Pergamon

Wat. Sci. Tech. Vol. 30, No. 8, pp. 259–267, 1994.

0273-1223(95)00006-2
0273–1223/94 $7·00 + 0·00

ALGAL FLOCCULATION-SEDIMENTATION BY pH INCREASE IN A CONTINUOUS REACTOR

H. Yahi*,**, S. Elmaleh* and J. Coma*

**Groupe de Génie des Procédés, Université Montpellier II, 34095 Montpellier Cedex 5, France*
***Institut de Chimie, U. S. T. H. B., Algiers, Algeria*

ABSTRACT

The effectiveness of microalgae flocculation by pH increase was investigated using the jar test procedure. The results indicated that pH values between 11.8 and 12 induced extensive flocculation without need of adding magnesium. pH was increased by sodium hydroxide or calcium hydroxide.In both cases, the total solids abatement was more than 95% producing sludge of excellent settleability and good mechanical resistance quantified by a destructive test. The next step was the operation of a continuous flocculator which might optionally be packed with granular sand or inert resin. It was shown that a fluidized bed or any other mechanical energy transfer device was not required to obtain more than 95% efficiency with a superficial upflow velocity of 30 m/h corresponding to a residence time through the whole unit of 5 minutes only.

KEYWORDS

Algae; flocculation; fluidized bed; oxidation pond; sedimentation.

NOMENCLATURE

A Absorbance
C_i Inlet concentration, ML^{-3}
G Velocity gradient, T^{-1}

INTRODUCTION

Upgrading of oxidation pond effluents by suspended solids removal has received important attention considering the potential economic value of microalgae and the probable development of high-rate ponds where the solids production is maximized. Moreover, considering the need of higher quality effluent from oxidation ponds, new European standards will request less than 30 mg/l total suspended solids. However, the solids–liquids separation is extremely difficult and most processes are relatively ineffective or require huge amounts of energy (Oswald, 1978).

Besides, a new process of algal flocculation in a fluidized bed has recently been proposed (Elmaleh *et al.*, 1991 ; Elmaleh *et al.*, 1992). The flocculation is induced by precipitation of magnesium hydroxide at pH values between 9.5 and 11.5. The required magnesium is provided by adding seawater or magnesium chloride or by a Mg^{++} liberating resin. The mechanical energy transferred to the suspension and a collection effect by the fluidized particles both enhance the formation of clusters.The clusters grow in a maturation zone above the fluidized bed and form a sediment in a multitubular settler. The extensive algal flocculation causes efficient solids abatement between 80 to 95% as the superficial upflow velocity is in the range of 7 to 30 m/h.

The purpose of this research is to test the effectiveness of flocculation by simple increase of pH without adding any magnesium, then to evaluate the potential of this flocculation in a continuous reactor which will not include a fluidized bed.

MATERIAL AND METHODS

Flocculators

Two units are operated, i.e., a Water Research Centre jar test and a continuous flocculator. The experimental procedure for the jar test runs is the following : 1 minute coagulation at G = 135 s^{-1} followed by 15 minutes flocculation at G = 35 s^{-1} and then 30 minutes settling.

The continuous flocculator is constituted by a cylindrical column which may be packed with sand or with an inert granular resin fluidized by the once-through flow of the suspension (Fig. 1 and Table 1). A 30° inclined settler is provided at the upper part of the column. The influent is admitted at the lower part of the reactor through a pipe oriented towards the bottom. A 5 N sodium hydroxide solution or, alternatively, a 50 g/l lime suspension is injected through a peristaltic pump which maintains pH constant owing to a feedback loop.

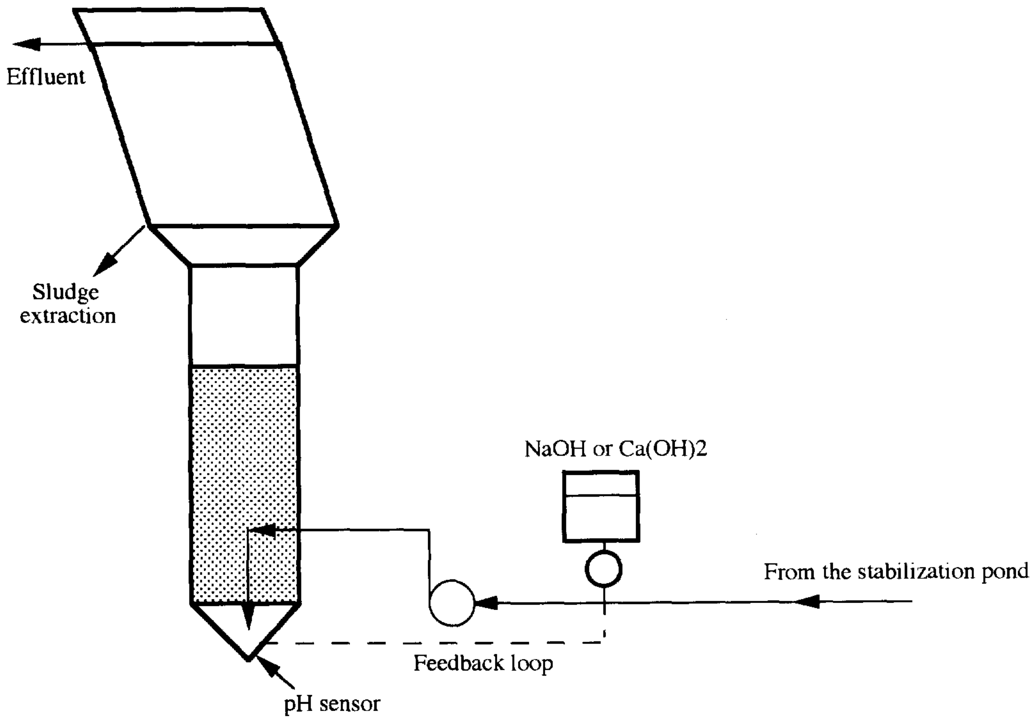

Fig. 1. Continuous flocculator.

TABLE 1. Characteristics of the Continuous Flocculator

Flocculator	Diameter, m	0.1
	Height,	2.1
	Cross-section area, m^2	0.0079
Settler	Lenth, m	0.28
	Width, m	0.24
	Height, m	0.65

TABLE 2. Main Characteristics of the Granular Media

	Resin	Sand
Type	Inert Duolite S5 TR	
Mean particle diameter, μm	800	250
Density of the material, kg/m3	1.17×10^3	2.65×10^3
Minimum fluidization velocity, m/h	2.3	2.4
Minimum fluidization velocity gradient, s^{-1}	40	120
Minimum fluidization Camp number	10^4	10^4

Inlet suspension

The suspension is directly pumped from the third and last stabilization pond of the Mèze, France, treatment plant. The pH remains between 8 and 9.5 while the suspended solids concentration is maximum in April reaching 1 g/l and minimum in January with 50 mg/l. As the continuous flocculation-sedimentation runs reach a steady state after a few minutes, the effluent variability does not induce any inconsistency in the experimental data.

Determinations

Suspended solids concentration is determined by measuring the 678 nm absorbance with a Roy 1201 spectrophotometer (Ayoub *et al.*, 1986). Absorbance is easily correlated to suspended solids concentration obtained in conformity with the Standard Methods (APHA, 1971). Solids abatement is quantified by:

$$E = \left(1 - \frac{\text{outlet solids concentration}}{\text{inlet solids concentration}}\right).$$

After a jar test run, the effluent concentration is defined as the supernatant concentration. In the continuous runs, the efficiency is directly derived from the concentration in the settler effluent.

Ca^{++} concentration and Mg^{++} concentration are determined by the EDTA titrimetric method.

RESULTS AND DISCUSSION

Jar test runs

The solids abatement is an increasing function of pH (Fig. 2).

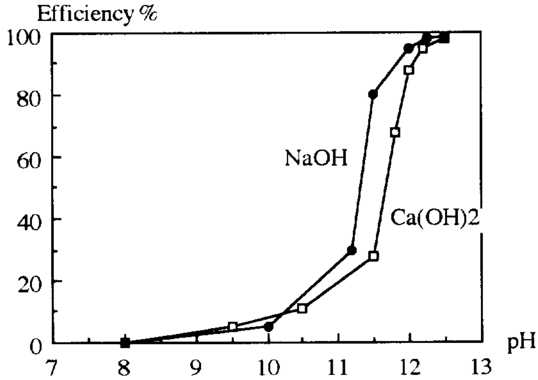

Fig. 2. Total solids abatement against pH. Ci=180 mg/l.

The flocculation is initiated at pH 10.5. At pH 12, a high efficiency plateau is reached where nearly all the measurable solids are eliminated. Mg^{++} concentration and Ca^{++} concentration decrease while the efficiency increases; the Mg^{++} abatement rate is however significantly higher (Fig. 3). Furthermore, it is worthwhile to notice that the flocculation becomes significant when the pH value is about the theoretical value of magnesium hydroxide precipitation, i.e., 11.3, while neglecting the suspension ionic strength (Alexeev, 1980). This result confirms the importance of magnesium hydroxide precipitation in the flocculation mechanism (Elmaleh *et al.*, 1991).

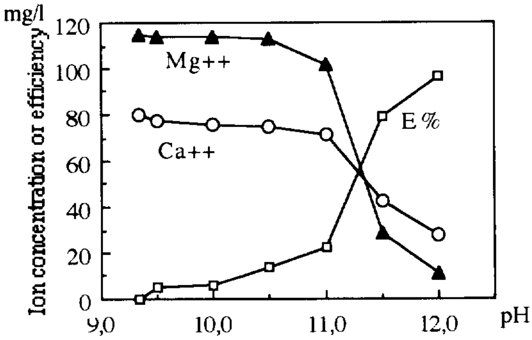

Fig. 3. Mg^{++} and Ca^{++} concentrations against pH. Ci=180 mg/l, pH increased by NaOH.

The solids abatement is slightly lower when pH is adjusted by lime instead of sodium hydroxide (Fig. 2). This is partly due to the difficult pH stabilization and regulation by lime whose solubility depends on the ions contained in the solution. Besides, it has been shown that $CaCO_3$ precipitation at a pH higher than 9.5 is not a predominant mechanism of the separation (Ayoub *et al.*, 1986 ; Elmaleh *et al.*, 1992).

The addition of seawater improves slightly the total solids abatement when pH is lower than 12 and seawater concentration under 40% (Fig. 4). This is in accordance with preceding results where it was concluded that seawater causes extensive algal flocculation at pH 11.5 (Elmaleh *et al.*, 1991). However when pH is higher than 12, no seawater is required. The effect is slightly more significant when pH is regulated by lime as seawater increases favourably the Mg^{++}/Ca^{++} ratio (Fig. 5). However, in both cases, microalgae flocculation is feasible by simple pH increase.

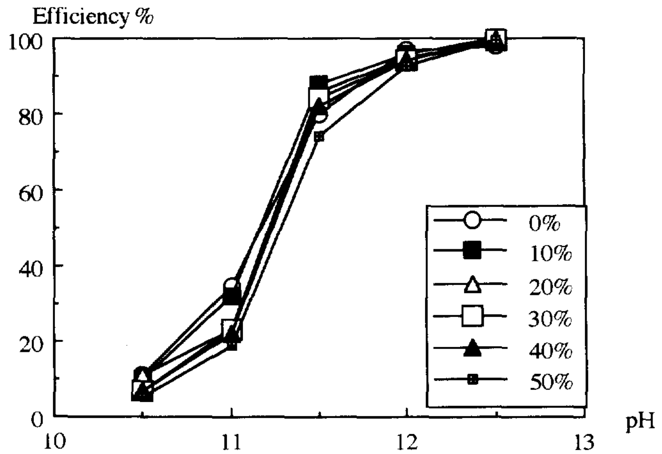

Fig. 4. Seawater concentration influence. Ci=180 mg/l, pH increased by NaOH.

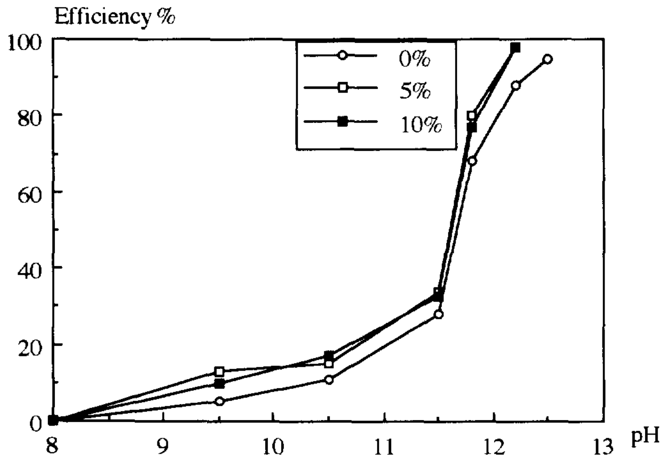

Fig. 5. Seawater concentration influence. Ci=180 mg/l, pH increased by lime.

The maximum settling velocity, obtained by following the Kynch procedure, increases with pH but decreases when seawater is added (Fig. 6). The floc mechanical resistance is tested by a destructive procedure derived from Jabbouri *et al.* (1989). After 10 minutes settling, the supernatant absorbance A_1 is measured. Then, mechanical energy is transferred by intense agitation in a jar test. After 10 minutes settling, the new supernatant absorbance A_2 is measured. The ratio A_2/A_1 quantifies the floc resistance. Values about 1 or slightly less than 1 mean a total resistance. All the flocs are totally resistant when velocity gradient is lower than 135 s^{-1} as displayed in Fig. 7 where the ratio A_{-2}/A_1 is plotted against G/G_0, G being the velocity gradient used in the destructive test and G_0 being a reference value, i.e. 35 s^{-1}.

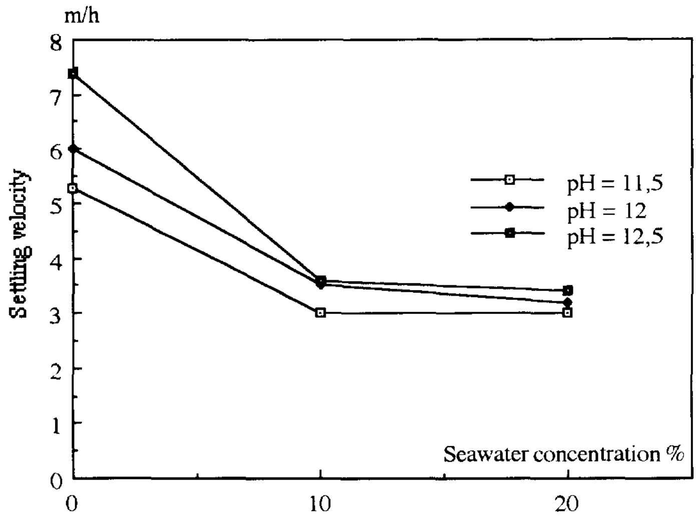

Fig. 6. Maximum settling velocity. pH increased by NaOH.

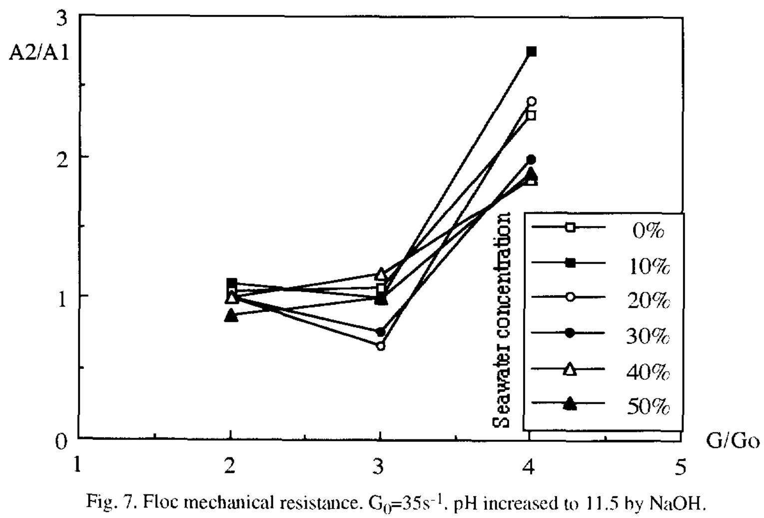

Fig. 7. Floc mechanical resistance. G_0=35s^{-1}. pH increased to 11.5 by NaOH.

As a matter of conclusion, the flocs formed by simple pH adjustment have higher settling velocity and are fairly resistant. In the following runs, no seawater will be added.

Continuous runs

The total solids abatement is more than 95 % and can be reached without fluidized bed (Fig. 8). The floc cohesion is so strong that the improvement by a fluidized bed is not significant. It is concluded that extensive flocculation can be induced at very low velocity gradient, e. g., in the empty column, therefore without the help of any mechanical energy transfer device; this result is due to the fact that the main process is the precipitation of magnesium hydroxide. The efficiency depends solely on pH value and is limited by the space time through the settler; however, even if the influent is low concentrated, the efficiency is significant and produces a high quality effluent (Fig. 9). The break point is about 30 m/h superficial upflow velocity through the flocculation column which is quite similar to the results obtained by injecting Mg^{++} into a fluidized flocculator (Elmaleh *et al.*, 1991 ; Elmaleh *et al.*, 1992). The mean residence time through the whole unit is then of 5 minutes only. Such good results must be taken into account with the low energy requirement quantified by the energy necessary to transport the suspension through a 2.75 m height empty column which means that the energy requirement is only 2.3 kWh per year. Besides, it is much easier to design and operate such an empty reactor than a fluidized bed. Furthermore, the need of a high pH value is not really a limitation. Upgrading of oxidation pond effluents is required during periods of high photosynthetic activity when high pH values, larger than 10.5, are commonly achieved (Friedman *et al.*, 1977). Moreover, the standard requires less than 30 mg/l suspended solids which can be reached by adjusting the pH between 11 and 11.5 (Fig. 10). The required base concentration is then 0.5 g/l of sodium hydroxide or 0.6 g/l of calcium hydroxide; this requirement depends on the ionic strength.

If the effluent needs to be neutralized before disposal, it could be conveniently done by simple air injection, the gaseous carbon dioxide will be absorbed and the pH decreased. If the water does not contain enough Mg^{++} nor Ca^{++}, it would be necessary to provide them by injecting seawater or any other source of these ions.

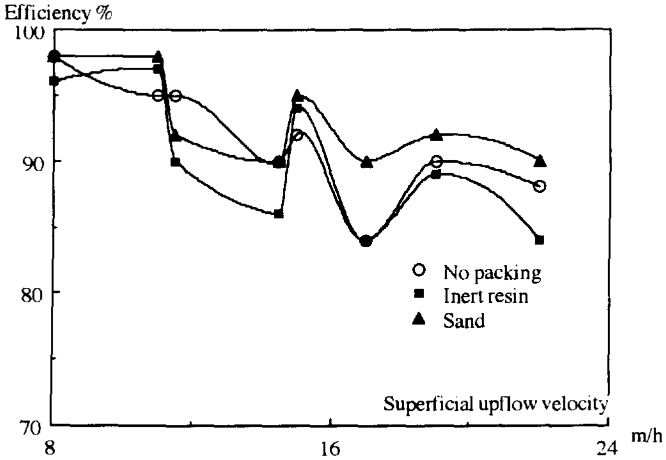

Fig. 8. Continuous flocculator efficiency, pH=11.5, fixed bed height=40cm, Ci=180mg/l, pH increased by NaOH.

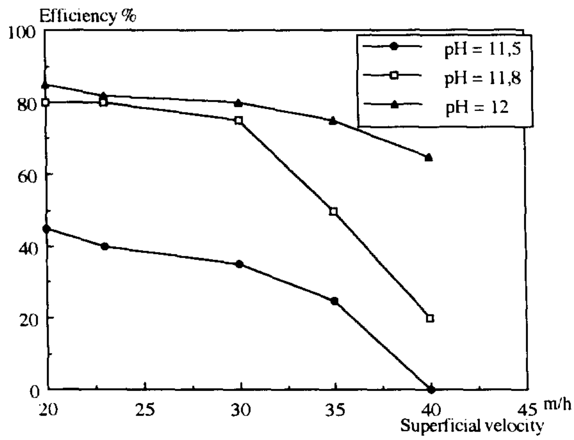

Fig. 9. Solids abatement through the empty column. Ci=60mg/l, pH increased by lime.

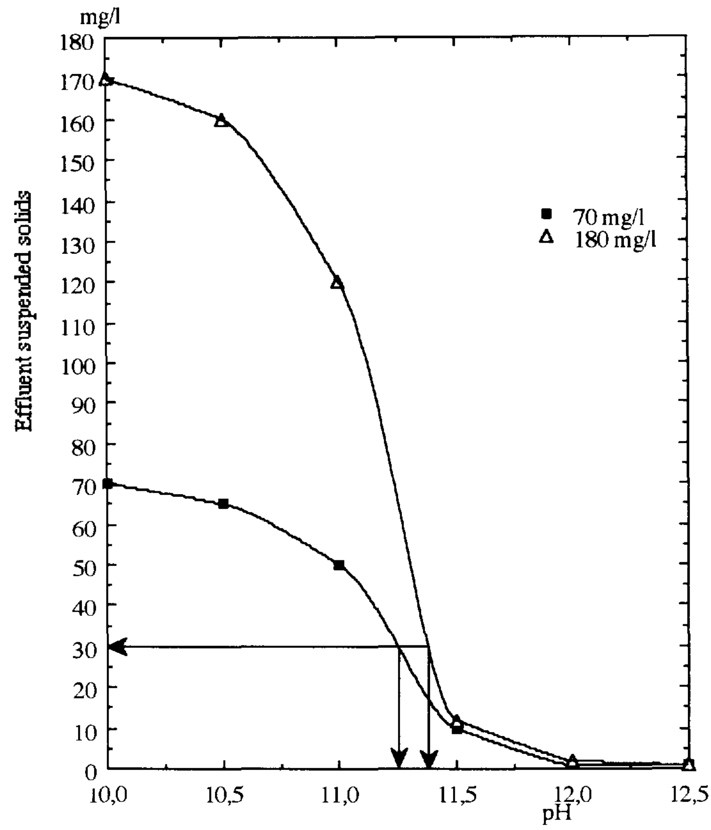

Fig. 10. Residual suspended solids concentration against pH.

CONCLUSIONS

(1) A high suspended solids abatement can be reached between pH values of 11.8 to 12 without adding any magnesium.

(2) The achieved extensive flocculation produces flocs of high settling velocity and excellent mechanical resistance.

(3) The process can be operated continuously without the help of a fluidized bed or any other mechanical energy transfer device.

REFERENCES

Alexeev, V. (1980). *Analyse Quantitative*. Editions Mir, Moscou.

American Public Health Association (1971). *Standard Methods for the Examination of Water and Wastewater.* American Public Health Association, Washington, DC.

Ayoub, M. G., Sang-Ill Lee and Koopman, B. (1986). Seawater induced algal flocculation. *Wat. Res.*, **20**, 1265-1271.

Elmaleh, S., Coma, J. and Borsato, J. (1992). Algal flocculation in a magnesium exchanger fluidized bed. *Wat. Sci. Tech.*, **26**, 1689-1696.

Elmaleh, S., Coma, J., Grasmick, A. and Bourgade, L. (1991). Magnesium induced algal flocculation in a fluidized bed. *Wat. Sci. Tech.*, **23**, 1695-1702.

Friedman, A. A., Peaks, D. A. and Nichols, R. L. (1977). Algae separation from oxidation pond effluents. *J. Wat. Pollut. Control Fed.*, **49**, 111-119.

Jabbouri, A., Elmaleh, S., Grasmick, A., Tréal, Y. and Coma, J. (1989). Caractérisation de la cohésion des flocs produits en lit fluidisé . *Env. Technol. Letters*, **10**, 167-172.

Oswald, W. J. (1978). The engineering aspects of microalgae. In : *CRC Handbook of Microbiology,* A.I. Laskins (Ed.), CRC Press, Boca Raton, pp. 519-552.