding 10 ml of ethanol. Typically, the composition of the CGAs was 65 to 77 percent of air and 23 to 35 percent surfactant solution, respectively. Tergitol 15-S-9 and NaDBS were at the lower end, while CPCl showed values at the upper end of the quality range.

3.7 CGA Batch Test Procedures

Batch tests were used during the first phase of the project to screen different surfactants for their capacity to float algae from their growth media with and without pretreatment of algae. The experimental arrangement for the CGA flotation batch tests is depicted in Figure 3.

3.7.1 General Procedure

One liter of algae solution with a pH of 7.0 to 7.9, and a temperature of 22±2 °C was poured into the glass cylinder. CGAs were generated and pumped through plastic tubing into a plastic one-liter graduated cylinder. The intake of the CGAs in the metal container was approximately 2 cm below the spinning disk between baffle and container wall. The position of the spinning disk was adjusted for optimum generation of CGAs. The usual procedure was to lower the container until the disk was almost visible while the disk was spinning. The first 200 ml of CGAs were discharged. The appropriate volume was measured in a plastic graduated cylinder, the CGA pump was stopped, and the intake switched to the graduated cylinder. The CGAs were pumped into the CGA batch flotation cell from the bottom. All valves were closed as soon as the appropriate CGA volume had entered the batch cell . The opening (8 mm diameter) at the bottom of the batch cell served as the inlet for the CGAs, and the outlet for the cleaned growth media, referred to as raffinate. The first 100 ml of raffinate were discharged, and the second 100 ml were sampled

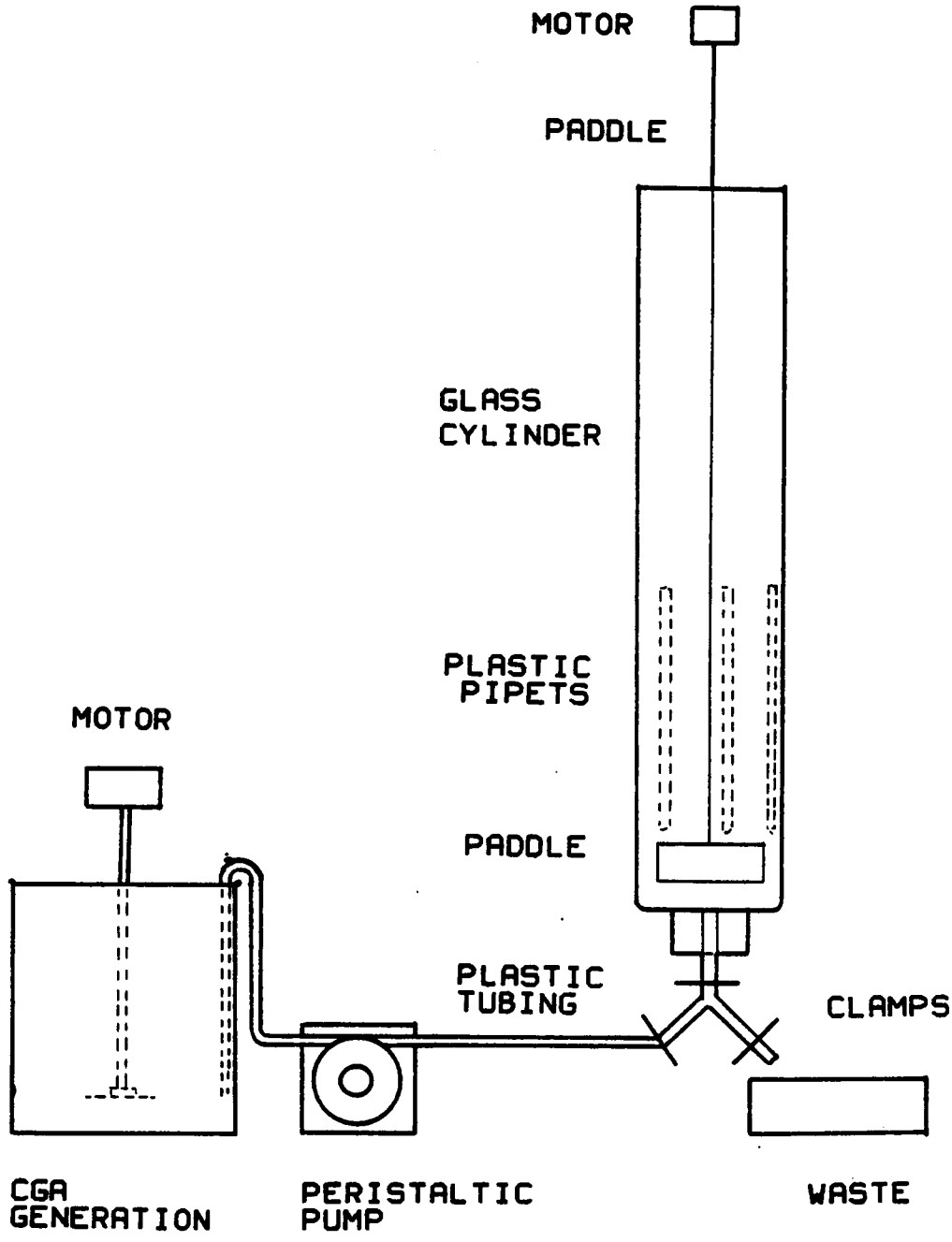


Figure 3. Schematic Diagram of CGA Batch Flotation.

and analyzed for TSS. TSS values were corrected for the presence of coagulants, where applicable, by filtering 100 ml of coagulant containing water of the same coagulant dose through a filter, and measuring TSS. Distilled water was used in these cases to prepare the control.

3.7.2 Mixing

The effect of mixing on the CGA batch flotation was investigated conducting a series of tests in which the algae solution was subject to mixing by a metal paddle (2.5 cm x 6.0 cm). The paddle rotated at a speed of 20 rpm, unless otherwise indicated. The experimental arrangement is depicted in Figure 3. Three plastic pipets mounted on a wire frame reduced vortexing. This construction provided the neccessary flexiblity for cleaning of the batch flotation cell.

3.7.3 Flocculation

Alum flocculation as a pretreatment step was investigated. The optimum dose for flocculation was predetermined using a Phipps and Bird six paddle mixing apparatus. Four different flocculant doses in the range of 60 to 120 mg/l as Alum were added to the algal solution. Mixing was provided for 20 min. at a speed of 20 rpm. The same test was then performed in the CGA batch flotation cell using the optimum dose. The test was continued as described under general procedure.

3.8 Procedures for Continuous Flow Studies

The general set-up for the continuous flow studies is depicted in Figure 4. The CGA supply valve was closed. Three liters of a well-mixed algae solution were stored in a plastic container and pumped at the appropriate flowrate through the continuous flow cell. The effluent algae solution was recycled for two minutes to provide a well mixed solution. The hydraulic head of the effluent was adjusted during this time to allow a froth built-up and overflow at the top of the continuous flow cell as soon as the CGAs, which were generated as previously described, were supplied to the system. The first 200 ml of CGAs were wasted at high a flowrate (150 ml/min) to conduct the tests with a constant CGA quality. The CGA pump was then adjusted to the appropriate flowrate. Recycling of the algae solution was stopped, and the CGAs were then pumped into the continuous flow cell from the bottom after opening the CGA supply valve. Algal solution was supplied from the side at the top of the column. The effluent raffinate left the column at the side of the bottom opposite the influent. The length of the flotation cell was fifty centimeters. The inlet and the outlet were four centimeters from the column ends. The level of the bulk solution was approximatly 3 cm above the influent. CGAs were delivered to the column through a glass tube of 4 mm diameter, 4 cm above the effluent for the raffinate, and the system was operated in a countercurrent mode. The uppermost centimeter of the glass column served as froth accumulation device. Froth was then subject to overflow and collection as shown in Figure 4. The temperature of the algae solution varied between 22 and 24 °C, at a pH of 7.0 to 7.9. The sample representing a continuous flow result for the raffinate was taken after 2.3 liters had passed the system with a total cell volume of 720 ml. Additional samples were obtained for the continuous flow operation tests. All samples and the influent algae solution were stored under refrigeration in brown 250 ml glass bottles. Froth collection was started after about 1.5 liters had passed the system. Froth samples were stored in white glass bottles of 100 ml volume. Flocculation and mixing was performed in a four-liter container as described under procedures for batch studies. The usual testing procedure

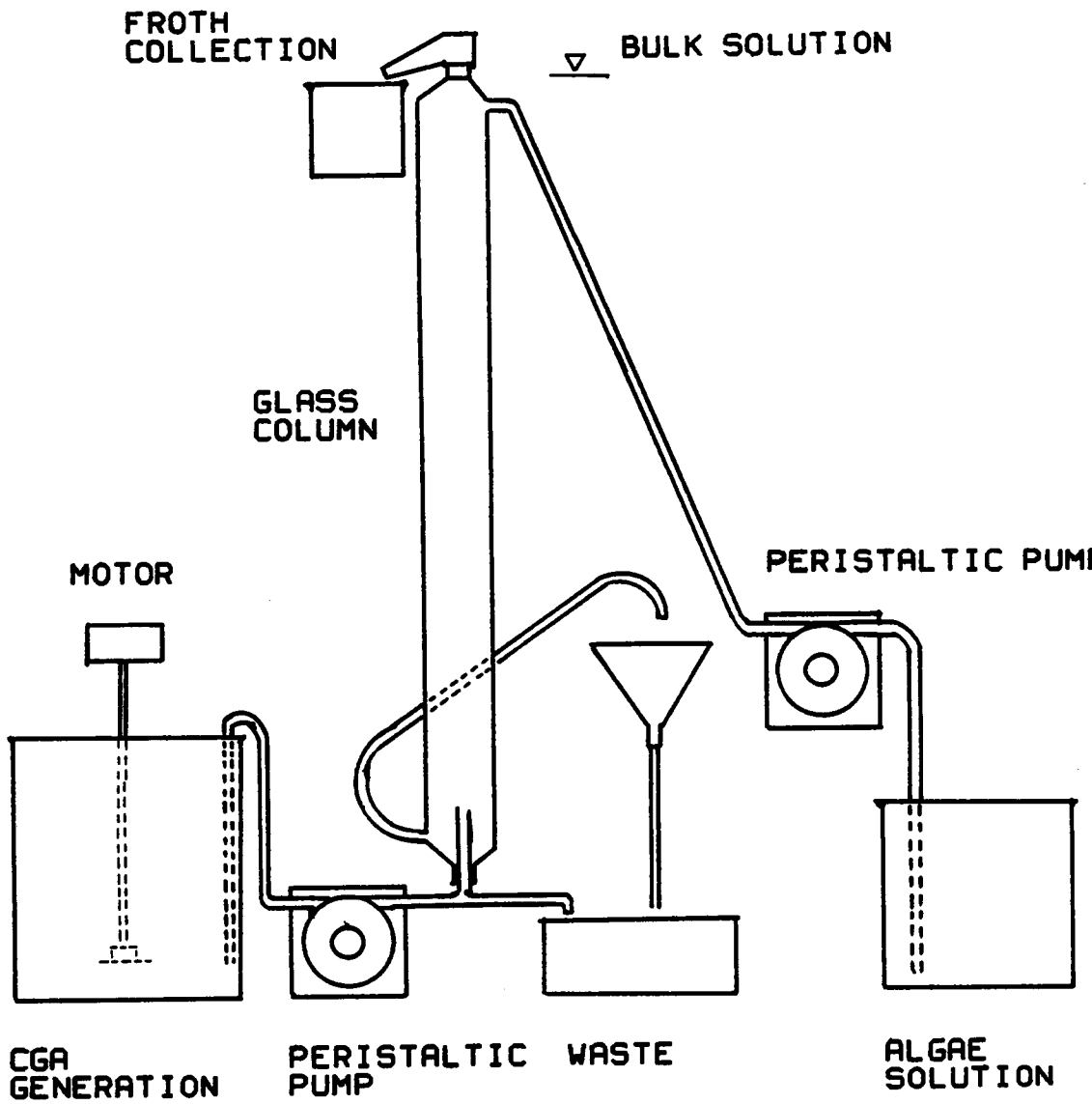


Figure 4. Schematic Diagram of CGA Continuous Flow Flotation.

was as follows: Tests were performed between noon and 5 ^{00} pm. Samples were refrigerated right after each test was finished. Initial steps for *Chlorophyll a* were followed by the initial steps for TSS measurements. Total organic carbon tests were performed not later than 8 hrs after sampling.

3.9 Surfactant Contamination of Treated Water

The presence of surfactant in the raffinate was a matter of concern. To quantify the surfactant concentrations in the raffinate and the froth for continuous flow operations, tests were performed using the same procedure as described above with one modification: Tap water at a temperature of 22 ± 2 °C replaced the algae solution.

3.10 Dissolved Air Flotation

Dissolved air flotation is an established technique for the removal of algae from water. The tests performed in this study were designed to serve as a reference for the new procedure using colloidal gas aphron flotation. The dimensions of the dissolved air flotation pressure chamber and the flotation cell are depicted in Figure 5. An algae solution of 1200 ml was filled into the pressure chamber which had a total volume of 2.5 liters and a diameter of 9.5 cm. Pressure of 50 psi was applied for 5, 15, 30 and 60 minutes while the liquid was agitated by rotating the unit two times every 2 minutes. A 100 ml volume was then discharged, and the next 1000 ml transfered through a 1.2 m plastic tubing (ø 8 mm) into a graduated glass cylinder of 5.5 cm diameter. The tubing was removed, the air bubbles allowed to raise for 60 sec. Then, 100 ml were wasted and 250 were

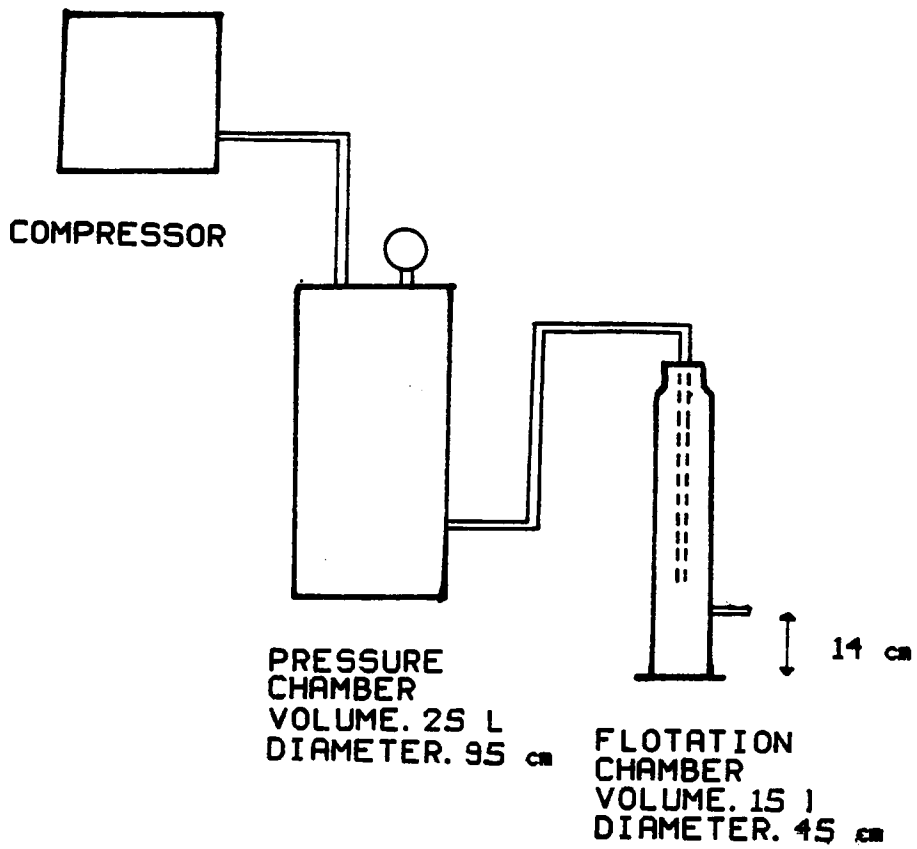


Figure 5. Schematic Diagram of Dissolved Air Flotation.

sampled in a brown glass bottle. The testing sequence was performed as for CGA continuous flow tests.

3.11 Biological Activity Tests

Oxygen uptake tests were performed to evaluate the potential effect of the surfactant Cetyl Pyrimidinium Chloride on the bioactivity in the receiving waters and to test for its biodegradability at concentrations observed in the raffinate. The general procedure is described in the Hach Manual for 6 Bottle Manometric Apparatus Model 2173B. The following modifications were made. Small glass tubes were inserted into the rubber seal caps and four additional holes of the same size as the original holes were punched into the seal caps to allow gas transfer, since the glass tubes covered the original holes. The original design showed problems with base overflowing and dripping into the sample, thus causing high pH and reducing bioactivity. The composition of the tested samples is listed in Table 2.

Table 2. Composition of Samples for Biological Activity Tests.

Constituent	Control ml	Sample ml
tap water	324	0
MLSS	36	36
CPCl (14 mg/l) solution	0	324

4.0 RESULTS

4.1 Overview

Several parameters were of interest while investigating the performance of algae separation. *Chlorophyll a* measurements were performed to quantify the removal of algae, since the change in *Chlorophyll a* values should be directly proportional to the removal of algae. *Pheophytin a*, a degradation product of *Chlorophyll a*, is a valuable indicator of algal age. It can also demonstrate changes in algal quality. It was first intended to report only *Chlorophyll a* concentrations. However, *Pheophytin a* concentrations for the raffinate were in several cases higher than *Pheophytin a* concentrations in the influent algae solution. To show overall removal of algal biomass and quantify changes in the composition of algal biomass during operation or storage, both total *Chlorophyll a* and *Pheophytin a* as well as *Pheophytin a* concentrations were reported. Total suspended solids (TSS) were measured to obtain information about biomass on the basis of dry weight measurements. This parameter is important, since most algae processing operations require a certain concentration to start with. Total organic carbon (TOC) measurements were used as an indicator of the change in organic matter. TOC concentrations provided valuable information about the built-up of surfactant in solution and helped to trace the fate of the surfactant during CGA

flotation. This was accomplished by comparing the readings to corresponding *Chlorophyll a* concentrations. Only total suspended solids were determined during preliminary batch studies.

4.2 Algal Age

Pheophytin a concentrations were in the range of 10 to 22 percent of total *Chlorophyll a* and *Pheophytin a* over the time investigated. These measurements started after algae had been cultured for one month in the aquaria. The lowest concentration was measured at the beginning of the continuous flow studies. *Pheophytin a* concentrations varied between 14 and 22 percent of *total Chlorophyll a* and *Pheophytin a* in influent algae solutions reported in this study. Aging of algae obviously took place over the time these studies were performed. However, comparison of results obtained on different days should be valid, since *Pheophytin a* percentages varied between 15 and 19 percent even on the day when the effect of influent algae concentration on continuous flow CGA flotation was studied. Whether CGA flotation preferentially removes live or dead algal material can be addressed by reporting *Pheophytin a* and total *Chlorophyll a* plus *Pheophytin a* concentrations. The filtrate appeared clear to the eye, thus implying that neither *Pheohytin a* nor *Chlorophyll a* broke through the filter.

4.3 Results of Batch Studies

Table 3 compares removal of the different separation processes investigated. Flotation of algae could not be accomplished using the anionic and non-ionic surfactants, Tergitol 15-S-9 and Soduim Dodecyl Benzene Sulfonate (NaDBS) respectively, although high volume ratios of CGAs to algae solution were applied. The cationic surfactants, Arquad T-50 and Cetyl Pyrimidinium Chloride (CPCl), yielded promising results. The removal efficiency using CGAs produced with Arquat T-50 and CPCl were in the same range as those obtained with a combined process of alum flocculation and sedimentation. It should be noted that flotation with Arquad T-50 could be achieved at a volume ratio of 0.25. Both applications of cationic CGA flotation showed higher removal efficiencies than dissolved air flotation.

Flocculation using alum as flocculant is often applied as a pretreatment or conditioning step for separation of algae together with dissolved air flotation. An investigation of this pretreatment step while dewatering Florida phosphate slime with CGA flotation has been reported.[41] The pretreatment in this study was performed using the pre-determined optimum dose for flocculation. After pretreatment, CGA flotation with all three types of surfactants, anionic, non-ionic and cationic, showed removal efficiencies of TSS above 90 percent, well above the results of alum flocculation and sedimentation. The dissolved air flotation equipment did permit testing dissolved air flotation in combination with flocculation as pretreatment.

Figure 6 shows the influence of the volume ratio of CGAs to algae solution on the separation of algae from growth media. As expected, cationic CGA flotation can accomplish better separation with increasing volume ratios. A higher volume of CGAs was pumped through the system, providing more bubbles for contact with algae and a well-mixed sample, thus reducing the disadvantage of possible stagnant volumes in the batch flotation cell. The effect of mixing on the removal of algae is depicted in Figure 7. Mixing obviously did not have a significant influence on

Table 3. Observed Removal Efficiencies for Batch Studies Quantified as Percent Removal of Total Suspended Solids.

Reference Removal Methods

Method Used	% Removal
dissolved air flotation pressure 50 psi, 30 min	60
alum flocculation, dose: 100 mg/l sedimentation 20 min	84

CGA Flotation without Pretreatment

Surfactant	Conc.	ml Used	Volume Ratio	Mixing	% Removal
NaDBS	0.7 g/l	500	0.5	no	0
Tergitol 15-S-9	2 ml/l	500	0.5	no	0
CPCl	0.7 g/l	500	0.5	no	64
CPCl	0.7 g/l	200	0.2	20 rpm	34
Arquad T50	2 ml/l	250	0.25	no	80

CGA Flotation with Pretreatment

Pretreatment	Surfactant	Conc.	ml Used	Volume Ratio	% Removal
alum flocculation dose 100 mg/l alum	CPCl	0.7 g/l	100	0.1	93
alum flocculation dose 100 mg/l alum	Tergitol	2 ml/l	100	0.1	92
alum flocculation dose 100 mg/l alum	NaDBS	0.7 g/l	100	0.1	91

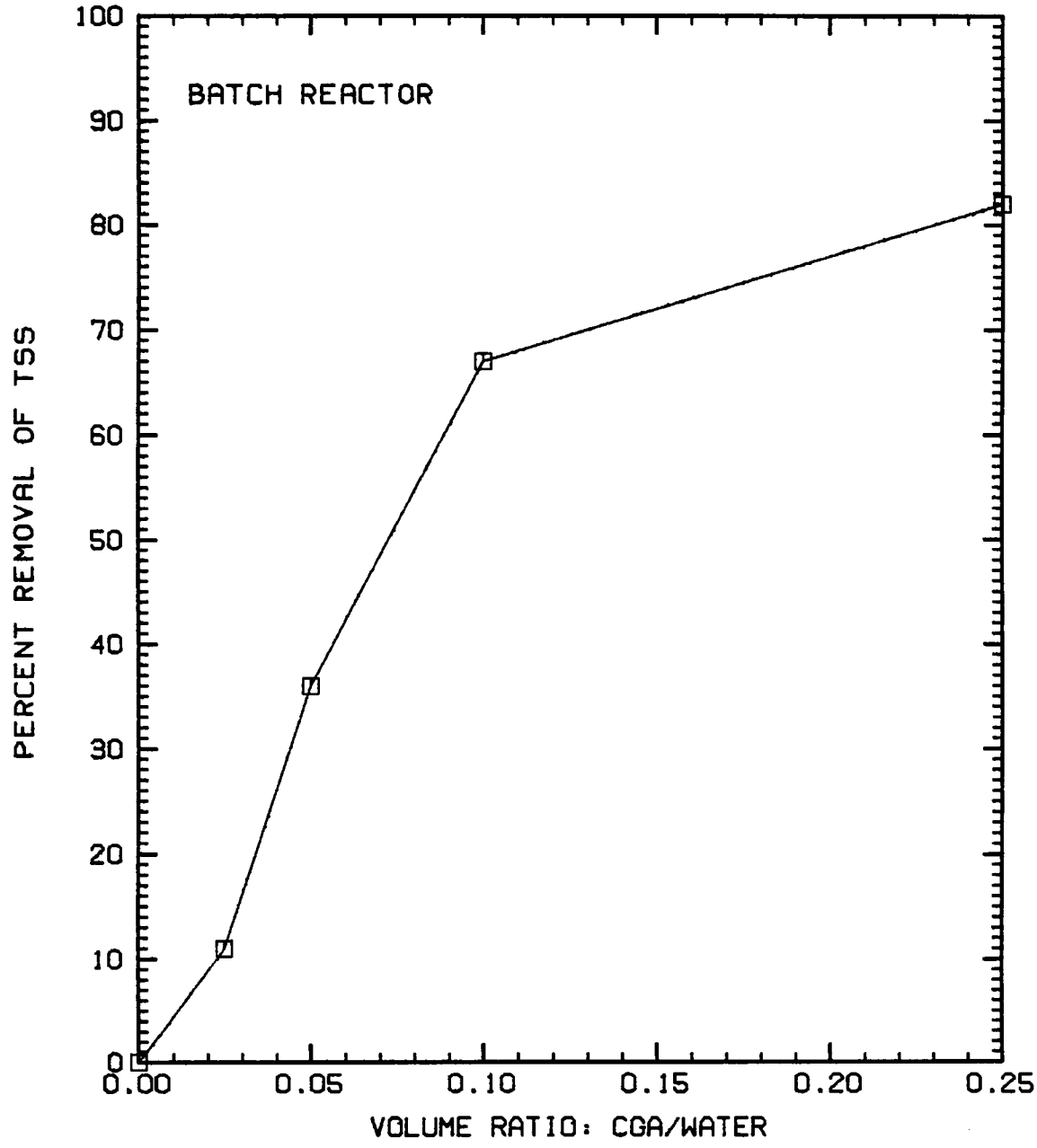


Figure 6. Effect of the Volume Ratio of CGA to Algal Solution on the Removal of TSS Using Arquad T-50 (2 ml/L) for Generation of CGA.

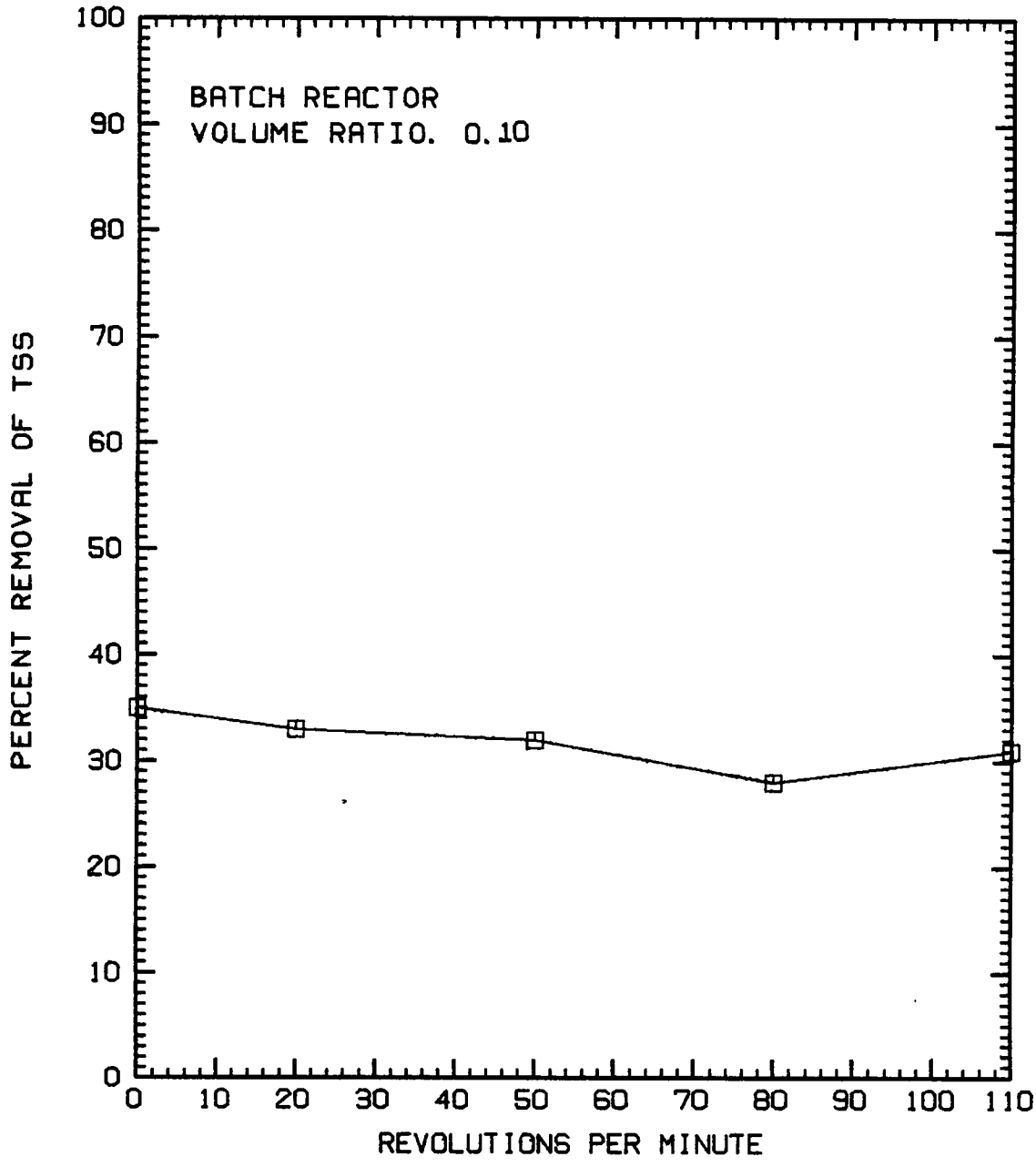


Figure 7. Effect of Mixing on the Removal of TSS using CPCl (0.7 g/l) for Generation of CGAs.

the removal efficiency. The volume ratio in this study was 0.1. Stagnant volumes were obviously not present when 100 ml of CGAs were pumped into the batch flotation cell.

4.4 Dissolved Air Flotation

Figure 8 shows the effect of time duration provided for gas uptake at 50 psi (3.4 atm) on the removal of algae. Values for the influent algae solution are reported at time zero. At equilibrium, air made up approximately 8 percent of the total volume at a pressure of 50 psi and a temperature of 20 °C. TOC readings constantly decreased with increasing time duration. Maximum *Chlorophyll a* and *Pheophytin a* removal was achieved at 30 min. The effluent concentrations varied between 15.4 and 20.4 mg/l. The concentration for the 60 min time duration increased slightly compared to the lowest concentration. *Pheophytin a* was about 50 percent of the total *Chlorophyll a* and *Pheophytin a*, except for the 60 min value where *Pheophytin* was 68% of total *Chlorophyll a* and *Pheophytin a.*

The effect of influent concentrations on the removal efficiencies achieved using dissolved air flotation (pressure: 50 psi, applied: 30 min) is depicted in Figure 9.
Approximately sixty percent of the TOC was removed at a relatively high influent algae concentration of 50 mg/l as TOC. Only twenty percent was removed when influent TOC was between 15 to 25 mg/l whereas 48% removal was achieved at the lowest influent concentration. Total *Chlorophyll a* and *Pheophytin a* removal was in the range of 55 to 70% over the whole range of influent algae concentrations. Even higher removal efficiencies of total suspended solids were obtained with values ranging between 55 and 85%.

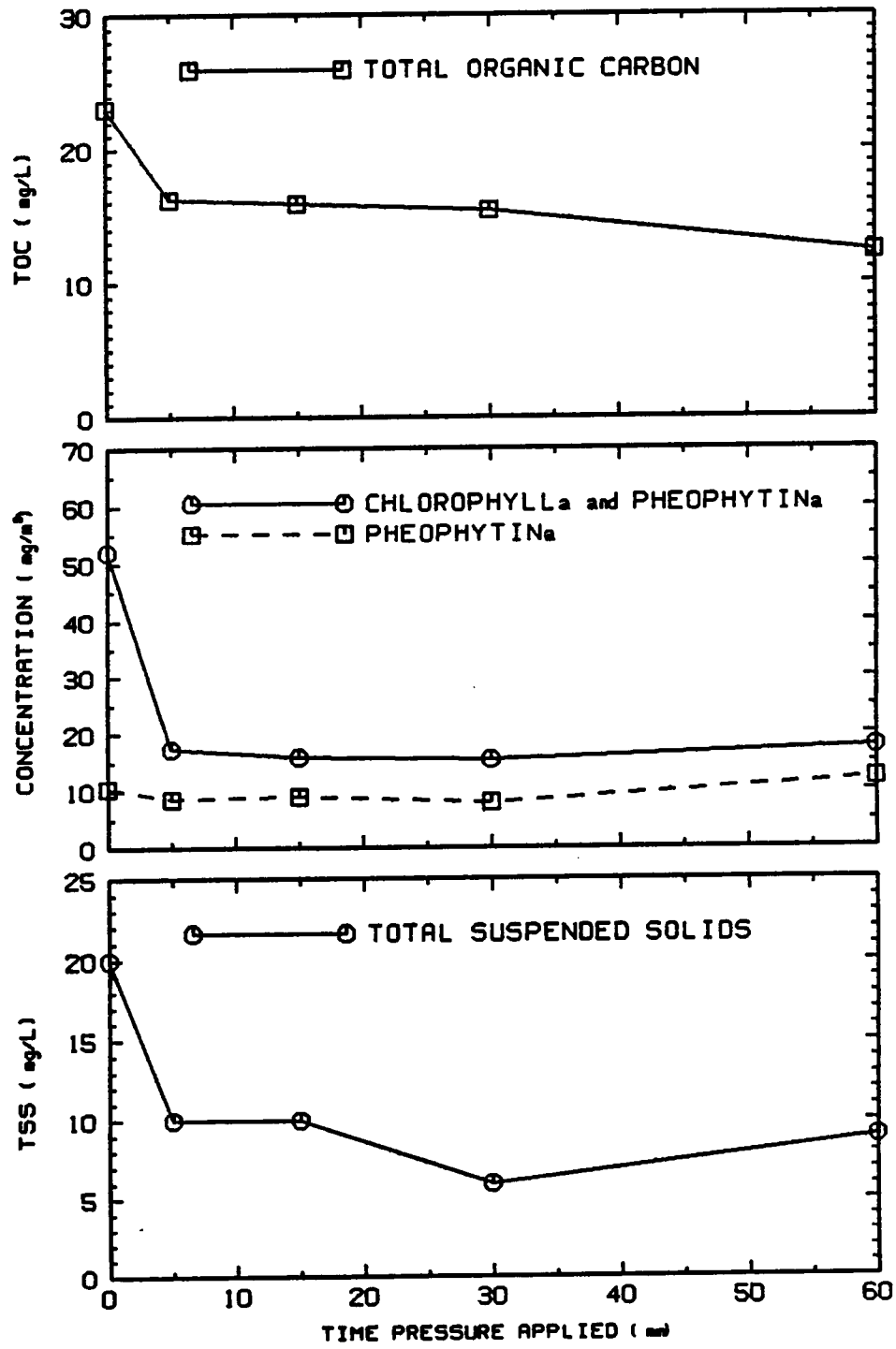


Figure 8. Effect of Time Pressure Applied for Gas Uptake Using Dissolved Air Flotation Batch Reactor for Removal of Algae (Pressure: 50 psi).

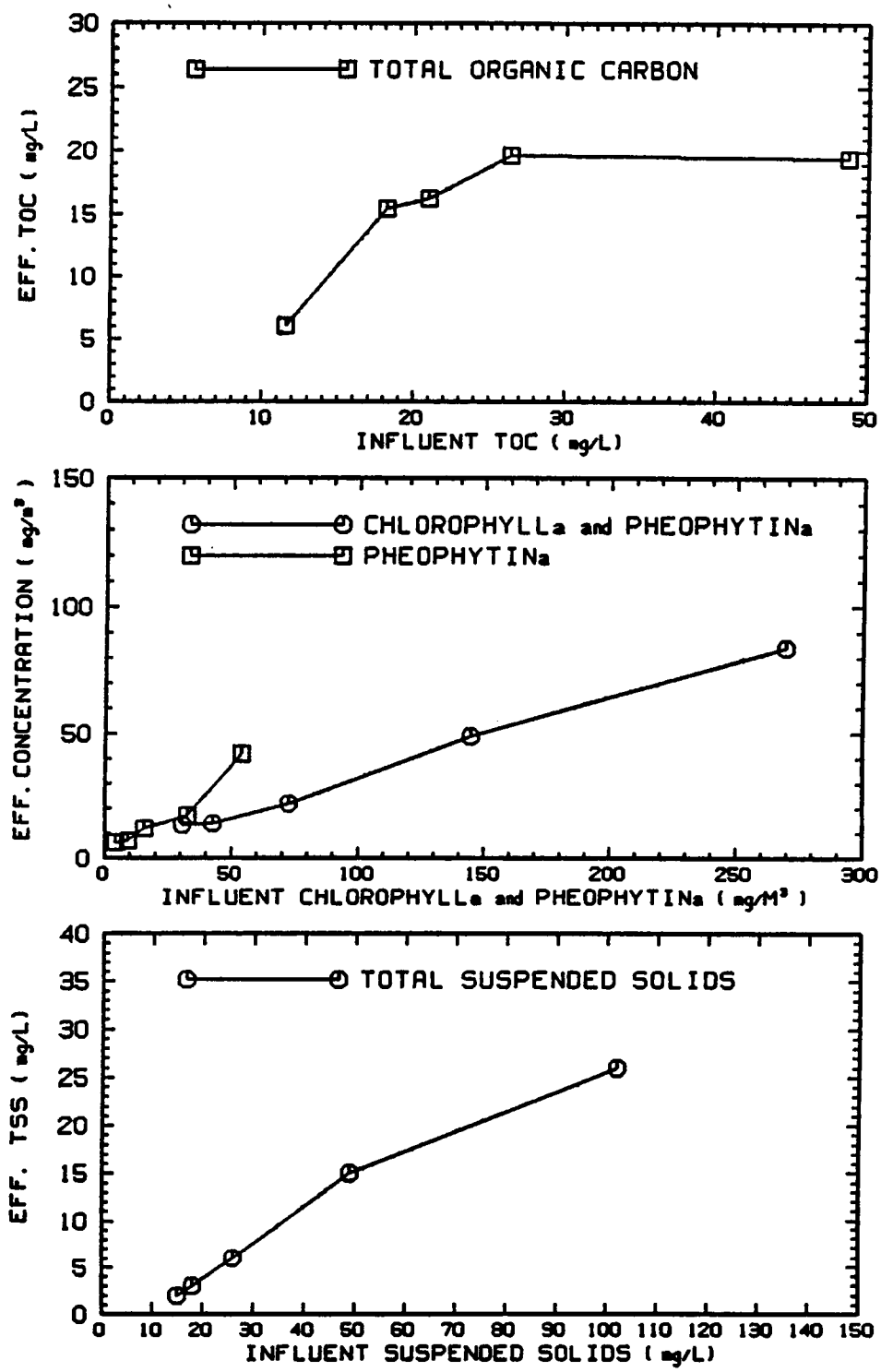


Figure 9. Effect of the Influent Concentrations on the Effluent Quality Using Dissolved Air Flotation (Pressure: 50 psi, 30 min).

4.5 *Results of Continuous Flow Studies.*

Arquad T-50 showed the most promising results for a "pure CGA flotation" application. However, TOC readings for a solution of 10 mg/l as TOC made up using Arquad T-50 were in the range of 9 to 25 mg/l, whereas Cetyl Pyrimidine Chloride showed very constant readings between 9.7 to 10.5 mg/l as TOC under the same conditions. Both surfactants had to be analyzed in the furnace mode using a Dohrmann DC 80 Total Carbon Analyzer. A potentially more accurate method for TOC measurements using phosphoric acid and potassium persulfate together with ultraviolet radiation for oxidation in a reaction vessel could not oxidize the surfactants within the time intervals controlled by the connected computer. This resulted in error messages and no reproducable results could be obtained.

Earlier studies by Honeycutt[34] were performed at the very high volume ratio of CGAs to algae solution of 1.0. This study focused on comparably lower volume ratios. The range investigated was between 0.01 and 0.1. Cationic surfactants have the disadvantage of high prime costs and biostatic and biocidal properties. However, this disadvantage could be overcome in case of successful separation of algae using very low concentrations of surfactant for generation of CGAs combined with very low volume ratios. The concentration of the surfactant used should be very low in the raffinate and the froth under these conditions. Moreover, results of surfactant uptake studies obtained in this study can also be helpful in designing other CGA flotation separation cells like troughs. Flotation in troughs is very common in environmental applications, and was also used for CGA flotation of Florida phosphate slimes.[41]

Figure 10 shows the results of continuous flow operations performed at a volume ratio of 0.02 (CGA/algae solution). This study was performed to determine what volume of algae solution had to pass the system to reach steady state, since the supply of algae solution was limited. The TOC concentrations show that the system operated at steady state after about two times the volume of the cell had passed the system. Since sampling was started after 2.3 liters had passed the system, the obtained results should be considered results at steady state.

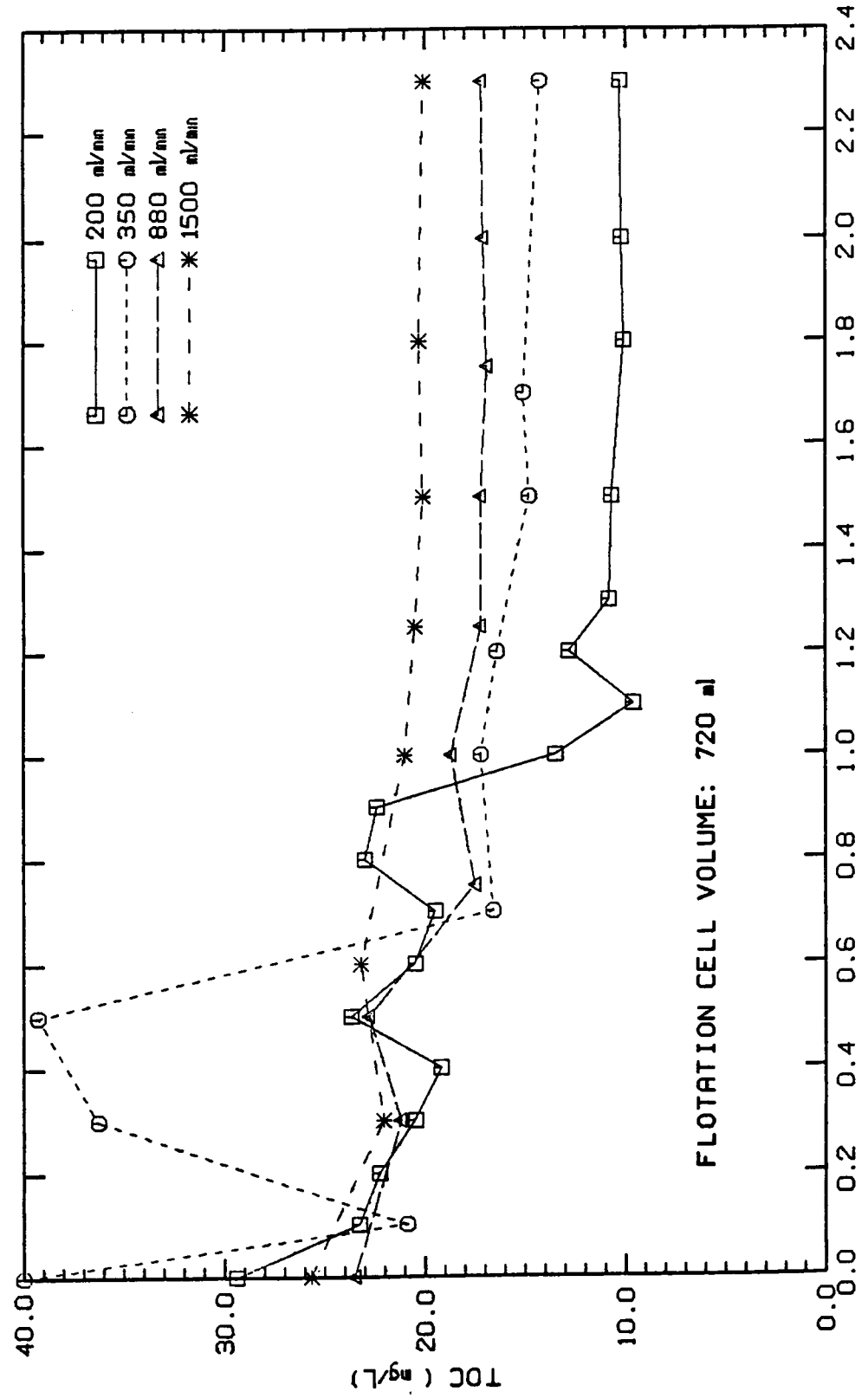


Figure 10. Effect of Flowrate on Effluent TOC Concentrations for Continuous Flow Operations, Volume ratio: 0.02 CGA/Algal solution.

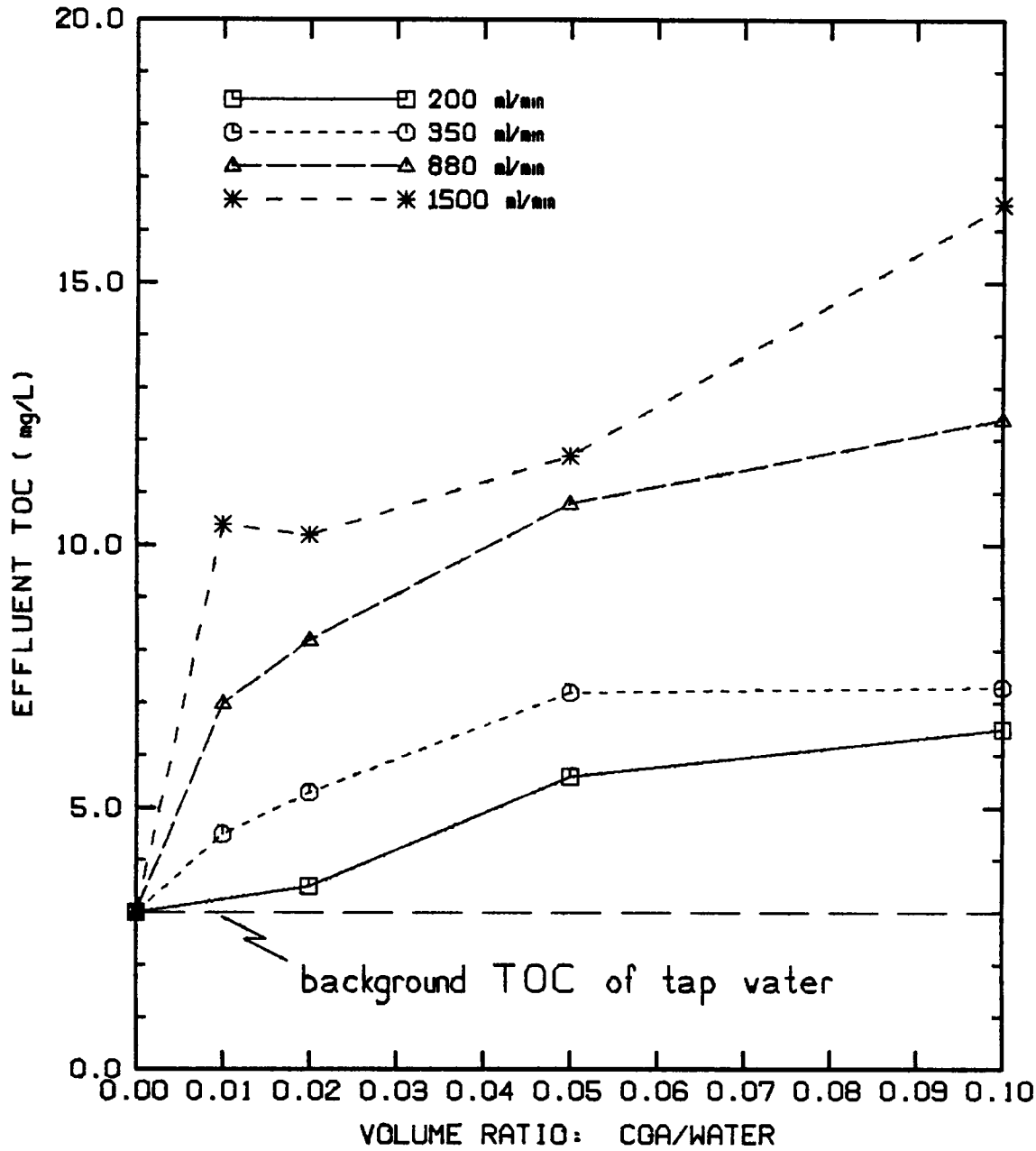


Figure 11. Effect of Flowrate on Surfactant Uptake by Tap Water Using CPCl (0.7 g/L) for Generation of CGAs.

Contamination of tap water with surfactant was studied to evaluate the effect of the flowrate on the fate of the surfactants during operation. Figure 11 shows the concentrations for the effluent water. Water has a background TOC of 3.0 mg/l when analyzed in the furnace mode of the Total Organic Carbon Analyzer. Concentrations are between 1.5 to 2.5 mg/l when the more precise method is used. TOC concentrations increase with increasing flowrates as well as increasing volume ratios.

Figures 12 through Figure 15 show the results of algae separation using CGA flotation for four flowrates. Values for influent algae solutions are reported at a volume ratio of zero. TOC reductions of approximately 60% were achieved at a flowrate of 200 ml/min throughout the three volume ratios used. The TOC concentrations dropped to a minimum TOC concentration for each flowrate studied and increased again at the highest volume ratio. The optimum volume ratio for TOC removal is in the range of 0.02 to 0.05. The concentration dropped as low as 9.2 mg/l at a flowrate of 350 ml/min. The concentrations for the two lower flowrates were in the range of 9.2 to 13.1 mg/l, while the higher flowrate concentrations ranged from 17.1 to 20.5 mg/l as TOC. TOC removal efficiencies decreased with increasing flowrates. Plots in the center show total *Chlorophyll a* and *Pheophytin a* as well as *Pheophytin a*. *Chlorophyll a* and TSS removal increaes with increasing volume ratios. No significant trends could be observed for either *Chlorophyll a* or TSS removal performance over the range of investigated flowrates.

Figure 16 shows the four TOC plots of Figure 12 through 15 on one page with an overlay of data obtained in the study of surfactant uptake by tap water. This figure shows the trade-off between algae removal and surfactant solubilisation during continuous flow operation of a CGA system. Removal efficiency of TOC decreased with increasing flowrates, since more surfactant was found in the raffinate at higher flowrates.

The effect of the influent algae concentration on the removal performance of CGA flotation is depicted in Figure 17. This study was performed at a flowrate of 350 ml/min for the algae solution and a volume ratio of 0.02. The plot for TOC implies there was a limit to TOC removal of approximately 8 mg/l. TOC removal was obviously less effected by influent TOC concentration than were *Chlorophyll a* and TSS removal. More than fifty percent of total *Chlorophyll a* and

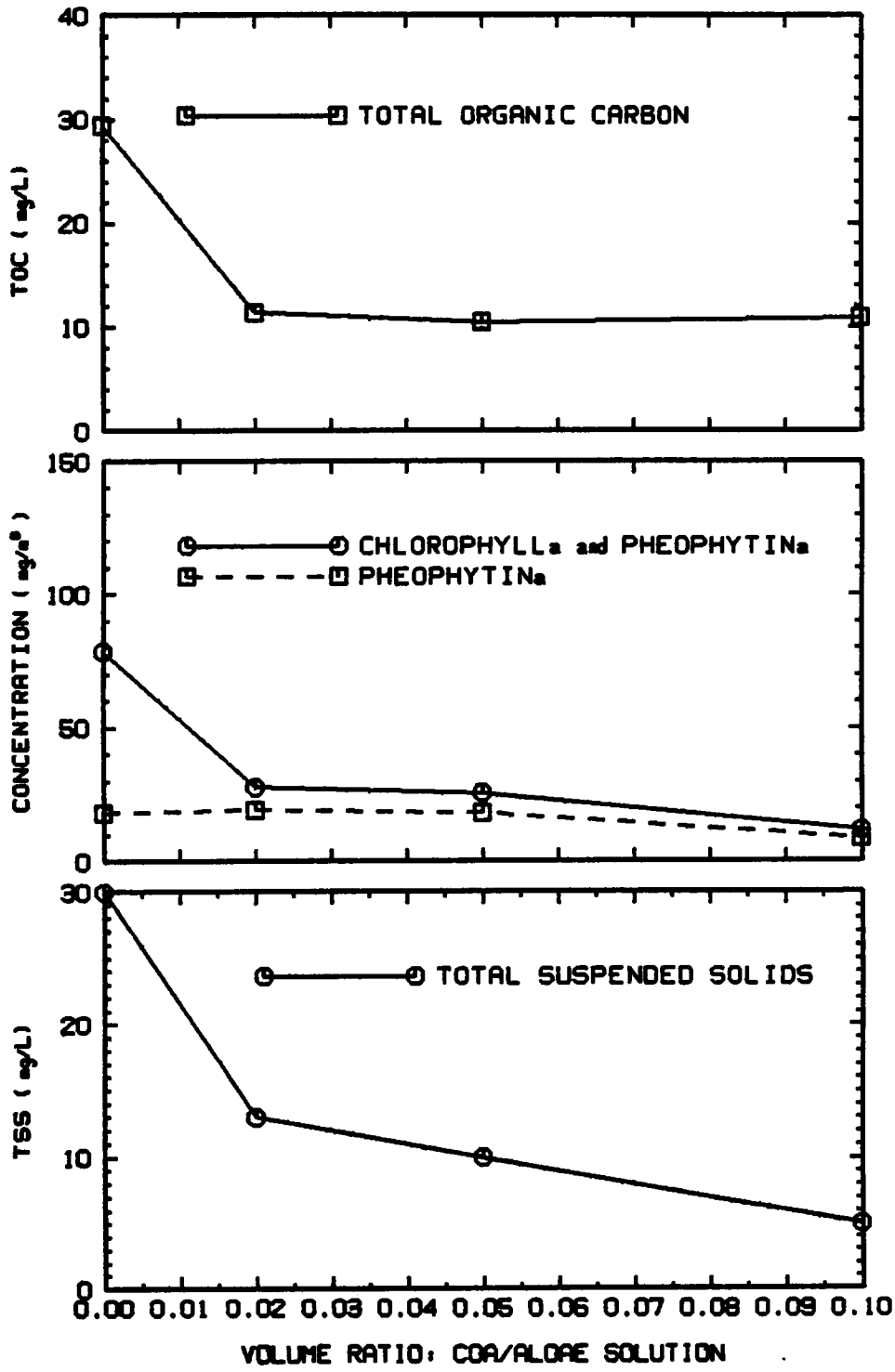


Figure 12. Effect of the Volume Ratio of CGA to Algal Solution on the Removal Efficiency Using CPCI (0.7 g/l) for Generation of CGAs, Flowrate: 200 ml/min.

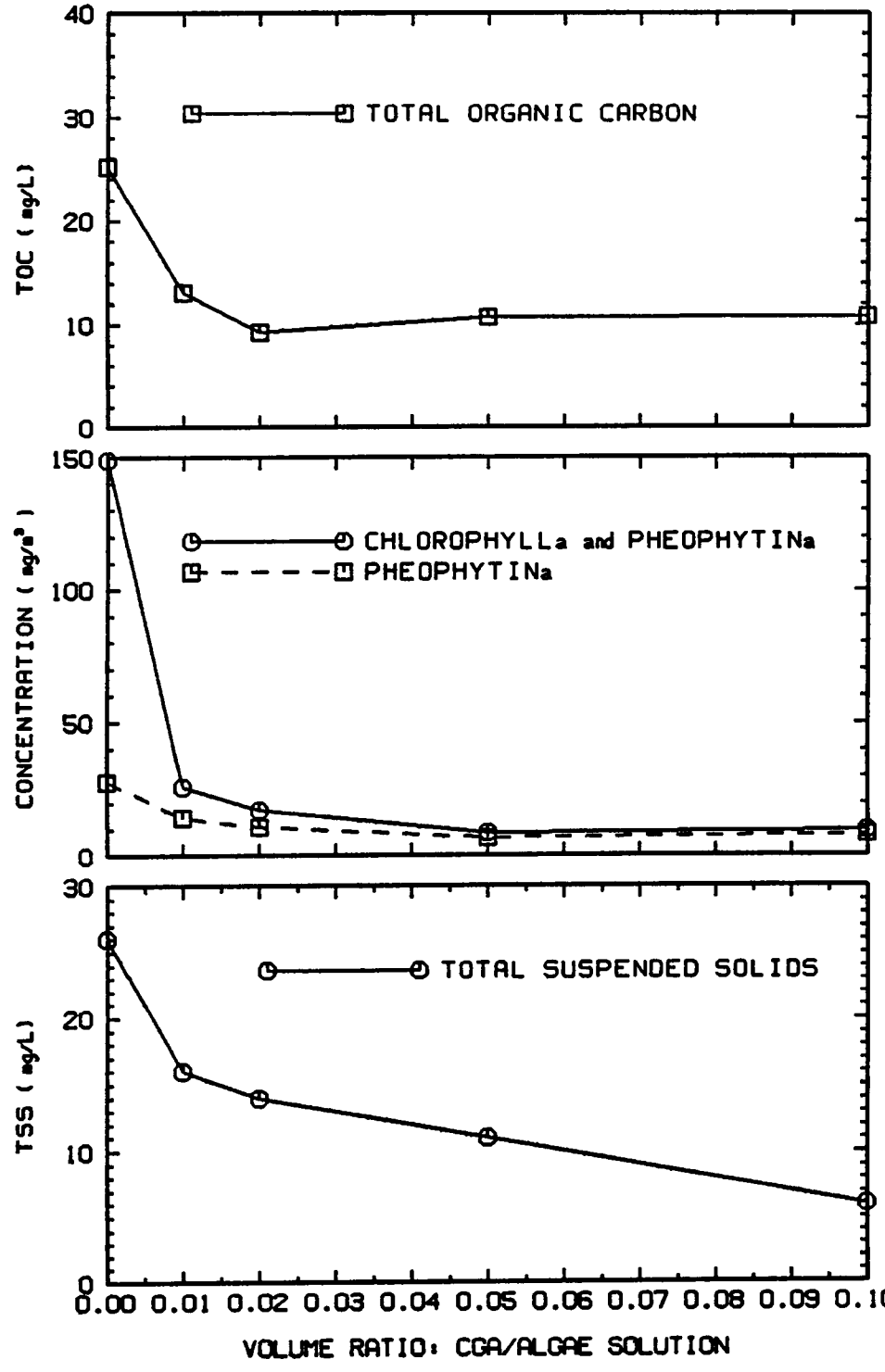


Figure 13. Effect of the Volume Ratio of CGA to Algal Solution on the Removal Efficiency Using CPCI (0.7 g/l) for Generation of CGAs, Flowrate: 350 ml/min.

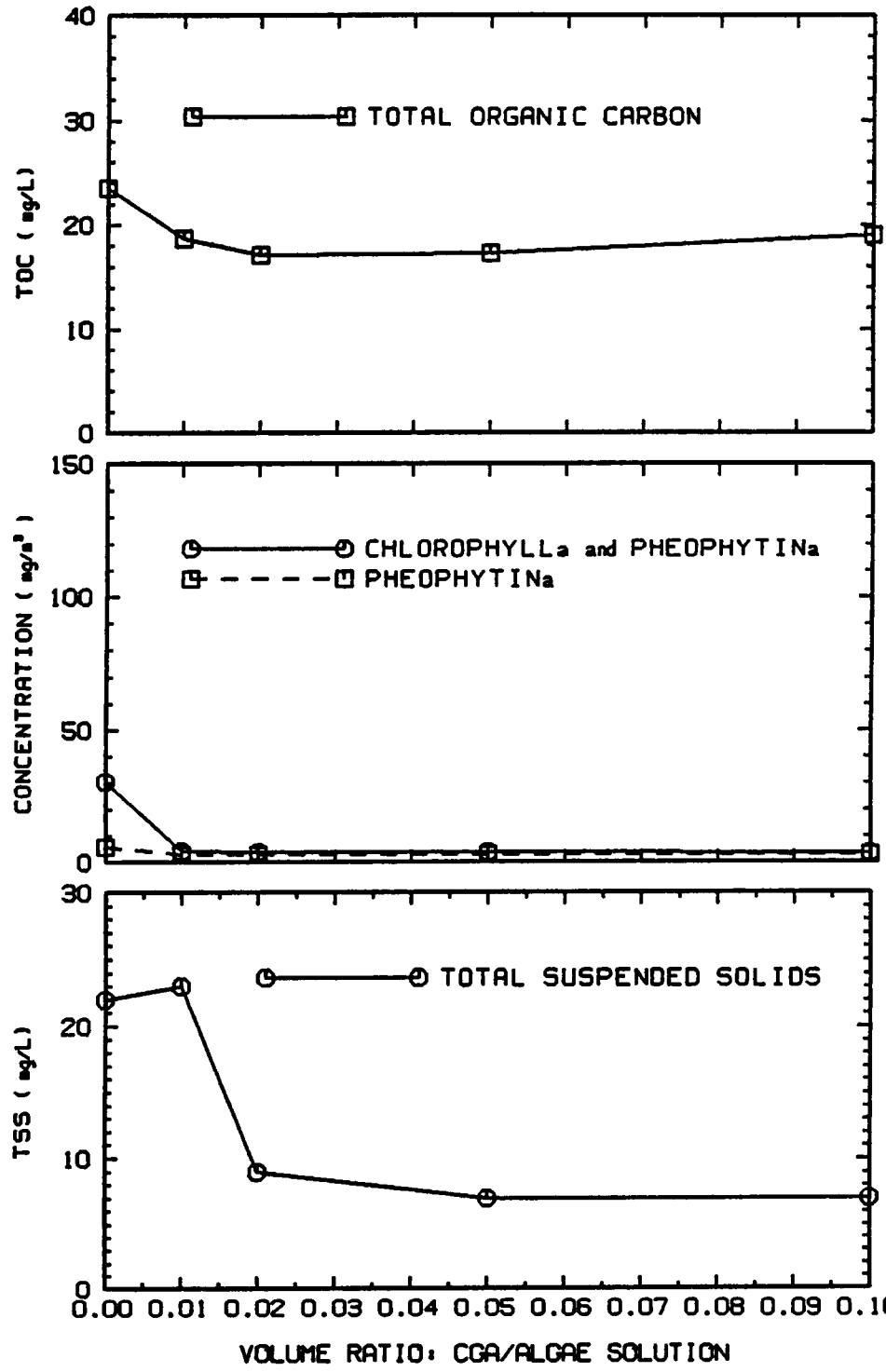


Figure 14. Effect of the Volume Ratio of CGA to Algal Solution on the Removal Efficiency Using CPCI (0.7 g/l) for Generation of CGAs, Flowrate: 880 ml/min.

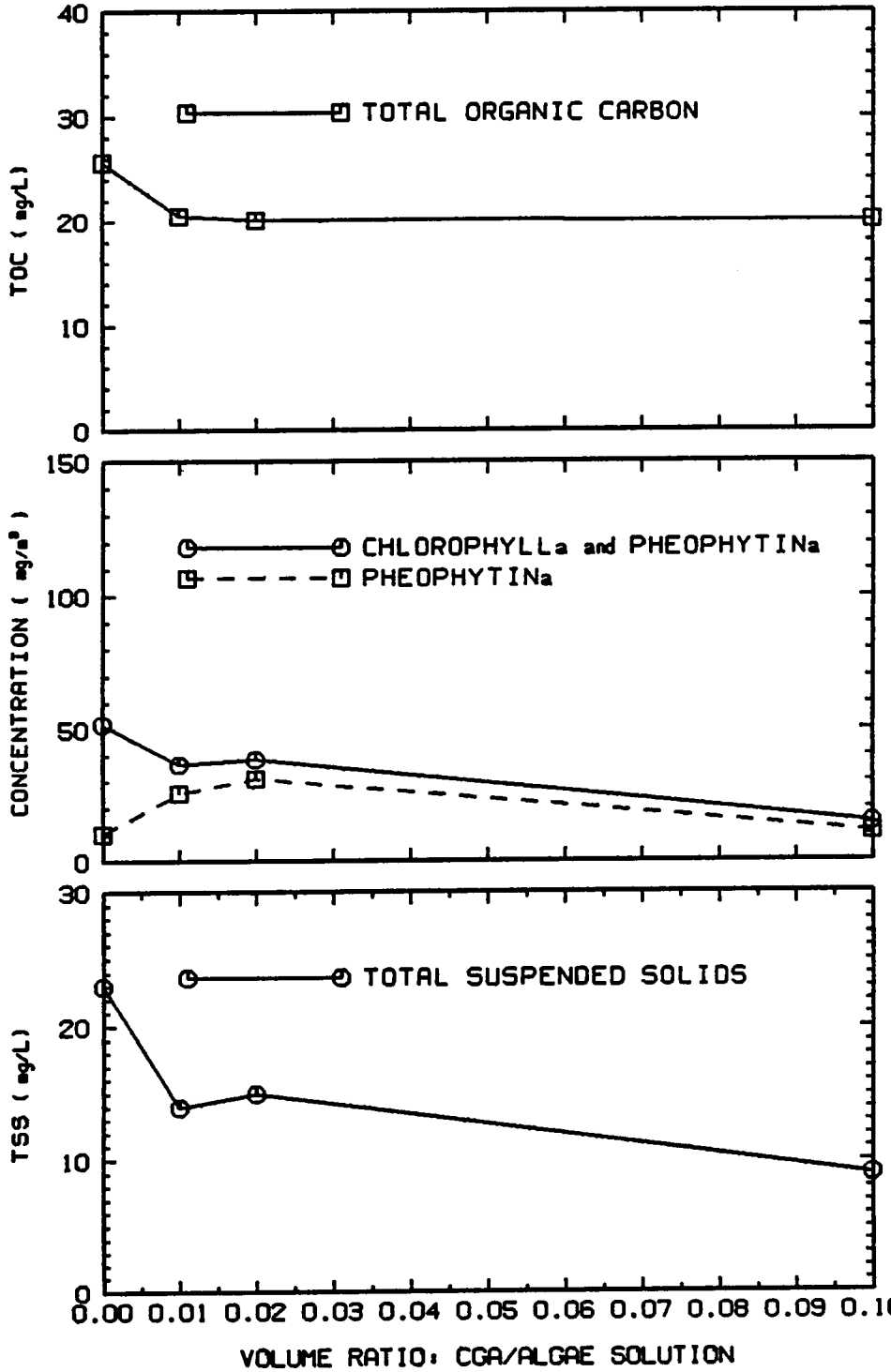


Figure 15. **Effect of the Volume Ratio of CGA to Algal Solution on the Removal Efficiency Using CPCl (0.7 g/l) for Generation of CGAs, Flowrate: 1500 ml/min.**

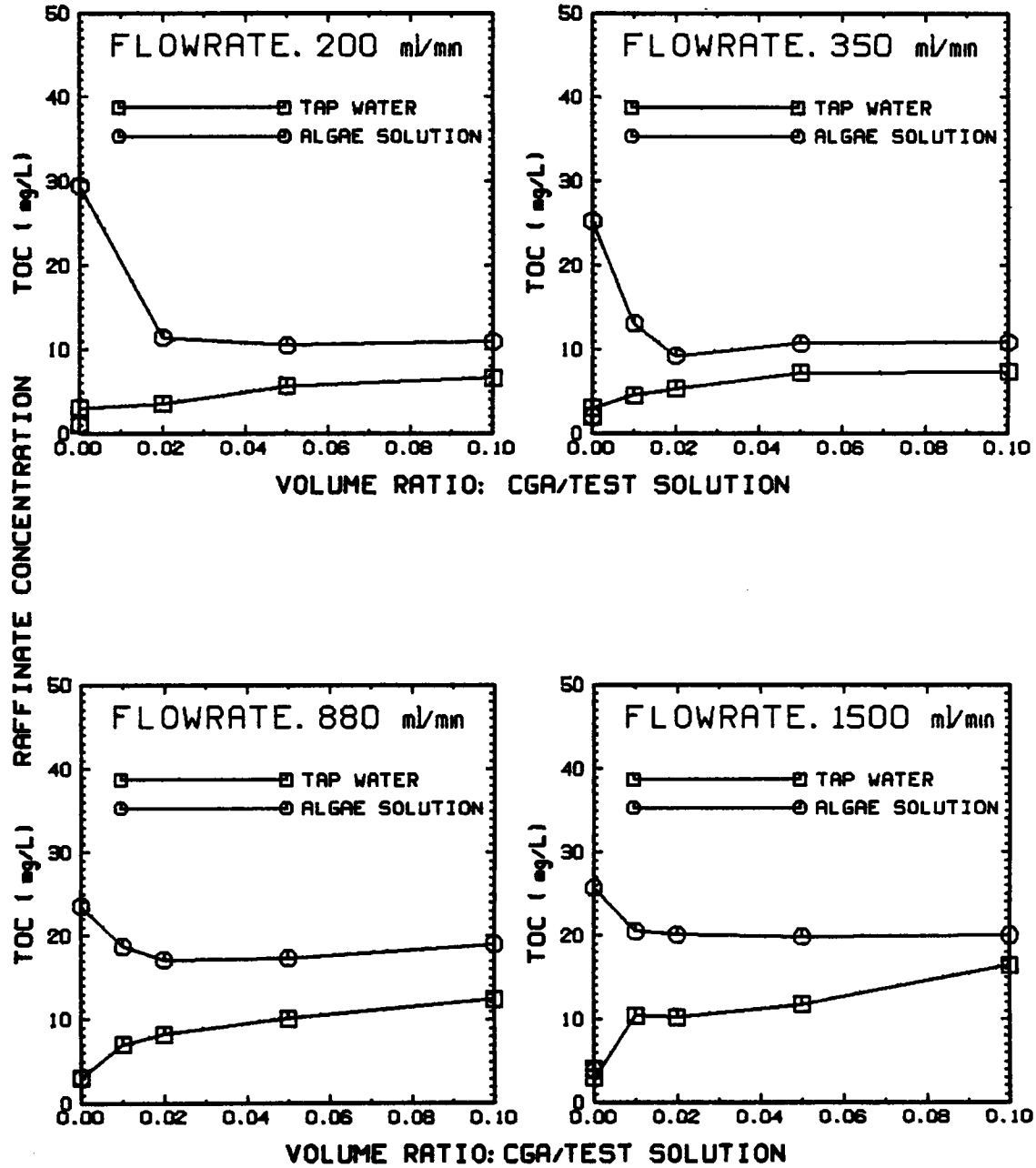


Figure 16. Estimation of TOC Substitution: Comparing TOC Removal during Continuous Flow Operation with Surfactant Uptake of Tap Water.

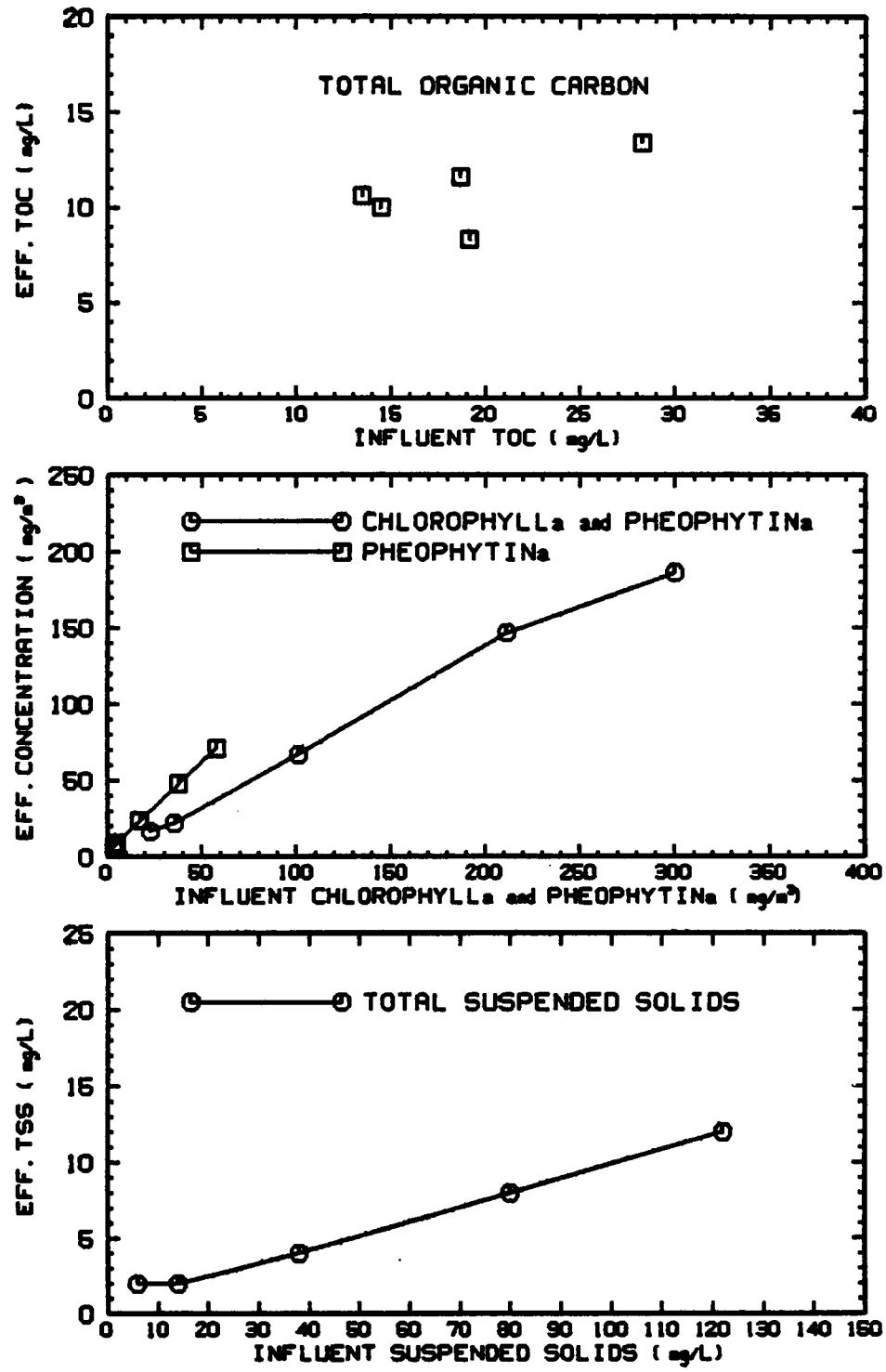


Figure 17. Effect of the Influent Concentrations on the Removal Efficiencies using CPCl (0.7 g/l) for Generation of CGAs 1 {Flowrate: 350 ml/min, Volume Ratio: 0.02 (CGAs/Algal Solution)}.

Pheophytin a was removed throughout this study. Residual, unremovable *Chlorophyll a* and *Pheophytin a* was approximately 5 mg/m^3. Almost no net removal of *Pheophytin a* could be expected. Total suspended solids removal was higher than ninty percent for all influent algae concentrations. Residual TSS were in the range of 2 to 3 mg/l.

Collection of froth and the determination of steady state values proved to be very difficult. Only about 20 ml could be collected at a volume ratio of 0.05 although collection began after 1.5 liters had passed the system. The froth volume collected was usually about half the volume of the CGAs supplied during the time period of collection. Overflow of froth was regulated by adjusting the hydraulic head of the effluent. As soon as the supply of CGAs started, the hydraulic head changed because the CGAs added to the overall feed volume to the flotation cell. Additional adjustments were very difficult to perform during operation, especially at the higher flowrates. The same problem occured at the highest volume ratio. TOC concentrations for the froth layer varied between 56 and 267 mg/l at a flowrate of 350 ml/min. Figure 18 shows TOC concentrations of the froth collected at a flowrate of 350 ml/min. The results of this study are from a series of experiments where only froth was collected and all other sampling was omitted. Optimizing the collection of froth again showed problems at the highest volume ratio. The low TOC concentration at a volume ratio of 0.1 was the result of overflowing water and subsequent diluting of the froth. Included in this figure are also the results for froth collected while tap water was used instead of algae solution. The sampling for the reading at the highest volume ratio was obtained after a careful adjustment of the hydraulic head and approximately 10 liters of water had passed the system, since the supply of water was not limited. TOC concentrations reported in Figure 18 were subject to the procedure as described in Chapter 3. However, observations of the collected froth showed that the algae settled out within 10 min, thus leaving a supernatant with TOC concentrations of 60 to 100 mg/l. The algae layer had TOC concentrations between 900 and 1500 mg/l. Total suspended solids measurement of the settled algae showed concentrations up to 11 g/l. The average value for six measurements was 6 g/l. Total *Chlorophyll a* and *Pheophytin a* concentrations were as high as 3500 mg/m^3 with an average of 2650 mg/m^3. Algal concentrations in the froth were up to 23 times the influent algal concentrations. Great variability was mostly due to the sampling technique, since

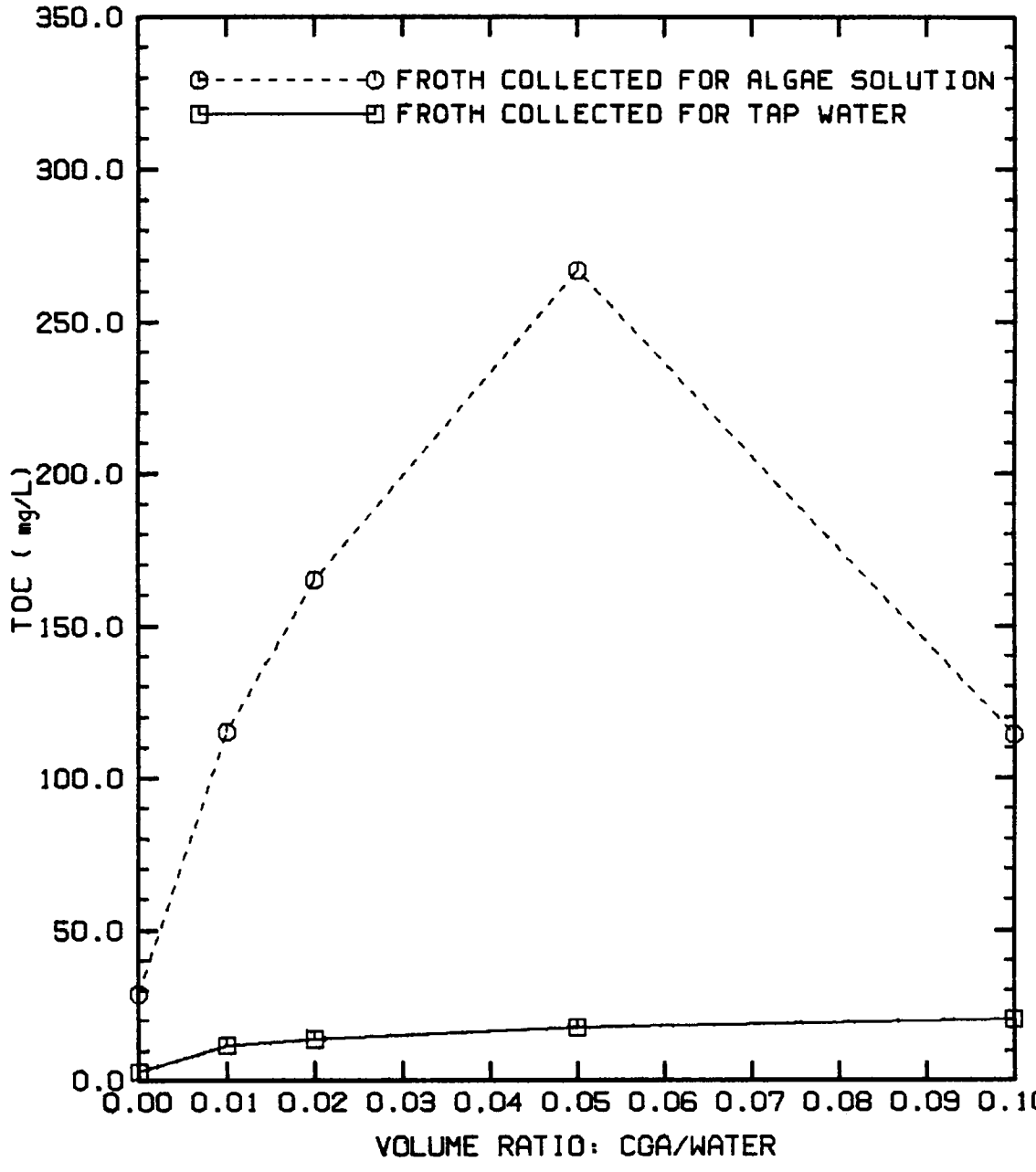


Figure 18. Effect of the Volume Ratio of CGA to Water on TOC Concentrations of Mixed Froth for Tap Water and Algae Froth Using CPCl (0.7 g/l) for Generation of CGAs.

only a thin layer of algae covered the bottom of a 20 ml bottle. One milliliter was measured by pipetting and then subjected to the procedures described in methods and materials.

4.6 Biological Activity Test Results

Continuous flow operations showed effluent TOC concentrations as low as 9.2 mg/l. Part of this TOC was organic carbon in form of surfactant molecules. A solution of 10 mg/l as TOC was prepared using CPCl and tested for biodegradation as well as biostatic or biocidal effects the biological activity test results are depicted in Figure 19. The presence of the cationic surfactant Cetyl pyrimidine chloride apparently reduced the rate of bioactivity. The controls showed higher daily oxygen uptake throughout the first six days, oxyggen uptake was aproximately equal during the next three days, before the samples with surfactant finally showed higher higher oxygen uptake than the controls. Total oxygen demand was equal after 12 days. The oxygen demand of the CPCl solution was approximately 25 mg/l higher than the oxygen demand of the controls.

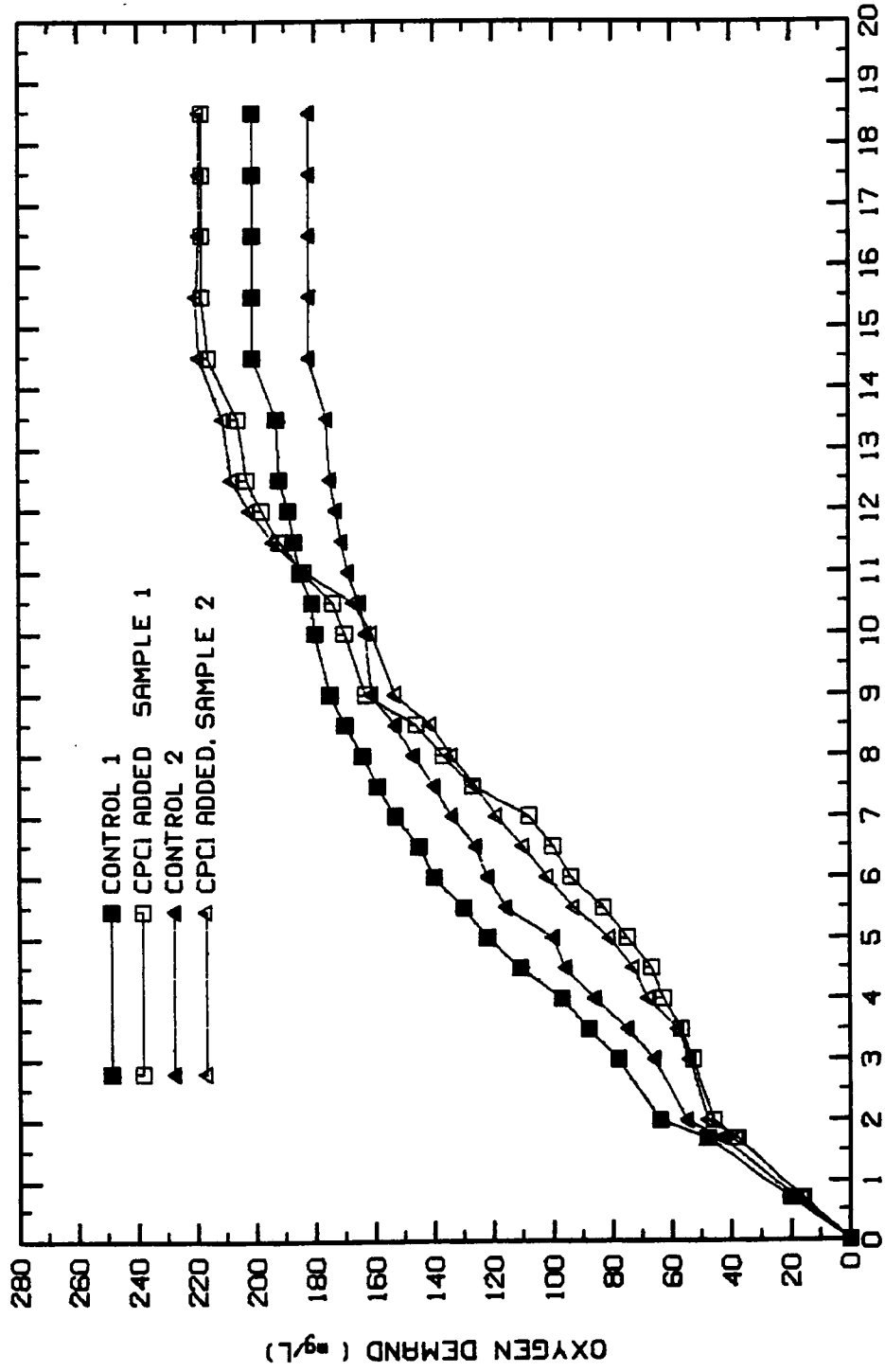


Figure 19. Effect of 14 mg/L Cationic Surfactant Cetyl Pyrimidinium Chloride on the Oxygen Uptake of Activated Sludge Microorganisms.

5.0 DISCUSSION

Results of the preliminary batch studies indicated that two different approaches can be taken while applying CGA flotation for algae removal. CGA flotation without any pretreatment or preconditioning step will only have satisfactory results using cationic surfactants. Algae have a negative surface charge. Charge interaction between algae surface and surfactant molecules is obviously responsible for the successful flotation of algae by cationic surfactants.[34] Cationic, non-ionic and anionic surfactants can be utilized for CGA flotation after the pretreatment of algae by alum flocculation. Pretreatment with alum flocculation will improve the removal efficiency of cationic CGA flotation. The results of these preliminary studies agree for the most part with findings by Honeycutt, but one observation was different.[34] Pretreatment with alum flocculation followed by batch CGA flotation using a anionic surfactant did not fail in this study, but showed over 90% removal. However, no removal could be observed in the continuous flow CGA flotation cell using alum flocculation followed by non-ionic and anionic CGA flotation. The pumping action of the peristaltic pump caused destruction of the flocs. Flowrates for this kind of CGA flotation have to be significantly reduced to avoid break-up of algae-alum flocs.

Cetyl Pyrimidinium Chloride was used in the countercurrent continuous flow operations, although separation of algae was less successful compared to Arquad T-50. A very dilute surfactant solution containing Arquad T-50 in a concentration of 10 mg/l as TOC showed great variations

when tested on the Total Organic Carbon Analyzer. A possible explanation for these results is the presence of micelles, i. e., formations of larger groups of surfactant molecules in spherical or rod-like shapes.[39]

Continuous flow studies show that CGA flotation can be operated at substantially reduced volume ratios of CGAs to algae solution. Even lower volume ratios should result in satisfactory separation and flotation of algae. Peristaltic pumps, used in this study, did not permit operation at lower flowrates. Several factors were responsible for increasing TOC values at higher flowrates as well as higher volume ratios. Higher volume ratios increased the number of small sized bubbles with a rising velocity lower than that of the downflowing algae solution, thus increasing the carryover of CGA bubbles. Higher volume ratios also slightly increased the downflow velocity, since a higher volume entered the cell during a given time interval. Higher flowrates resulted in a higher downflow velocity, thus preventing the rise of even bigger bubbles to the top of the flotation cell. This effect was apparent at a flowrate of 1500 ml/min. The downflow velocity of the algae solution was about 2.6 cm/sec. Assuming a size distribution of bubbles of 25 to 100 micron in diameter, the rising velocity would be between 0.34 and 5.4 cm/sec. Only a small percentage of bubbles, namely bubbles with a diameter of 70 microns or bigger, have a buoyancy force that can overcome this downflow velocity and show up as a froth layer at the top, even at the lowest volume ratio used. No carryover should take place at a flowrate of 200 ml/sec, resulting in a downflow velocity of the algae solution of 0.35 cm/sec. Diffusion of surfactant molecules from the shell of a CGA to the bulk solution is probably responsible for surfactant loss in the effluent during operation at such low flowrates.

Comparison of dissolved air flotation with CGA flotation is only valid when the volume of air for flotation is equivalent in both processes. Dissolved air will make up for approximately 7.5 percent of the total volume at a pressure of 50 psi and 22 °C. A volume ratio of 0.1 will provide about the same amount of air via CGAs. The quality of CGAs generated with CPCl was in the range of 73 to 75 percent of air in the total volume. CGA flotation is very effective for algae removal at this volume ratio but has limitations with respect to TOC reductions. Dissolved air flotation has, of course, less limitations with repect to minimum TOC values, since no additional

organic matter is involved in the process. CGA flotation achieved better removal of *Chlorophyll a*, comparing the results of Figure 12 through 15 to Figure 9. Both methods removed TSS to a similar extent. Removal of algae will vary with influent algae concentrations for both applications.

Suggestions for improvements of "pure CGA flotation" include use of a shorter column to reduce contact time of CGAs with algae solution, use of a skimmer to prevent algae flocs from falling back into the solution and operation at reduced flowrates as well as reduced volume ratios. A trough construction should be applied in case CGA flotation is combined with alum flocculation. Design criteria should focus on the reduction of surfactant uptake by the bulk solution.

The influence of the surfactant on the algae-froth mixture should be explored. Results of this investigation indicate a decrease of algal quality in the presence of higher concentrations of cationic surfactant. *Pheophytin a* concentrations are higher for some raffinates at a flowrate of 1500 ml/min than for the corresponding reading for the influent algae solution. Biological activity of activated sludge microorganisms in waters where CPCl was present at a concentration similar to the one found in the raffinate indicate CPCl exhibited biocidal and biostatic properties, even at such low concentrations. Presence of surfactant in water also reduced the oxygen transfer from air into the liquid, since the surfactant molecules tend to accumulate at the liquid/gas interface. CPCl is biodegradable, however it did not degrade within a short period of time. Sheets[42] performed BOD_5 tests on CPCl, and did not detect any degradation. The theoretical oxygen demand of a 10 mg/l CPCl solution is 28 mg/l, and approximately the same amount was taken up in this study. The presence of the cationic surfactant resulted in a 25 percent inhibition of bioactivity during the first three days. No negative effects on the bioactivity can be expected after four days. Future investigations should focus on the use of a less harmful surfactant and substantially reduced volume ratios.

6.0 CONCLUSIONS

The results presented and discussed in the previous sections allow the following conclusions to be drawn:

1. Separation of algae from growth media can be successfully achieved by CGA flotation using a cationic surfactant for generation of CGAs. Separation was not achieved using anionic and non-ionic surfactants.

2. Pretreatment of algal solutions by alum flocculation increases the separation efficiency of a CGA flotation process using a cationic sufactant.

3. Pretreatment of algal solutions by alum flocculation also yields successful separation of algae from growth media using anionic and non-ionic surfactants for CGA generation. Removal efficiencies are similar to those processes where cationic surfactants are used.

4. The separation of algae from growth media is enhanced by higher volume ratios of CGAs to algal solution.

5. Volume ratios can be significantly reduced without substantial negative effects on the separation performance in countercurrent continuous flow processing, as compared to batch processing.

6. The froth formed is sufficiently stable to keep the floated algae from sinking back into the bulk solution.

7. Applications of CGA flotation for algae separation and harvesting are mostly limited by the presence of surfactant in the raffinate.

8. The cationic surfactant Cetyl Pyimidinium Chloride will inhibit microbial activity of activated sludge, as measured by oxygen uptake, at concentrations similar to those found in the raffinate of these experiments.

BILIOGRAPHY

1. Kumar, H. D. and Singh, H. N., **A Textbook on Algae.** The MacMillan Press Limited (1979).

2. James M. Montgommery, Consulting Engineers, **Water Treatment and Design.**, John Wiley & Sons, Inc. (1985).

3. Shelef, G., Moraine, R. and Sandbank E., Physico-chemical treatment of pond effluents for unrestricted agricultural reuse with recovery of algae as protein source: Pilot and field scale experiments. **Progress in Water Technology 1-2** (10):231-246 (1978).

4. Bare, W. F. Rance, Jones, Norman B. and Middlebrooks, E. Joe, Algae removal using dissolved air flotation. **Journal Wat. Poll. Control Fed. 47** (1):153-169 (1975).

5. Becker, E. W., and Heussler, P., Foreword. In **Arch. Hydrobiol. Beih. Ergebn. Limnol. 20**:V-VI (1985).

6. Klute, R.and Neis, U., Coagulation of algae and subsequent removal by filtration or flotation. **Water Supply 1** (1):157-162 (1983).

7. Zabel, T., Advantages of dissolved air flotation for water treatment. **Journal AWWA 77** (5):42-46 (1985).

8. Lawler, D. L., Removing particles in water and wastewater. **Environ. Sci. Technol. 20** (9):856-861 (1986).

9. Benemann, J., Koopman, B., Weissman, J., Eisenberg, D. and Goebel, R., Developement of microalgae harvesting and high-rate pond techniques in California. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, pp. 457-495 (1980).

10. Friedman, A. A., Peaks, D. A. and Nichols, R. L., Algae separation from oxidation pond effluents. **Journal Wat. Poll. Control Fed. 49** (1):111-119 (1977).

11. Heusler, P., Development and results of the Peruvian-German Microalgae Project. **Arch. Hydrobiol. Beih. Ergebn. Limnol. 20**:1-8 (1985).

12. Horstman, U., The use of microculture in aquaculture. **Arch. Hydrobiol. Beih. Ergebn. Limnol. 20**:153-156 (1985).

13. Shelef G., High-rate algae ponds for wastewater treatment and protein production. **Water Science and Technology 14** (1-2):439-452 (1982).

14. Benemann, J. R., Weissman, J. C., Koopman B.L. and Oswald W. J., Energy production by microbial photosynthesis. **Nature 268**:19-23 (1977).

15. Lincoln, E. P., Resource recovery with microalgae. **Arch. Hydrobiol. Beih. Ergebn. Limnol. 20**:25-34 (1985).

16. El-Fouly, M., Abdalla, F. E., El-Baz, F. K., Experience with algae production within the Egypto-German Microalgae Project. **Arch. Hydrobiol. Beih. Ergebn. Limnol. 20**:9-15 (1985).

17. Dilov, C., Georgiev, D. and Bozkova, M., Cultivation and application of microalgae in the Peoples Republic of Bulgaria. **Arch. Hydrobiol. Beih. Ergebn. Limnol. 20**:35-38 (1985).

18. Soong, P., Production and development of *Chlorella* and *Spirulina* in Taiwan. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, pp. 97-113 (1980).

19. Fox, R. D., The cultivation of *Spirulina* as part of an integrated village health system. **Arch. Hydrobiol. Beih. Ergebn. Limnol. 20**:17-24 (1985).

20. Shelef, G. and Soeder, Introduction. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, p. x (1980).

21. Venkataraman, L. V., Nigam, B. P., and Ramanathan, P. K., Rural oriented fresh water cultivation and production of algae in India. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, pp. 81-95 (1980).

22. Van Vuuren, L. R. S. and Van Duuren, F. A., Removal of algae from wastewater maturation pond effluents. **Journal Water Poll. Control Fed. 37**:1256-1262 (1965).

23. Lincoln, E. P. and Hill, D.T., An integrated micro-algae system. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, pp. 229-244 (1980).

24. Levin, G. V., Clendenning J. R., Gibor, A. and Bogar, F. D., Harvesting algae by froth flotation. **Applied Microbiology 10**:169-175 (1965).

25. Goluek, C. G. and Oswald, W. J., Harvesting and processing sewage-born planctonic algae. **Journal Water Poll. Control Fed. 37**:471-498 (1965).

26. Mohn, F. H., Experiences and strategies in the recovery of biomass from mass cultures of microalgae. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, pp. 547-571 (1980).

27. Koopman, B. and Lincoln, E. P., Autoflotation harvesting of algae from high-rate pond effluents. **Agricultural Wastes 5** (4):231-246 (1983).

28. Moraine, R., Shelef, G., Sandbank, E., Bar-Moshe, Z. and Shvarzburd, L., Recovery of sewage borne algae: flotation, and centrifugation techniques. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, pp. 531-545 (1980).

29. Berk, Z., Thermal dewatering of algal slurries. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, p. 576 (1980).

30. Sorgeloos, P., Potential of converting microalgae into brine shrimp *Artemia*. **Arch. Hydrobiol. Beih. Ergebn. Limnol. 20**:147-149 (1985).

31. Becker, E. W. and Venkataraman, L. V., Production and processing of algae in pilot plant scale experiences of the Indo-German project. **Arch. Hydrobiol. Beih. Ergebn. Limnol. 20**:35-50 (1985).

32. Oswald, W. J., Algal production-problems, achievements and potential. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, pp. 1-20 (1980).

33. Castillo S., J., Merino M., F. and Heussler, P., Production and ecological implications of algae mass culture under Peruvian conditions. In **Algae Biomass, Production and Use**, ed. Shelef, G. and Soeder, C., Elsevier/North Holland Biomedical Press, New York, pp. 123-134 (1980).

34. Honeycutt S. S., Wallis, D. A., Sebba, F., A technique for harvesting unicellular algae using colloidal gas aphrons. **M. S. Thesis, Virginia Tech**, Blacksburg, Va. (August 1983).

35. Sebba, F., Microfoams - An unexploited colloidal system. **Journal of Colloidal and Interface Science 35**:643-646 (1971).

36. Sebba, F., Investigation of the modes of contaminant capture in CGA (MGD) foams, **U.S. Department of Interior, Office of Water Research and Technology**, OWRT/RU-82/10 (1982).

37. Sebba, F., An improved generator for micron-sized bubbles. **Chemistry and Industry** 3:91-92 (1985).

38. **Standard Methods for the Examination of Water and Wastewater, Sixteenth Edition.** , American Public Health Association, Washington D.C. (1985).

39. Swisher, R. D., **Surfactant Biodegradation**, Marcel Dekker, Inc., New York (1970).

40. Hach Chemical Company, **6 Bottle Manometric Apparatus Model 2173B Manual** (1977).

41. Sebba, F. and Alexander, S. F. and De Moor, T., Use of colloidal gas aphrons in treatment of Florida Slimes. **Florida Institute of Phosphate Research**, Project 82-02-027 (1982).

42. Sheets, W. D. and Malaney, G. W., The COD values of syndets, surfactants and builders. **Perdue Conf. 11**:185-196 (1956).

Appendix

Table 4. Raw Data for Dissolved Air Flotation Studies.

Time Study

	TOC	Chlorophyll a & Pheophytin a	Pheophytin a	TSS
Time Pressure Applied min	mg/L	mg/m^3	mg/m^3	mg/L
0	23.1	52.0	10.4	20
5	16.2	17.3	8.6	10
15	15.9	15.8	9.0	10
30	15.4	15.4	7.9	6
60	12.3	17.7	12.1	9

Influent Concentration Study

TOC		Chlorophyll a & Pheophytin a		Pheophytin a		TSS	
mg/L		mg/m^3		mg/m^3		mg/L	
Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
11.6	6.1	30.8	13.5	4.4	6.3	15	2
21.0	16.3	42.8	13.9	9.2	7.1	18	3
18.2	15.5	72.6	22.1	15.8	12.0	26	6
26.4	19.7	144.6	49.0	32.7	17.3	49	15
48.7	19.5	269.6	83.9	54.1	41.9	102	26

Table 5. Raw Data for Preliminary Continuous Flow Studies.

Continuous Flow Performance Study, Volume Ratio 0.02, Surfactant CPCl (0.7 mg/L)							
Flow Rate							
200 ml/min		350ml/min		880 ml/min		1500 ml/min	
Volume Passed Liter	TOC mg/L	Volume Passed Liter	TOC mg/L	Volume Passed Liter	TOC mg/L	Volume Passed Liter	TOC mg/L
0.0	29.4	0.0	40.0	0.0	23.5	0.0	25.7
.100	23.3	.100	20.9	.300	21.2	.300	22.1
.200	22.3	.300	36.3	.500	22.8	.600	23.2
.300	20.5	.500	39.3	.750	17.5	1.000	21.0
.400	19.2	.700	16.6	1.000	18.7	1.250	20.5
.500	23.7	1.000	17.2	1.250	17.2	1.500	20.1
.600	20.5	1.200	16.4	1.500	17.2	1.800	20.3
.700	19.5	1.500	14.8	1.750	16.9	2.300	20.1
.800	23.0	1.700	15.1	2.000	17.1		
.900	22.4	2.300	14.3	2.300	17.2		
1.000	13.5						
1.100	12.6						
1.200	12.8						
1.300	10.8						
1.500	10.7						
1.800	10.1						
2.000	10.2						
2.300	10.3						

Sufactant Uptake by Tapwater				
Volume Ratio	0.01	0.02	0.05	0.10
Flow Rate ml/min	TOC mg/l	TOC mg/l	TOC mg/l	TOC mg/l
0.0	3.0†	3.0†	3.0†	3.0†
0.01	-	4.5	7.0	10.4
0.02	3.5	5.3	8.2	10.2
0.05	5.6	7.2	10.8	11.7
0.1	6.5	7.3	12.4	16.5

† background TOC of tap water

Table 6. Raw Data for Continuous Flow CGA Flotation Studies (Flowrate Study).

CGA Flotation Using CPCL (0.7 mg/L) for Generation of CGAs, Flowrate 200 ml/min.

	TOC	Chlorophyll a & Pheophytin a	Pheophytin a	TSS
	mg/L	mg/m^3	mg/m^3	mg/L
Influent Conc.	29.4	78.5	18.1	30
Volume Ratio				
0.02	11.4	27.8	19.3	13
0.05	10.5	25.6	18.2	10
0.1	10.9	11.8	8.8	5

CGA Flotation Using CPCL (0.7 mg/L) for Generation of CGAs, Flowrate 350 ml/min.

	TOC	Chlorophyll a & Pheophytin a	Pheophytin a	TSS
	mg/L	mg/m^3	mg/m^3	mg/L
Influent Conc.	25.2	149	27.9	26
Volume Ratio				
0.01	13.1	25.9	14.3	16
0.02	9.2	17.3	10.8	14
0.05	10.7	8.7	6.8	11
0.1	10.8	9.6	7.9	6

Table 7. Raw Data for Continuous Flow CGA Flotation Studies (Flowrate Study Contiued).

CGA Flotation Using CPCL (0.7 mg/L) for Generation of CGAs, Flowrate 880 ml/min.

	TOC	Chlorophyll a & Pheophytin a	Pheophytin a	TSS
	mg/L	mg/m^3	mg/m^3	mg/L
Influent Conc.	23.5	30.6	5.8	22
Volume Ratio				
0.01	18.7	4.1	2.9	23
0.02	17.1	3.8	2.9	9
0.05	17.3	3.7	2.8	7
0.1	19.0	3.4	3.0	7

CGA Flotation Using CPCL (0.7 mg/L) for Generation of CGAs, Flowrate 1500 ml/min.

	TOC	Chlorophyll a & Pheophytin a	Pheophytin a	TSS
	mg/L	mg/m^3	mg/m^3	mg/L
Influent Conc.	25.7	52.0	10.4	23
Volume Ratio				
0.01	20.5	36.6	25.5	14
0.02	20.1	38.4	31.0	15
0.5	19.8	21.2	15.7	12
0.1	20.0	14.4	10.9	9

Table 8. Raw Data for Continuous Flow CGA Flotation Study (Concentration Study).

Influent Concentration Study							
TOC		Chlorophyll a & Pheophytin a		Pheophytin a		TSS	
Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
19.2	8.3	22.6	3.3	16.8	6.7	6	2
13.5	10.6	35.6	5.0	22.1	8.9	14	2
14.5	10.0	101.4	17.3	66.8	23.8	38	4
18.7	11.6	211.5	38.1	146.6	47.9	80	8
28.3	13.4	300.0	58.0	186.0	71.1	122	12

Table 9. Raw Data for Biological Activity Study.

O_2 Uptake				
Time	Control 1	Sample 1	Control 2	Sample 2
Days	mg/L	mg/L	mg/L	mg/L mg/L
0	0	0	0	0
.7	20	16	18	16
1.7	48	38	43	38
2	64	46	55	48
3	78	53	66	54
3.5	88	57	75	58
4.0	97	63	86	68
4.5	111	67	96	73
5.0	122	75	100	81
5.5	130	83	116	93
6.0	140	94	122	102
6.5	145	100	126	110
7.0	153	108	134	119
7.5	159	127	140	126
8.0	164	137	147	134
8.5	170	146	153	141
9.0	175	163	161	153
10.0	180	170	163	161
10.5	181	174	165	167
11.0	185	184	169	183
11.5	187	192	171	194
12.0	189	198	173	202
12.5	192	203	175	208
13.5	193	206	176	211
14.5	201	216	182	219
15.5	201	218	182	220
16.5	201	218	182	219
17.5	201	218	182	219
18.5	201	218	182	219

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