

TABLE 4. Weekly maximum air temperatures °F at eight locations along an elevational gradient in the Rattlesnake Hills 1967.

Date	Sites							
	1	2	3	4	5	6	7	8
4/17	78	76	77	73	70	60	66	60
4/24	80	76	76	78	71	78	63	61
5/1	77	74	77	74	73	58	66	64
5/8	88	87	86	84	81	72	74	73
5/15	98	94	93	91	89	78	79	76
5/22	107	107	105	103	98	92	91	88
5/29	100	100	99	96	92	—	82	82
6/5	98	99	98	96	95	82	80	78
6/12	102	102	102	97	96	84	84	80
6/19	114	109	109	108	104	99	96	93
6/26	113	112	104	106	106	102	98	95
7/3	112	112	111	112	106	101	100	98
7/10	116	116	114	116	111	105	96	100
7/17	117	118	116	116	112	106	100	102
7/24	110	112	110	110	106	103	99	96
7/31	112	112	110	110	106	96	96	96
8/7	112	112	110	112	106	101	99	97
8/14	116	114	114	116	111	116	102	100
8/21	119	118	116	117	114	108	106	105
8/28	107	110	106	106	104	96	97	95
9/5	114	113	112	112	110	94	96	100
9/11	105	102	-----	102	100	-----	-----	91
9/18	103	102	100	100	98	96	95	90
9/25	106	104	103	101	100	89	92	91
10/2	101	98	96	95	95	-----	-----	78
10/9	84	85	85	85	82	76	82	79
10/16	83	85	84	73	80	70	74	73
10/23	79	79	76	76	76	55	57	68
10/30	68	72	71	69	67	63	64	61
11/6	82	84	81	79	77	76	68	67
11/13	67	68	65	63	60	50	57	58
11/20	66	65	62	65	65	59	60	53
11/27	67	67	66	67	64	-----	60	58
Average	97.0	96.5	94.8	94.2	91.7	85.0	83.2	82.0

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Froth Flotation for Harvesting *Chlorella* Algae

In recent years, considerable research has been directed toward finding a feasible method for the mass harvesting of unicellular algal suspensions. The benefits of such an economical process would be tremendous in the area of food production, as algae have a high protein value. Nutrient removal and recovery would be an added benefit because algae have a high nitrogen-phosphorus composition. Many methods have been investigated, including dissolved-air flotation, flocculation and sedimentation, and centrifugation. Thus far, however, none of these methods has proven economically feasible, especially when an end product suitable for human or animal consumption was desired.

This study was initiated to investigate the possibility of using froth flotation as a method of algal harvesting and was carried out in conjunction with a dairy waste project being conducted at Washington State University's Knott Dairy Farm. The dairy waste project involves various methods of treatment of dairy manure wastes. The final treatment step consists of a polishing lagoon in which *Chlorella vulgaris* is the dominant algal form. The influent to this pond is rich in nutrients which become concentrated in the algae cells. Removal of the algae would be highly desirable since their discharge into any receiving water would constitute a significant organic loading on the stream. The additional benefit of algae harvesting could then be realized by the use of the recovered product as an animal food or crop fertilizer, thus creating a semi-closed nutrient system.

In the initial study, water samples containing the algae were brought to the laboratory and tested. These samples were observed to froth quite readily, probably as a result of a natural frothing agent produced by the *Chlorella vulgaris* itself.

Later, the effects upon harvest efficiency by the variation of certain parameters such as (1) pH, (2) temperature, (3) addition of a frothing agent and (4) frothing dosage were investigated.

Mechanism of Froth Flotation

Froth flotation is a highly complex phenomenon involving numerous parameters. These parameters include concentration of material to be frothed, temperature, oxygen content of the solution, types of frothers and their concentrations, and pH. Although mineral froth flotation has been practiced for over fifty years, it is still regarded by many workers as an art rather than a science.

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Several theories have been presented to explain froth flotation. However, the simple mechanism shown in Figure 1 has found general acceptance in the mineral processing industry. A long-chained, monomolecular, dipolar hydrocarbon coats the particle in suspension. The hydrocarbon then links to the air bubble. Thus, the particle is attached to the air bubble.

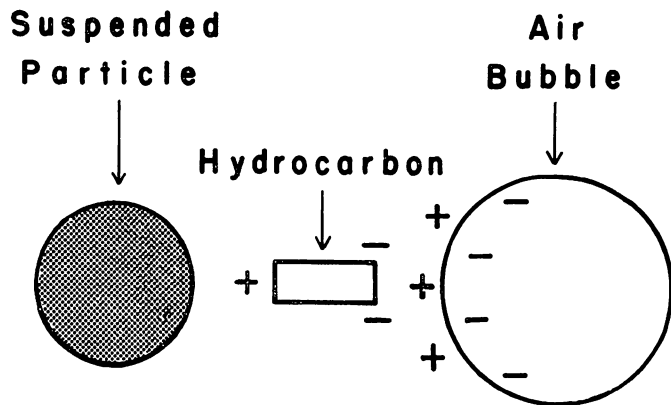


Figure 1. Possible froth flotation mechanism.

Materials and Methods

Algae culture

The algae to be harvested were obtained from the dairy waste lagoon just before the tests were to be made (1 to 3 hours). Preliminary investigation had shown that there was little difference between the harvesting efficiencies of lagoon cultures compared to the harvest efficiencies of laboratory grown *Chlorella vulgaris* when harvesting conditions were equated.

Froth flotation apparatus

The froth flotation apparatus is shown in Figure 2. Frothing was accomplished by using a Wemco-Fabergren Mineral Tester. This laboratory-scale device is used for mineral separations by froth flotation. It was equipped with a 2600 ml capacity Pyrex bowl with an overflow lip approximately 14 cm wide. A small pan was placed under the lip to collect the froth overflow. A Reliance tachometer was attached and all tests were run at 3500 rpm impeller speed. Air was introduced into the bowl through the impeller shaft, and a valve attached to the stationary shaft of the unit controlled the air introduced into the test sample. The impeller had a vigorous mixing and shearing effect creating small bubbles in large volume.

pH adjustment

For high and low pH levels, 3N sodium hydroxide and 3N hydrochloric acid were added respectively. Measurements of pH were made with a Beckman portable pH meter.



Figure 2. Froth flotation apparatus.

Temperature adjustment

Temperatures were adjusted by utilizing refrigeration, a variable temperature room, and, in some instances, a hot plate.

Frothing agents

Various frothing agents and coagulants including pine oil, sodium oleate, oleic acid, linoleic acid, sodium chloride and ferric sulfate were tested in preliminary investigations. However, only sodium oleate appeared to be of any value. Sodium oleate was tested at various concentrations at normal pH and at 1 ppm at various pH values.

Harvesting procedure

The sample to be tested was poured into the frother bowl. The machine was then started with the air valve closed. This provided highly turbulent mixing, but no intro-

duction of air. Chemical addition and pH adjustment, in that order, were performed. Next, the air valve was opened to allow frothing to occur. The froth produced overflowed into the collecting pan. A small scraper was used to help move the froth to the overflow lip. When frothing ceased or the bubble load appeared nil, the operation was discontinued. After the froth returned to liquid, the volume of overflow was noted. Also, time was recorded from the start of the frothing until the overflow returned to a liquid. Samples of both the overflow and the original algal solution were taken for analysis. Total Kjeldahl nitrogen was used as an indicator of algae removal (Standard Methods, 1965). The bowl and impeller were thoroughly cleaned and rinsed after each test to prevent carryover of chemicals to the next batch.

Results and Discussion

Preliminary investigation

Before any intensive work was undertaken with any specific frothing agents, several compounds were investigated. These chemicals are in widespread use in the mineral processing industry as frothing agents. Compounds such as xanthates were eliminated from consideration due to their toxicity, odor, or other such undesirable characteristics. Oleic acid, sodium oleate, pine oil, sodium chloride, linoleic acid and ferric sulfate were tested in several batches both separately and in combination. The pH was also varied. Oleic acid, and linoleic acid destroyed the natural frothing of the culture at all pH values. Pine oil, sodium chloride, and ferric sulfate had no effect upon the natural frothing; however, sodium oleate appeared to increase the bubble load of the froth. For these reasons, sodium oleate was the only compound extensively investigated in subsequent tests.

Effect of pH on harvesting

In the first tests, harvesting efficiency versus pH with no chemical addition was investigated. The overflow bubble characteristics at high and low pH values were markedly different from those at natural pH (9.2) and 7.0. At high and low pH, the bubbles were very large and did not collapse readily as indicated by the total time of the frothing operation. At pH 9.2 and 7.0, frothing occurred quite rapidly. The bubbles were relatively small and returned to the liquid form fairly rapidly.

The largest percentage of total nitrogen removed occurred at a pH of 3.0 with 75.2 per cent removal, as shown by Figure 3.

Effect of temperature on harvesting

Four samples each were tested at 10, 15, 20, and 25°C. In these experiments the natural pH was 9.8. As indicated by Figure 4, the per cent of nitrogen removal varied only slightly. Temperature had essentially no effect on harvesting efficiency.

Effect of frother on harvesting

Sodium oleate in varying concentrations was investigated as a method of improving flotation. The greatest nitrogen reduction occurred at a frother concentration of 2.5 ppm. The natural pH 9.5 was used in this series of tests (Figure 5).

In later experiments, 1.0 ppm of sodium oleate was added to each batch and the pH of the algal solution was varied. As occurred at previous pH values, the froth characteristics were best at, or near, natural pH (9.8), as shown in Figure 6.

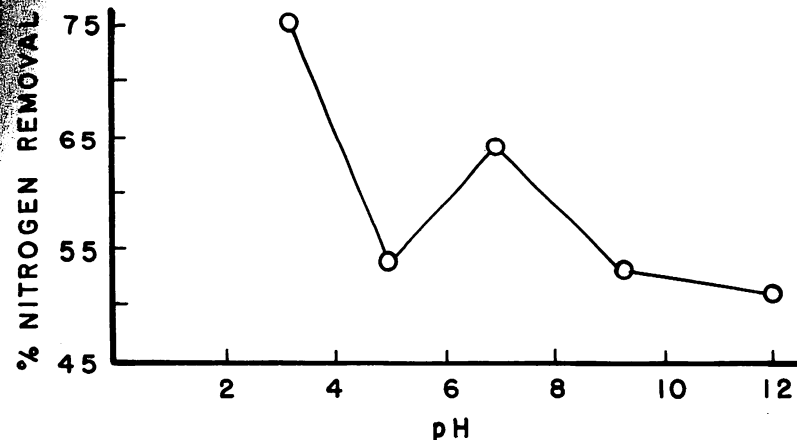


Figure 3. Nitrogen removal as a function of pH.

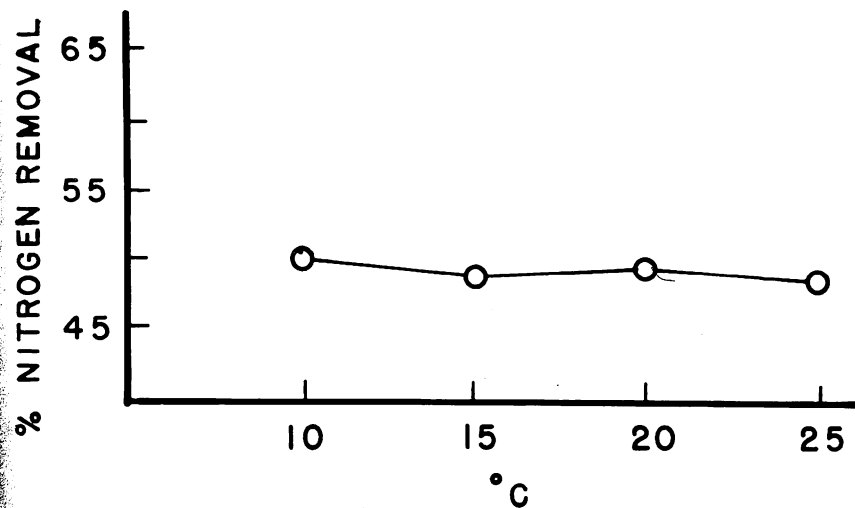


Figure 4. Nitrogen removal as a function of temperature.

Multiple flotations

A series of three flotations were performed at natural pH, 9.5. The froth of the first stage was the influent of the second, etc.

The removal of nitrogen of each stage based on the influent to that stage was 55.3, 54.0, and 60.9 per cent respectively for the first, second, and third stages. Overall removal based on the original algal solution was 55.4, 29.9, and 18.2 per cent for the first, second, and third stages respectively. The concentration of the algal solution increased after each frothing operation, and after three stages the nitrogen concentration was 270.2 mg/l compared to 84.0 mg/l for the original solution.

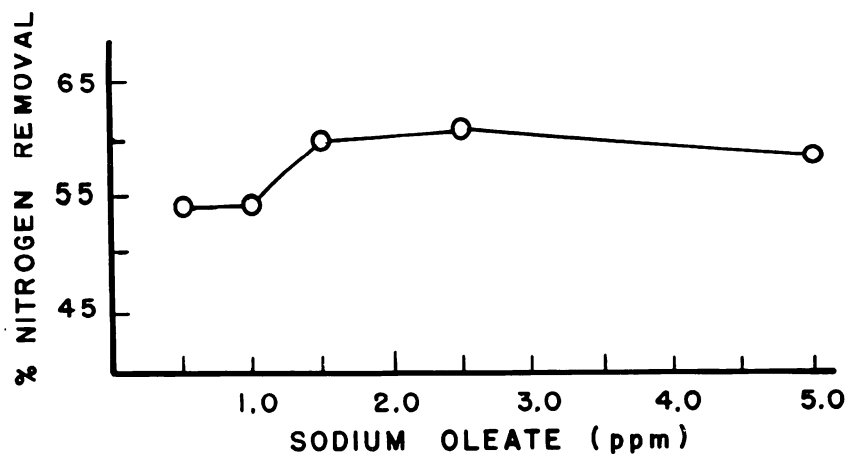


Figure 5. Nitrogen removal at a pH of 9.5 as a function of sodium oleate concentration.

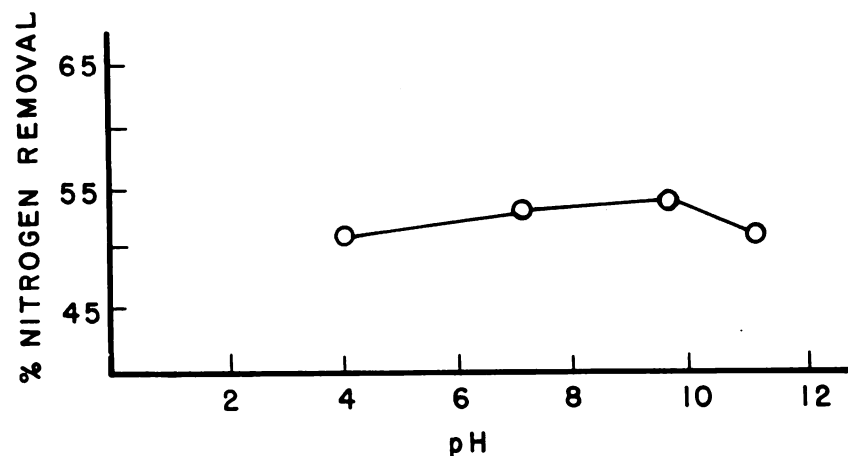


Figure 6. Nitrogen removal with 1 ppm sodium oleate as a function of pH.

Economic Considerations

Levin and Barnes (1964) estimated the cost of a different harvesting procedure based on the recovery of 0.5 per cent solids content in the froth harvested. Since this is the approximate yield that could be expected, their figure of \$75.00 per ton could be applied to this process. However, their cost of chemicals was above \$50.00 per ton, and taking into consideration the costs of drying, a figure of \$70.00 per ton total cost would be unreasonable.

Conclusions

The pH was found to have a significant effect on both the efficiency of the frothing operation and the froth characteristics. At high and low pH values, the froth was very

stable and took a relatively long time to collapse. At or near natural pH, frothing time was short and bubble collapse took place quite rapidly. It was concluded that temperature had no effect on the frothing operation.

With the addition of sodium oleate, frothing of the algal solution increased. Total nitrogen removal remained about the same as with no chemical addition. The maximum removal efficiency with sodium oleate occurred at natural pH, 9.5, in a concentration of one ppm. Frothing without any chemical additions produced the most efficient harvesting. Thus, the addition of sodium oleate, although improving the frothing characteristics, resulted in less process efficiency.

The results of multiple flotation showed that each stage removed approximately 50 to 60 per cent of the total nitrogen input to that stage. Single-stage frothing operation preceding another harvesting technique, such as centrifugation, also has definite possibilities for application.

No explanation can be offered for the failure of many widely used frothing agents. Oleic and linoleic acids are widely used in the mineral processing industry but were of no value when used in the algal suspension. However, frothers might not be expected to perform in an organic system as they do in an inorganic system, because as other workers such as Gaudin (1962) have pointed out: (1) microorganisms are much smaller than mineral particles, (2) the specific weight of the organism is close to that of the liquid itself, (3) bubble encounter is probably less likely because of the first two reasons, and (4) an organic system is constantly changing, making it difficult to balance frothing dosages.

The next step will be to undertake a pilot study actually to determine the feasibility of this process on a larger scale. This later study can also provide a base for a realistic economic evaluation.

Acknowledgments

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