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EXPERIMENTS WITH EXTRACTS FROM CACTUS, ALOE AND MARINE ALGAE IN BRAZIL

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THE ROLE OF NATURAL POLYELECTROLYTES AS COAGULANT AIDS -
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ABSTRACT

The utilization of polyelectrolytes for flocculation of turbid waters improves settling rates and filter performance. The volume of sludge produced is much smaller and the treated water is less corrosive. However, the cost of synthetic polyelectrolytes are relatively high and many of them still present doubts with respect to potential long term negative health effects to consumers. On the other hand, natural polyelectrolytes extracted from native plants are shown to be as effective as their synthetic similars, less expensive and probably free of toxic compounds which may raise public health concern.

With the objectives of stimulating the development of natural polymers in tropical countries, assessing their efficiency on turbidity removal and determining the appropriate technical and operational procedures for their use as coagulant aids, an investigation was conducted with some selected Brazilian native plants.

Utilizing very simple extractive methods, coagulant solutions were prepared from "Opuntia Ficus Indica" ("Cactus da India"), "Alóes Vera" ("Babosa") and marine algae of the Sargassum species.

The coagulant solutions were tested in combination with commercial alum, and the optimum conditions for flocculation of a low turbidity water were determined through jar-testing and pilot plant studies.

The results obtained from the experiments demonstrated the ability of the tested polymers to improve turbidity removal and to reduce alum dosages when properly utilized as coagulant aids for water flocculation.

Tropical countries may consider the implementation of national programmes for the evaluation of the flocculant plants' potential as well as to develop appropriate methods for polyelectrolyte production and the conditions under which they can be effectively applied as coagulant aids for water clarification.

KEY WORDS

Natural polyelectrolytes, Coagulation-flocculation, Turbidity, Water treatment, Chemical treatment, Chemical products.

1. INTRODUCTION

The use of polyelectrolytes has been substantially increased during the last three decades to improve flocculation, sedimentation and filtration of drinking water, flocculation of wastewater as well as in the processes of elutriation, chemical conditioning and drying of domestic and industrial sludges.

A large array of commercial synthetic polyelectrolytes are now available including cationic, anionic and nonionic structures with molecular weight as high as 10^7 . Most of them are based on polyacrylamide and its copolymers with polyacrylic acid and on polyamines.

The use of polyelectrolytes in water treatment seems to have been started about 4 000 years ago. Some references in the Sanskrit literature refer to crushed nuts of a tree (Nirmali tree or Strychnos potatorum) which were used in India about 2 000 BC for water clarification. The coagulation effects provided by these nuts has been explained by the presence of some water soluble organic polymers^{1/}. Presently several organic compounds such as starch and starch derivatives, cellulose compounds, polysaccharide gums, and proteinaceous material are considered effective as coagulants or coagulant aids. These compounds are naturally occurring polyelectrolytes and can be referred to as biocolloids with ionizable sites. Jahn^{2/} provides a long list of natural coagulants occurring in seeds, sap of stems, banks, twigs, roots and tubes describing chemical compositions, traditional uses and coagulating properties.

2. OBJECTIVES

One of the main problems in water treatment is the excessive volume of sludge which accumulates in the sedimentation tanks. This constitutes an environmental hazard since the volume of sludge to be disposed of is much larger than the volume of solids coming in with the raw water due to the usual large amounts of coagulant added during the coagulation process. The use of polyelectrolytes will not only reduce the amount of sludge formed but will produce sludge with higher dewatering capacity, reducing both the ecological problems related to the final disposal and the operational costs of treatment plants.

However, most developing countries are not able to profit from these advantages because synthetic polymers need to be imported, are very expensive or because kinetics of flocculation is poorly understood to allow for their use in a sound and effective way.

On the other hand, in most tropical developing countries there exists a large variety of native plants capable of furnishing natural polymers to be utilized in water treatment without many of the inconveniences caused by its synthetic similars.

The general objective of this study is to stimulate tropical countries to analyze their potential to produce natural polymers and to establish the conditions under which they can be effectively applied as coagulant aids for water clarification.

The specific objectives were to study three of the most promising Brazilian native plants in order to:

- (a) determine the most simple and effective way to extract coagulant solutions from them;

- (b) determine the rate kinetics of flocculation of alum and the natural polymers in static reactors (jar test);
- (c) verify the efficiency of flocculation of the polymer solutions as coagulant aids in a continuous flow system.

3. PLANTS USED AND THEIR CHARACTERISTICS

After the screening tests performed with several Brazilian plants, it was decided to pursue the study with only the three most promising ones: Opuntia ficus indica ("Cactus"), Aloe vera ("Babosa") and marine algae from the group phaeophyceae, Sargassum spp.

3.1 OPUNTIA FIGUS INDICA

The "cactus" belong to the Cactaceae family, genus cactales (Opuntiales). They originated in the dry regions of North and South America, but now they can be found everywhere. In Australia, Cabo and South Africa the adaptation was so strong that eradication has been causing difficulties to the local authorities. In Brazil they can be found everywhere, mainly in the dry "caatinga" of the northeast and along the atlantic coast, (figures 1 and 2). The chemical composition of the "cactus" obtained after several extractions and purifications is basically the following:

- simple isokinolenic alkaloides made of: Analime, Analidine, Analimine, Analonidine, Carnegine, Gigantine, Lophacrine, O-metil-d-analonidine, Petotine, and Cafeine;
- mucilage, a kind of gelatinous substance which may confer to the "cactus" species their flocculant properties;
- betalaines as betacianines and betaxantines;
- other substances in smaller quantities as: saponines, triterpenes, organic acids, traces of fructose, glicose, sacarose, maltose and refinose;
- other organic acids as maleic, citric and isocitric (1 to 3% of dry weight);
- fatty oils (about 6,8% in seeds);
- polifenols as Kercetine and Kaemp phenol.

"Cactus" tissues are rich in gummy components which are excreted during hot and dry periods. By hydrolysis these components can furnish arabinose, xilose, galactose and galacturonic acid in the proportion of 6:2:3:1.

In rural Peru, the mucilage extracted from "cactus" leaves are utilized for domestic clarification of drinking water. Kirchmer et al. in a paper published by CEPIS - Centro Panamericano de Ingenieria Sanitaria y Ciencias del Ambiente, Lima, Peru, describe the use of coagulant aids extracted from "cactus" in water clarification^{4/}.

3.2 ALOE VERA

The Aloe belong to the Liliacea family which has about 180 different species. The most common are the following ones: Aloe Vera (A. vulgaris or A.

barbardesis), *A. chinensis*, *A. perryi*, *A. ferox* and *A. saponaria*. They originated from the arid regions of Africa, mainly the Cape Province. In Brazil the aloes are known as "babosa" and are cultivated as ornamental plants (figure 3).

The dry residue extracted from the leaves is called "aloe", which is composed of aloine and aloeharz. Aloine is a glico-aloemodinantrone as shown in figure 4:

The Aloeharz contain types of tannic residues, acetic acid and arabinose, according to the molecular structure shown in figure 5.

No reference has been found with regard to the use of aloe plants for preparation of coagulant solutions to be used for water clarification. Their inclusion in this experiment was due to the similarity between concentrated solutions of synthetic polyelectrolytes and the gelatinous substances liberated by the leaves of "babosa" when broken apart or cut.

3.3 BROWN SEAWEED, SARGASSUM SPP.

The marine brown algae from the phaeophycene group, *Sargassum* spp. is abundant along the coast of South and North America.

The Botanic Department, University of Sao Paulo, Brazil has been exploring the productivity of brown algae along the coast of Sao Paulo State (figures 6 & 7) in an extension of about 600 km^{5/}. The exploration of *Sargassum* spp. (*s. cymosum*, *s. stenophyllum* and *s. vulgare*) along the coast, will provide around 400 tons of algae every 6 to 8 months allowing for a production of sodium alginate of about 20 tons per year. Depending on the season, and on the depth of growth, the brown seaweed contains from 10 to 25% as dry weight of alginic acid.

The alginic acid, (C₆ H₈ O₆) is a polymer with molecular weight of about 240 000. It is formed by two monomers: acid poli-d-manuronic and acid poli-L-guluronic. These monomers are linked together as copolymers of the types (-M-)_m, (-G-)_m, (-M-G-)_m in the same molecule as shown in figure 8^{6/}.

The sodium alginate has a very small toxicity and is normally used as food additive (thickener and gelling agent) and in the pharmaceutical industry. The maximum acceptable daily intake (ADI) is 25 mg/kg of body weight as alginic acid^{7/}. If an average of 60 kg of body weight is assumed, 1.5 grammes will be allowed to be taken per person per day without causing adverse effects.

Several studies were made in England^{8/}, Peru^{4/} and in Chile^{9/} confirming the efficiency of sodium alginate as coagulation aid in the clarification of turbid waters.

4. PREPARATION OF POLYMER'S SOLUTIONS

Several methods for the preparation of the polymer's solutions were tried, including extraction by ethanol through an Soxhlet apparatus. However, for the sake of simplicity and with the objective of providing methods that could be easily adapted to conditions of developing countries, only the simplest and least expensive preparation methods were utilized for the purpose of this experiment. The methods of preparation used were the following:

4.1 CACTUSFLOC VI (prepared from Opuntia ficus indica)

The fleshy stems, including the bark were cut in cubes of about 1cm, dehydrated between 50 and 60°C during 24 hours and then grinded. The fine powder obtained after sieving (Siever Tyler #200) was diluted in distilled water and filtered in a Gooch apparatus. The solution presented a green colour due to the chlorofilated compound present in the plant.

4.2 BABOSAFLOC V (prepared from A. vera)

The same preparation method was followed for the preparation of the aloe polymer solution. The single exception was that drying was made at a higher temperature, i.e. 60-70°C.

4.3 SODIUM ALGINATE (prepared from Sargassum spp.)

The extraction of alginic acid from the seaweed was done by the method of alkaline precipitation, according to the following steps:

- seaweed washed to eliminate sand and other residues;
- drying in open air;
- oven drying at 45°C until constant weight;
- a weighed portion of dry algae submitted to digestion in distilled water at 55°C for 10 minutes to eliminate potassium and iodine salts;
- portion kept in a 0.5% calcium chloride solution for 30 minutes and washed in distilled water;
- portion macerated in a 0.5% sodium chloride solution during 10 minutes at 60°C;
- idem with a 10% sodium carbonate, during 30 minutes under continuous agitation;
- the impure suspension of alginate was allowed to rest for 24 hours;
- dilution with distilled water to 50% of the initial concentration and pH adjusted to 9.0;
- cellulose and other solids were separated by sieving (sieve Tyler #60) and digested in a 2% sodium carbonate solution at 70°C for 10 minutes to extract the remaining insoluble alginate. After filtration through sieve (Tyler #60), the two filtrates were mixed together;
- a 1% solution of sodium hypochloride was added under continuous agitation until attaining pH=2.0. Sodium alginate precipitates in the form of white flocs;
- the suspension was put at 50°C in order to allow for the liberation of excess chlorine from the sodium hypochlorite;
- the suspension was filtered, and the sodium alginate precipitate was purified by dissolution in a 2% sodium carbonate solution until neutral pH was reached;

- the sodium alginate was precipitated by adding ethanol allowing formation of flocs of high density;
- the flocs were again separated by filtration and oven dried at 40°C until constant weight;
- the dry, flexible laminar flocs were grinded to form a light brown powder of sodium alginate, completely soluble in cold water.

5. EXPERIMENTAL SET UP

Two sets of experiments were performed by using aluminium sulphate and solutions of polymers extracted from the plants. The first set was made in a jar test apparatus with the objective of determining the flocculation kinetics parameters, and the second, to verify the capacity of the polymers solution in removing turbidity in a continuous flow system.

5.1 KINETIC PARAMETERS AND ASSESSMENT OF FLOCCULATION EFFICIENCY

The equations used in this experiment for rate kinetics and efficiency determinations are the following^{10/}:

(a) for a "plug flow" or batch reactor ("jar test")

$$\frac{N_0}{N_1} = \frac{1}{1 - e^{-K_C G} + e^{K_A G T} - K_C G} \quad [1]$$

where: N_0 = Turbidity (JTU), proportional to number concentration of primary particles entering the reactor

N_1 = As above, leaving the reactor

$\frac{N_0}{N_1}$ = Flocculation efficiency in the batch reactor

G = Velocity gradient (s^{-1})

K_A = Overall flocculation constant or general aggregation constant (adimensional)

K_B = Floc breakup constant (s)

T = Average detention time of particles in the reactor (s)

$$K_C = \frac{K_A T e^{-K_A G_{op} T}}{1 - e^{-K_A G_{op} T}} \quad [2]$$

$$K_C = \frac{K_B}{K_A} \quad [3]$$

Equation [2] is the first partial derivative of equation [1], with respect to G , set equal to zero, and G_{op} is the mean velocity gradient at the maximum rate of turbidity removal. Equations [1], [2] and [3] will allow for the determination of the kinetic parameters K_A , K_B and K_C in static (jar test) reactors.

(b) for continuous flow stirring tank reactors

for a single reactor:

$$\frac{N_o}{N_1} = \frac{1 + K_A G_1 T_1}{1 + K_A G_1 T_1 (1 - e^{-K_C G_1})} \quad [4]$$

for two reactors in series:

$$\frac{N_1}{N_2} = \frac{[1 + K_A T_1 G_1 (1 - e^{-K_C G_1})] (1 + K_A T_2 G_2)}{1 + K_A T_1 G_1 (1 - e^{-K_C G_1}) + K_A T_2 G_2 (1 - e^{-K_C G_2}) (1 + K_A G_1 T_1)} \quad [5]$$

and
$$\frac{N_o}{N_2} = \frac{N_o}{N_1} \frac{N_1}{N_2} \quad [6]$$

where G_1 and G_2 - velocity gradients in the first and second reactors, respectively

T_1 and T_2 - average detention times in the first and second reactors, respectively

N_1/N_2 - flocculation efficiency in the second reactor

N_o/N_2 - flocculation efficiency in the system composed of two tank reactors in series

5.2 RAW WATER AND CHEMICALS

Due to the large and continuous variation of the raw water available for the experiments it was decided to work with a synthetic water prepared with tap water, kaolinite (kaoline N.F. powder, J.T. Baker, USA, Lot n° 324 179), and sodium bicarbonate (powder, J.T. Baker, Lot n° 00200).

The artificial water was prepared in order to attain the basic average characteristics from the natural waters supplying metropolitan Sao Paulo:

Turbidity = N_1 = 15 NTU
 Alkalinity = 10 - 11 mg/l as $CaCO_3$
 pH = 6.4 to 7.4

A commercial granular aluminium sulphate was used with the following composition by weight of dry aluminium sulphate:

Total soluble aluminium: 14,5% as Al_2O_3
 Total soluble iron: 21.4% as F_2O_3
 Free alumina: 0.74% as Al_2O_3

5.3 MATERIALS AND EQUIPMENT

5.3.1 STATIC EXPERIMENTS

The static tests were performed in a multiple stirring apparatus (Phipps & Bird, Inc., Richmond, Va, six jars, two litres each). Each one of the jars

were equipped with a siphon allowing for collecting samples at a constant depth of 3 cm from the liquid surface. The jars were also equipped with rectangular baffles to provide small scale turbulence and to avoid vortex formation. (figures 9 and 10). The correlation between paddle rotation and velocity gradient shown in figure 11 was determined through a torsion balance method.

Turbidity measurements were made with a turbidimeter model HACH 2100-A (Hach Chemical Co., Ames, Iowa, USA) with standards calibrated in Jackson Turbidity Units (JTU).

A digital potentiometer (model E-603, Metrohm Herisau, Switzerland) with glass electrodes (Metrohm Herisau, Switzerland) was used for pH measurements. Zeta potential measurements were made to support the choice of best flocculation dosage of aluminium sulphate and polyelectrolyte solutions. For this purpose, electrophoretic mobility measurements were made through a zetameter equipped with a Riddick electrophoresis cell (Zeta Meter, Inc., New York, USA).

5.3.2 CONTINUOUS FLOW EXPERIMENTS

A pilot plant was designed and constructed to carry out this experiment (figures 12 and 13). The basic units of the system are the following: two make-up tanks with a total capacity of 765 litres; two injectors (for dosing solutions of aluminium sulphate and polyelectrolytes); a plug-flow reactor for initial mixing; two flocculation chambers in series; one settling tank and a triangular weir for level control. The plant was operated with a flow of 2000 ml/min (0.033 l/s or 2.88 m³/day), allowing capacity for continuous operation of more than 4 times the average total detention time of the system (about 80 minutes). A short description of the main units follows:

(a) Rapid mixing units:

Two rapid mixing units in series were provided in order to introduce the coagulants into the water and to provide adequate mixing. Each one of the units were composed of two parts: an injector in PVC designed according to Vrale and Jordan^{11/} (figure 14) and a plug flow reactor in flexible latex with a detention time of 30 seconds and a velocity gradient of about 820 s⁻¹ (Camp Number higher than 20 000).

(b) Flocculation units:

Flocculation was performed through two continuous flow stirring tank reactors in series with a volume of about 41 litres and an average hydraulic detention time of about 20.5 minutes each.

The velocity gradient in each tank reactor was established according to the equation:

$$G = 203.7 N_R^{3/2} \quad [7]$$

where: G = velocity gradient (s⁻¹)
 N_R = paddle rotation (RPS)

Paddle rotation could be varied from 0 to 140 rpm allowing for a velocity gradient in the range of 10 to 700 s⁻¹.

Figures 15, 16 and 17 show the flocculation units, the tank reactors and the turbine mixer used in each one of the tanks.

(c) Settling tank:

An upflow settling tank was installed after the flocculation units. It was made of 42 square pipes with 3 cm sides allowing for a total settling area of 1.5m^2 . The critical overflow rate was very low (about $10\text{ m}^3/\text{m}^2\text{ day}$) allowing for a laminar flow with a Reynolds Number of 26.5.

5.4 PROCEDURE

The synthetic water was prepared daily by adding the appropriate amounts of kaolinite and sodium bicarbonate to tap water, and maintained under continuous agitation in the make up tanks. The stock solutions of aluminium sulphate and polyelectrolytes were also prepared daily with concentrations of 0.5%.

5.4.1 JAR TESTS

The procedure adopted for the jar test experiments is as follows:

- the 6 beakers were filled with 1500 ml of the synthetic water;
- the stirring apparatus was set at $G = 500\text{ s}^{-1}$;
- the appropriate volume of aluminium sulphate solution was added and mixing was allowed for 30 seconds;
- the appropriate volume of polyelectrolyte solution was added and mixing was allowed for another 30 seconds. Tests performed with aluminium sulphate alone were allowed 60 seconds of initial mixing;
- the stirring speed was set to $G = 100\text{ s}^{-1}$ for 30 minutes;
- the suspension was allowed to settle for 20 minutes. Samples were taken (from 3cm below the surface) after 1, 3, 5, 7, 9, 12, 15 and 20 minutes of settling.

5.4.2 CONTINUOUS FLOW TESTS

The pilot plant was operated with aluminium sulphate and with the polyelectrolytes according to the best conditions determined in the jar test experiments. Since the overall average detention time of the system was about 80 minutes it was allowed a minimum of 90 minutes to attain steady state conditions. After that, samples were collected from the effluents from the first and second reactors and from the settling tank. The values of turbidity and pH reported are the arithmetic average of 6 samples collected afterwards at 15 minutes interval.

Efficiencies of flocculation achieved in the pilot plant can be compared with the theoretical values provided by equations [4], [5] and [6] (utilizing the values of K_A , K_B and K_C for the coagulants in consideration obtained from the static experiments) where:

- N_0 = raw water turbidity = 15 JTU
- N_1 = turbidity of a sample collected from the first reactor after 20 minutes settling in a beaker
- N_2 = idem from the second reactor

N_D = turbidity from a sample collected from the effluent of the settling tank
 N_0/N_1 = efficiency of flocculation in the first reactor
 N_1/N_2 = " " " " " second "
 N_1/N_2 = " " " " " two reactors in series
 N_0/N_D = " " " " " system

6. RESULTS AND DISCUSSION

6.1 BATCH EXPERIMENTS

Figure 18 shows the efficiency of turbidity removal as function of alum dosage and the time flocculated samples collected were allowed to settle. It can be seen that a dosage of 20 mg/l of alum allowed for a maximum of N_1/N_0 equal to 27 (final turbidity $N_1 = 0.56$ JTU, removal higher than 96%). With the optimum alum dosage and 20 minutes of settling after flocculation, the following data could be obtained utilizing Figure 19 and equations [1], [2] and [3].

$$\begin{aligned} G_{\text{optimum}} &= 145 \text{ s}^{-1} \\ K_{\text{optimum}} &= 1.87 \times 10^{-5} \\ K^A &= 4.69 \times 10^{-9} \text{ s} \\ K^B &= 2.48 \times 10^{-4} \text{ s} \\ K^C & \end{aligned} \quad [8]$$

Figures 20 to 23 are related to the studies made with alum and cactusfloc VI. It can be seen (figure 20) that the best results were achieved with 20 mg/l of alum and 1.0 mg/l of polymer (N_1/N_0 maximum equal to 33.0, final turbidity 0.45 JTU). It can also be noticed from figure 20 the slight anionic characteristic of the cactus polymer, allowing for a negative increase in the electrophoretic turbidity of the kaolin suspension. This is probably caused by absorption of the polymer in the kaolin particles through bridging with Al^{+++} cations already adsorbed at the interface. There was a quick formation of high density flocs which allowed for good clarification after 10 minutes of settling as shown in Figure 21.

Figure 22 shows the effect of alum dose and pH on turbidity removal. For a dosage of 20 mg/l of alum it was needed an initial pH of about 10.0 in order to achieve optimum flocculation. This is probably due to the low alkalinity of the artificial water and the need to introduce negative charges in order to react with the relatively high concentration of Al^{+++} .

With the data provided by figure 23, it was possible to determine for alum and cactusfloc the following values:

$$\begin{aligned} G_{\text{optimum}} &= 150 \text{ s}^{-1} \\ K_{\text{optimum}} &= 1.97 \times 10^{-5} \\ K^A &= 3.35 \times 10^{-9} \text{ s} \\ K^B &= 1.70 \times 10^{-4} \text{ s} \\ K^C & \end{aligned} \quad [9]$$

Figures 24 to 27 show the effect of babosafloc V on turbidity removal. The almost constant electrophoretic mobility with increasing dosage indicates the nonionic characteristic of this polymer (figure 24).

Concentrations of alumen of 10 and 15 mg/l were not enough to attain good flocculation with babosafloc V. The best conditions were obtained with 20 mg/l of alum and 1.5 mg/l of babosafloc V allowing for $N_0/N_1 = 35$ as shown in figure 25 (final turbidity 0.43 JTU).

Figure 26 shows the pH dependence on the flocculation with babosafloc V. Values of pH between 10 and 10.5 allowed for the best conditions for flocculation.

From figure 27 the following data can be obtained:

$$\begin{aligned} G_{\text{optimum}} &= 135 \text{ s}^{-1} \\ K_{\text{optimum}} &= 2.20 \times 10^{-5} \\ K_{\text{A}} &= 4.07 \times 10^{-9} \text{ s} \\ K_{\text{B}} &= 1.85 \times 10^{-4} \text{ s} \\ K_{\text{C}} &= 1.85 \times 10^{-4} \text{ s} \end{aligned} \quad [10]$$

The sodium alginate polymer has shown the best performance even with reduced dosages of aluminium sulphate. With 5mg/l of alum and 2 mg/l of alginate it was obtained $N_0/N_1 = 50$ allowing for a final turbidity of 0.30 JTU after 20 minutes settling (figure 28). The best efficiency however was achieved with 20 mg/l of alum and 6.0 mg/l of alginate as shown in figure 29 ($N_0/N_1 = 88$ and final turbidity 0.17 JTU).

Figure 30 shows that best flocculation conditions are attained within a narrow range of relatively low pH values (between 5.0 and 5.5), which may suggest the use of sodium alginate for clarification of coloured waters. On the other hand sodium alginate needed more energy to achieve optimum flocculation conditions ($G = 160 \text{ s}^{-1}$ as compared to cactus with $G = 150 \text{ s}^{-1}$ and aloe with $G = 135 \text{ s}^{-1}$). The data obtained from figure 31 allows for the following calculations:

$$\begin{aligned} G_{\text{optimum}} &= 160 \text{ s}^{-1} \\ K_{\text{optimum}} &= 1.95 \times 10^{-5} \\ K_{\text{A}} &= 4.07 \times 10^{-9} \text{ s} \\ K_{\text{B}} &= 1.26 \times 10^{-4} \text{ s} \\ K_{\text{C}} &= 1.26 \times 10^{-4} \text{ s} \end{aligned} \quad [11]$$

The K_{C} coefficient can be considered as indicative of floc strength and be used to compare the relative capability of different flocculants to remove turbidity in the coagulation-flocculation process. Figure 31 is a plot of the data obtained with the flocculants tested, showing that at the optimum velocity gradient the values of K_{C} are smaller for the polymers utilized in conjunction with alum than when alum was utilized alone. It can also be seen that the sodium alginate-alum solution, which provided the better water quality has shown the smallest value of K_{C} ($1.26 \times 10^{-4} \text{ s}$)

6.2 CONTINUOUS EXPERIMENTS

Several tests were made in the pilot plant utilizing dosages of alum and polyelectrolytes closer to the optimum dosages determined in the jar test experiments. However due to problems with the motors of the flocculation units running at higher speed, it was not possible to perform the tests at the optimum velocity gradients determined for each one of the coagulants used. The experiments were performed with velocity gradients and Camp Numbers ($G \times T$) suggested by Camp^{12/4} and Hudson^{13/4}, respectively G between 20 and 40 s^{-1} and GT higher than 10^4 .

The best results obtained are the following:

Aluminium sulphate (mg/l)	Polyelectrolyte (mg/l)	N_o/N_2	N_o/N_2	N_2 (JTU)
20.0	-	6.2	15.0	1.0
20.0	cactusfloc:1.0	6.0	16.7	0.9
30.0	babosafloc:2.0	4.2	9.4	1.6
5.0	sodium alginate:5.0	6.8	18.7	0.8

It should be noticed that the sodium alginate produced a final water with 0.8 JTU ($N_o/N_2 = 18.7$ or removal efficiency of 95%) with only 5.0 mg/l of alum. On the other hand the performance of the babosafloc was very poor attaining a removal of only 89% with 30 mg/l of aluminium sulphate. With 20 mg/l of alum the maximum attained with babosafloc (1.5 mg/l) was a final turbidity of 3.1 JTU ($N_o/N_2 = 4.8$ or removal efficiency of 79%).

7. CONCLUSIONS AND RECOMMENDATIONS

This experiment and several others 2/,4/,14/,15/,16/,17/ demonstrated that natural polyelectrolytes are effective as coagulant aids and can be used with advantage over their similar synthetics under technical and probably economical point of view. The solutions prepared from Opuntia ficus indica (cactusfloc VI) and Aloe vera (Babosafloc V) improved water clarification when used as coagulant aids with alum.

The solutions prepared with sodium alginate extracted from marine algae Sargassum spp when utilized as coagulant aids with alum provided the best clarification (98% in the static tests and 95% in the pilot plant) of all polymers tested and provided a reduction of the optimum alum dosage from 20 to 5 mg/l.

The static experiments have also shown that the natural coagulant aids allowed for a more rapid floc formation with density and settling velocities higher than flocs formed with alum alone.

The pilot plant confirmed the results obtained in the static experiments mainly with respect to the high performance of the sodium alginate as coagulant aid. It is probable that a much better result would have been obtained if the pilot plant were operated at the optimum velocity gradients as determined by the jar-test experiments, for each one of the natural coagulants tested.

It is recommended that tropical countries evaluate their potential for production of natural coagulants, promote the realization of pilot studies to assess the performance of the most promising plants as coagulant aids and stimulate the industrial production of natural polymers.

While considered as safe under the toxicological point of view, not enough studies have been made to date that effectively demonstrate the short and long term effects of natural polyelectrolytes on public health. Therefore, it is recommended that chemical/analytical investigations as well as toxicological studies are made for newly developed natural coagulants before they are allowed to be utilized in the treatment of public water supplies.

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FIGURE 1 - OCCURRENCE OF OPUNTIA FICUS INDICA
IN THE STATE OF SAO PAULO - BRAZIL



FIGURE 2 - OPUNTIA FICUS INDICA AND ITS FRUIT



FIGURE 3 - ALOE VERA

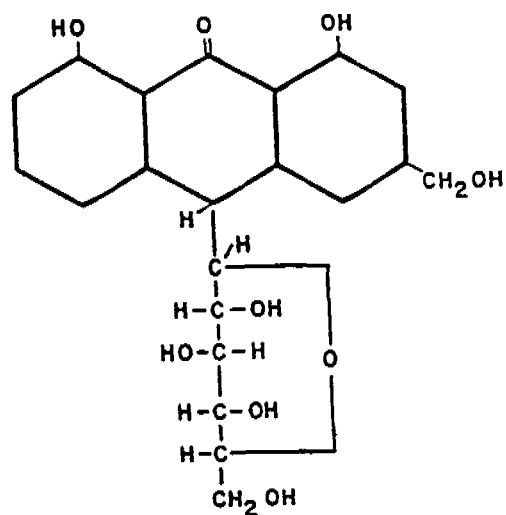


FIGURE 4 - MOLECULAR STRUCTURE OF ALOINE

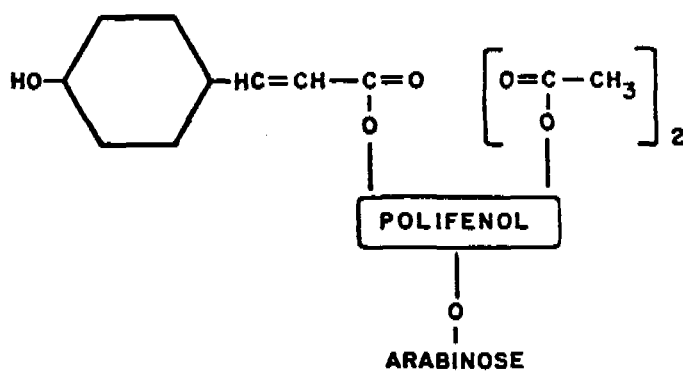


FIGURE 5 - PROBABLE MOLECULAR STRUCTURE OF ALOEHARZ



FIGURE 6 - OCCURRENCE OF BROWN SEAWEED (SARGASSUM SPP.)
IN THE COAST OF THE STATE OF SAO PAULO, BRAZIL



FIGURE 7 - BROWN SEAWEED COLLECT IN THE STATE OF SAO PAULO
BRAZIL, FOR THE PRODUCTION OF SODIUM ALGINATE

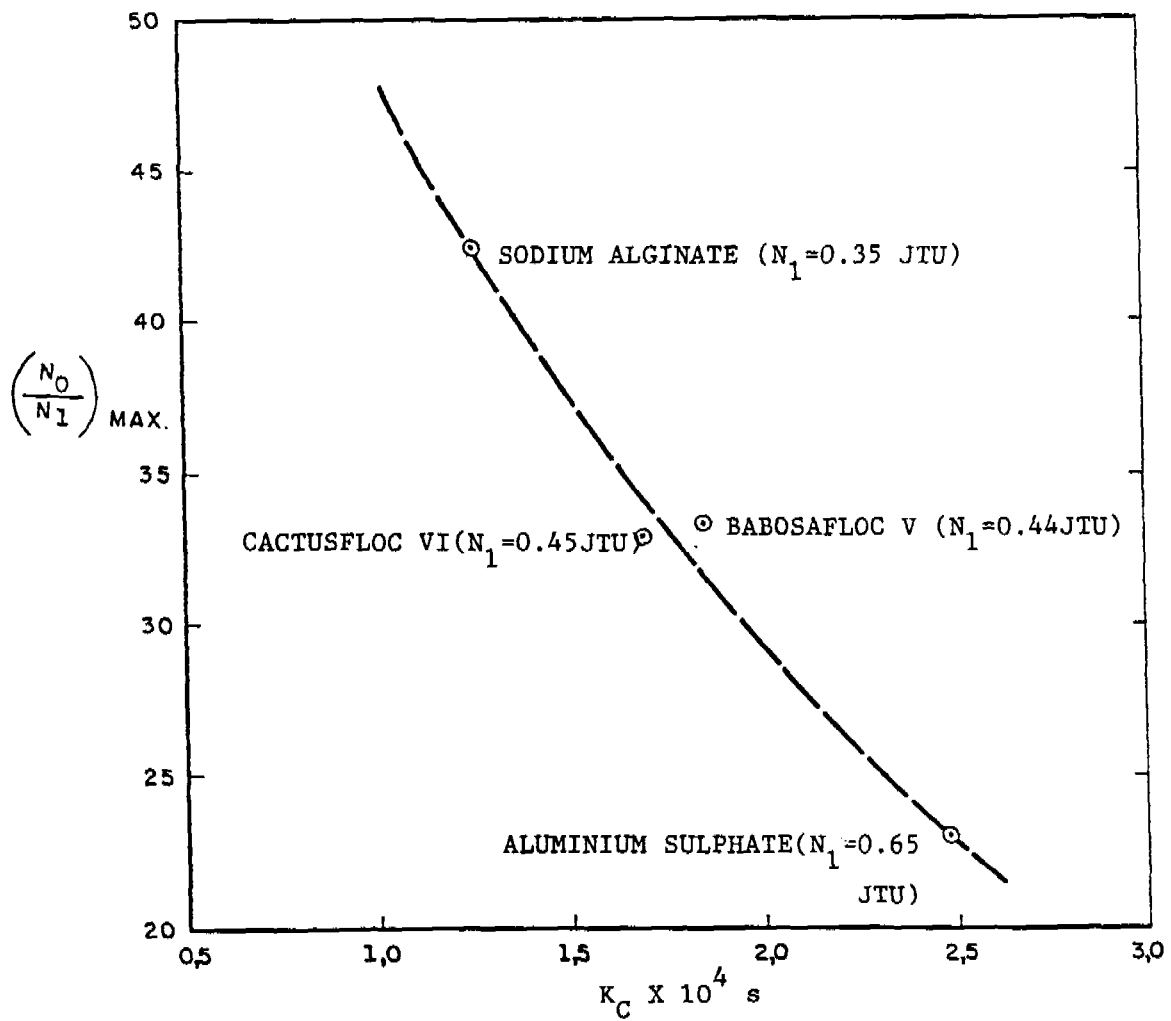


FIGURE 32 - CORRELATION BETWEEN K_C AND THE MAXIMUM EFFICIENCY OF FLOCCULATION

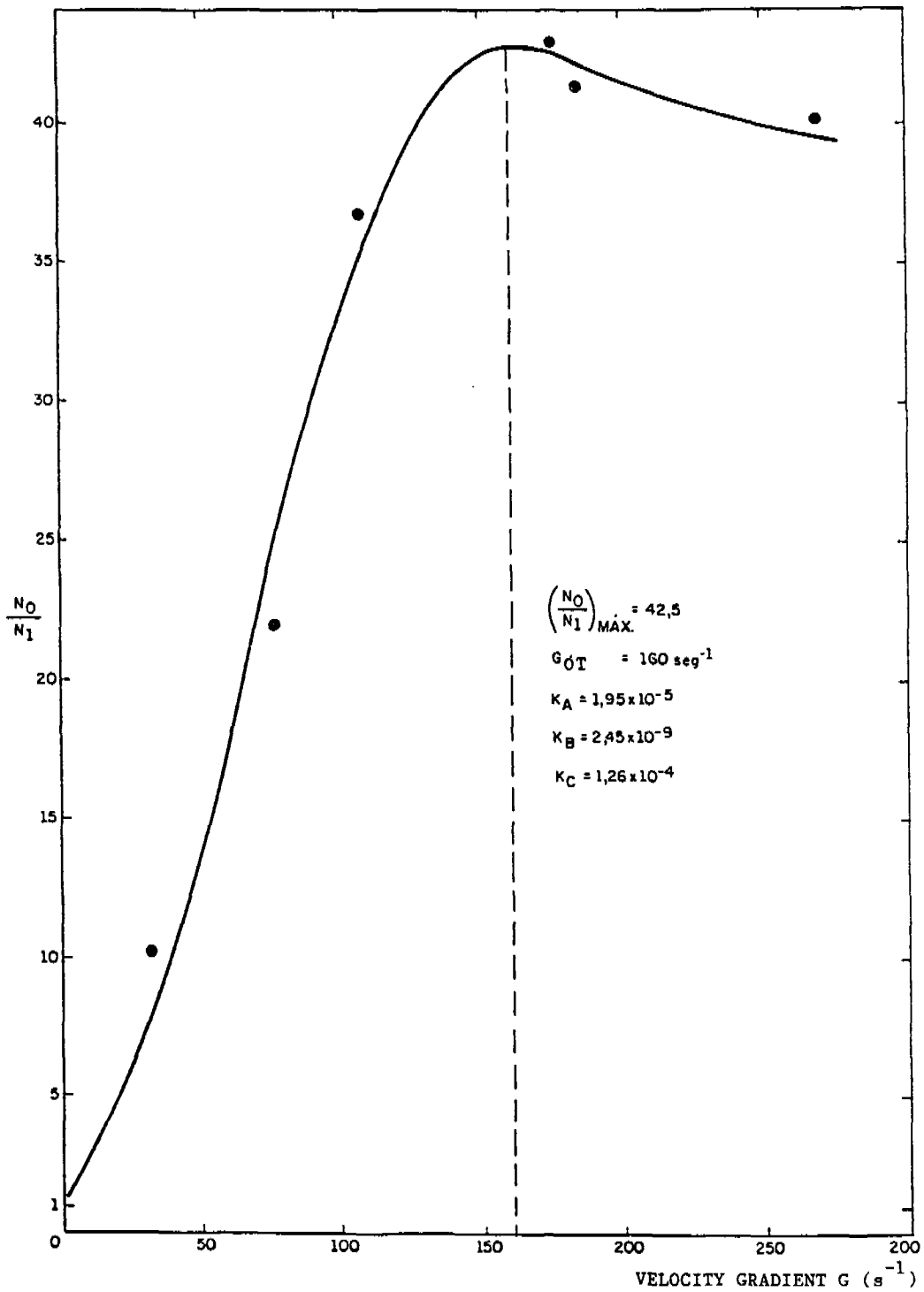


FIGURE 31 - EFFICIENCY OF FLOCCULATION X VELOCITY GRADIENT
 (20 mg/l ALUM AND 1.0 mg/l SODIUM ALGINATE)

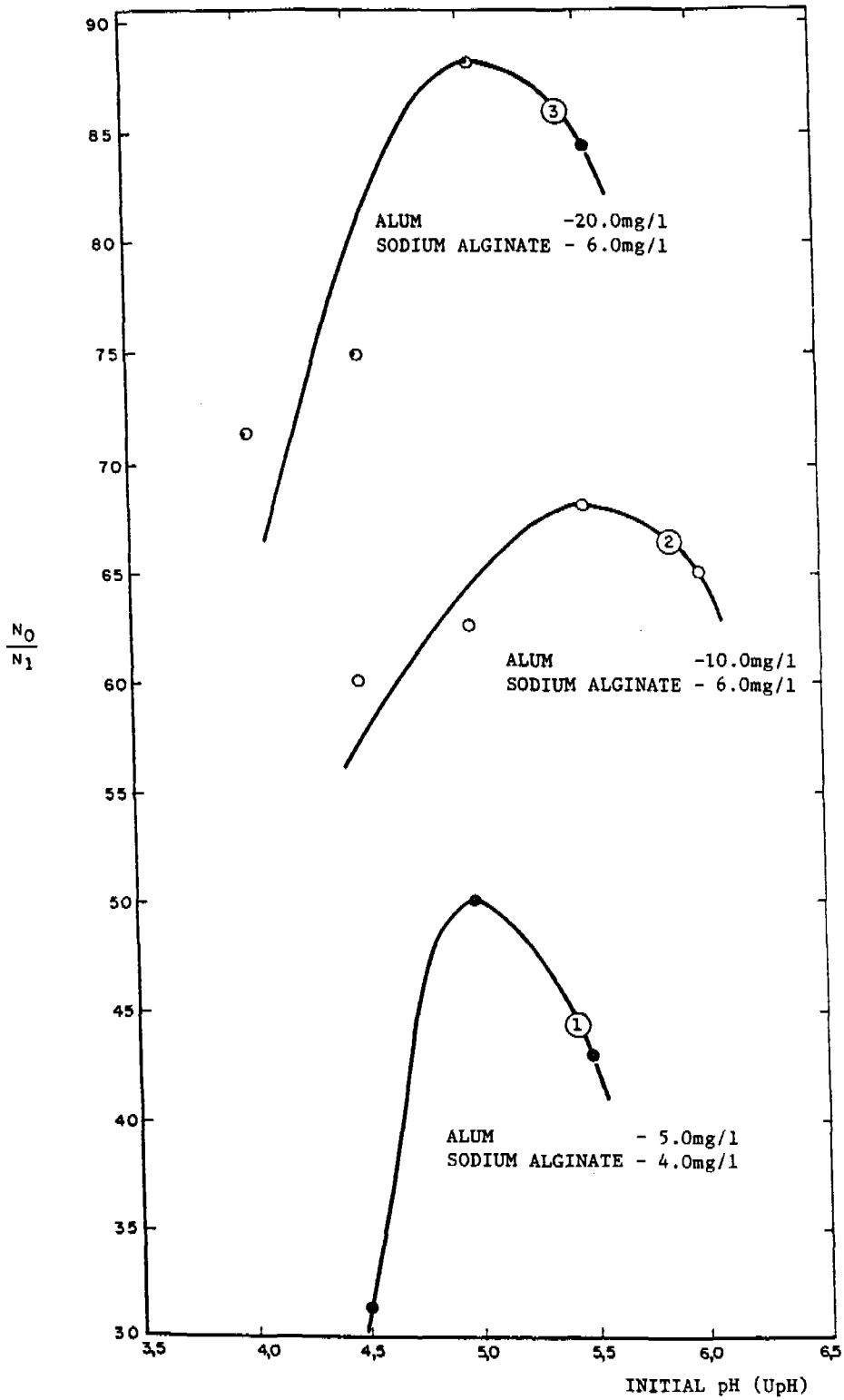


FIGURE 30 - EFFICIENCY OF FLOCCULATION AS FUNCTION OF INITIAL pH AND DIFFERENT DOSAGES OF ALUM AND SODIUM ALGINATE.

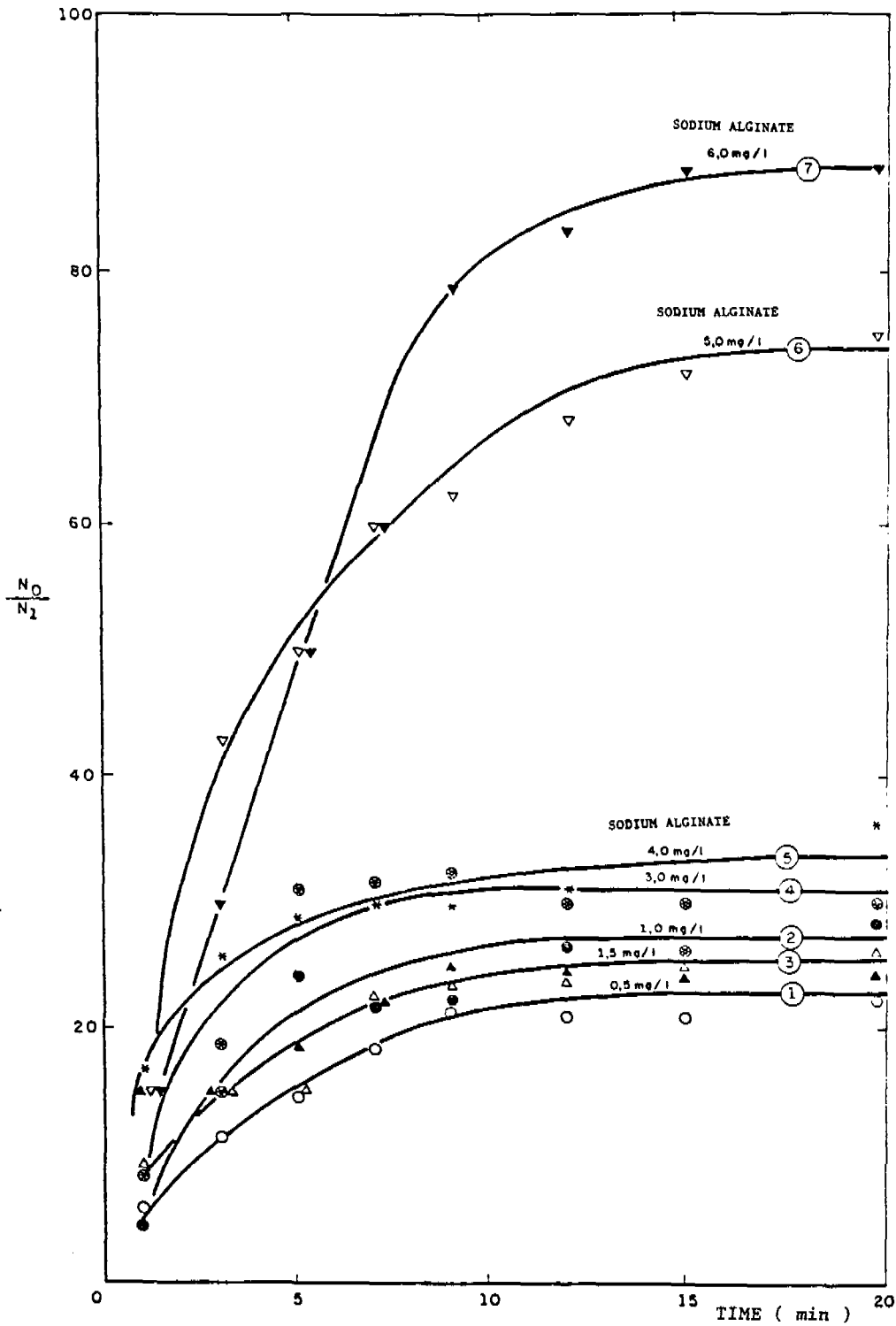


FIGURE 29 - EFFICIENCY OF FLOCCULATION AS FUNCTION OF TIME WITH 20 mg/l ALUM AND INCREASING DOSAGES OF SODIUM ALGINATE

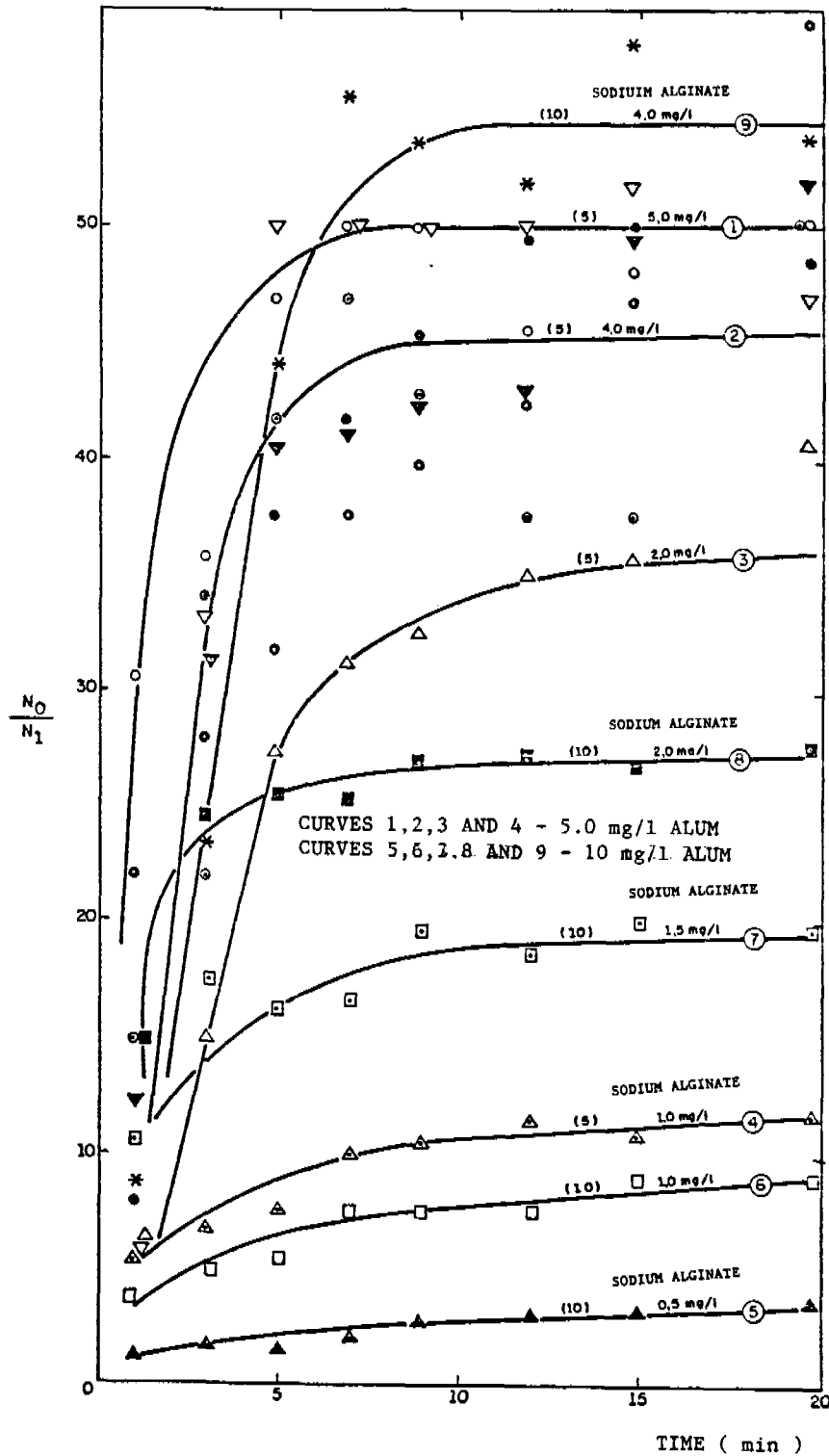


FIGURE 28 - EFFICIENCY OF FLOCCULATION AS FUNCTION OF SETTLING TIME WITH 10 AND 15 mg/L OF ALUM AND INCREASING DOSAGES OF SODIUM ALGINATE

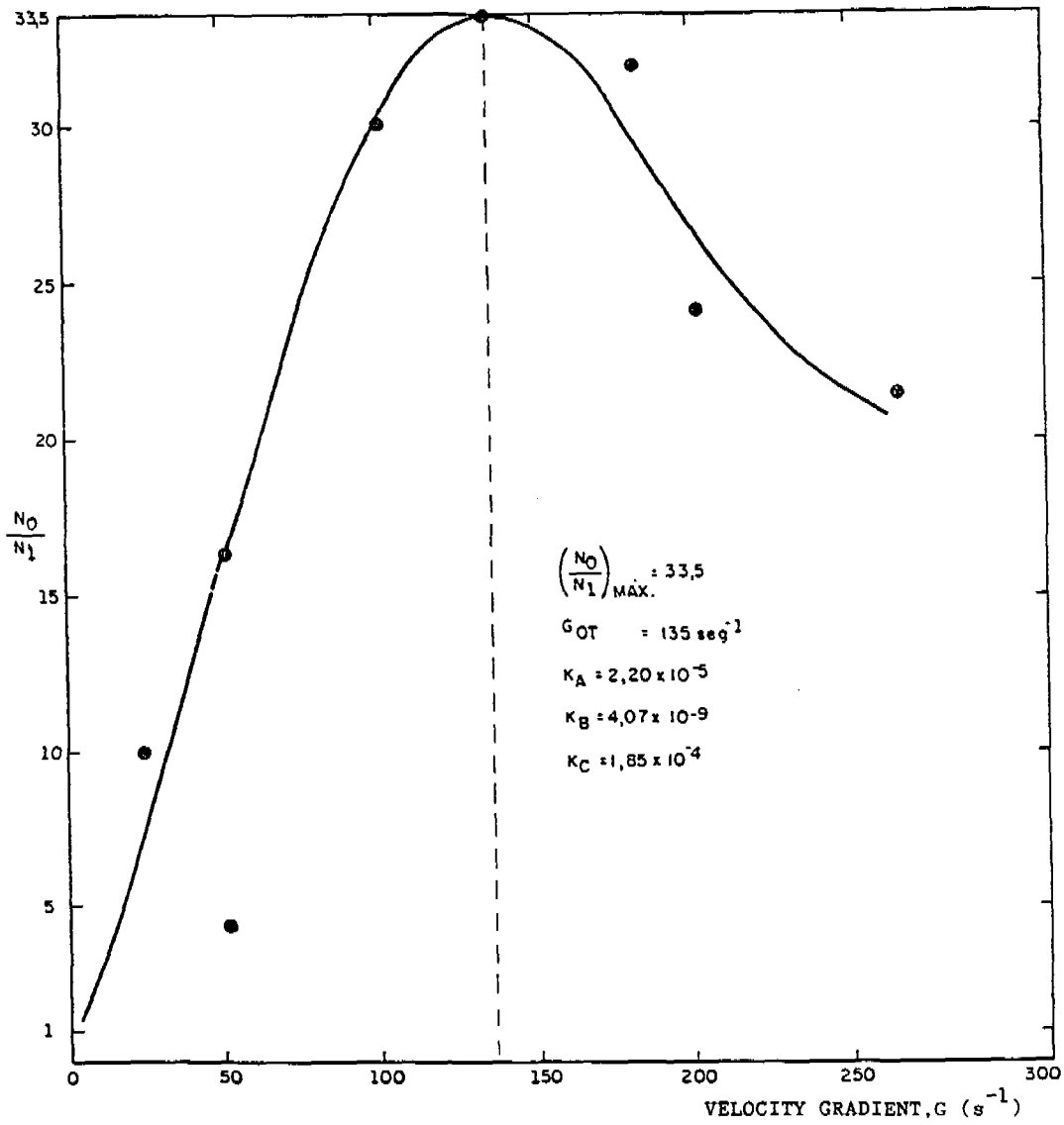


FIGURE 27 - EFFICIENCY OF FLOCCULATION X VELOCITY GRADIENT
 (20 mg/l ALUM AND 1.5 mg/l OF BABOSAFLOC V)

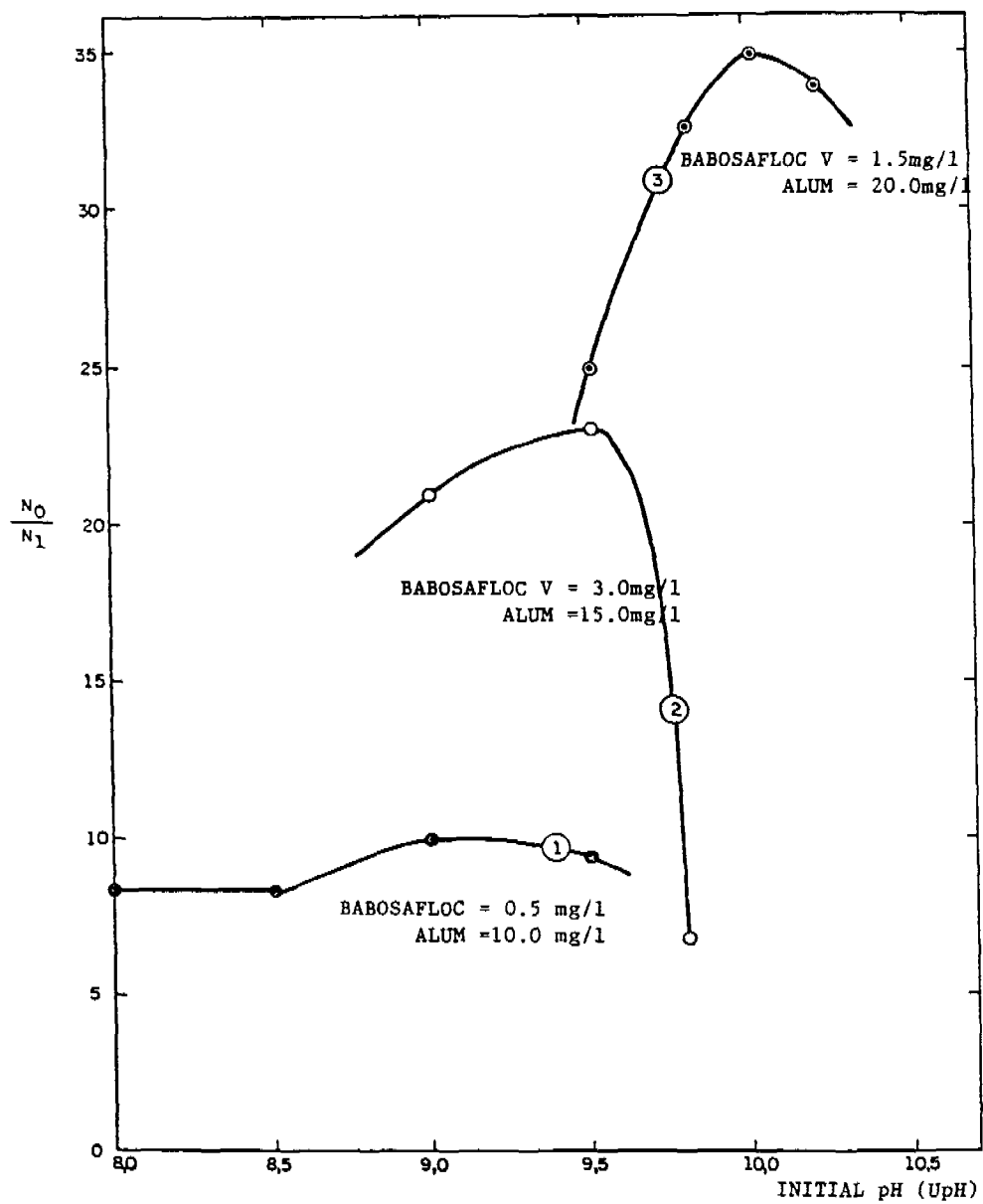


FIGURE 26 - EFFICIENCY OF FLOCCULATION AS FUNCTION OF pH AND DIFFERENT DOSAGES OF ALUM AND BABOSAFLOC V (SETTLING TIME = 20 min)

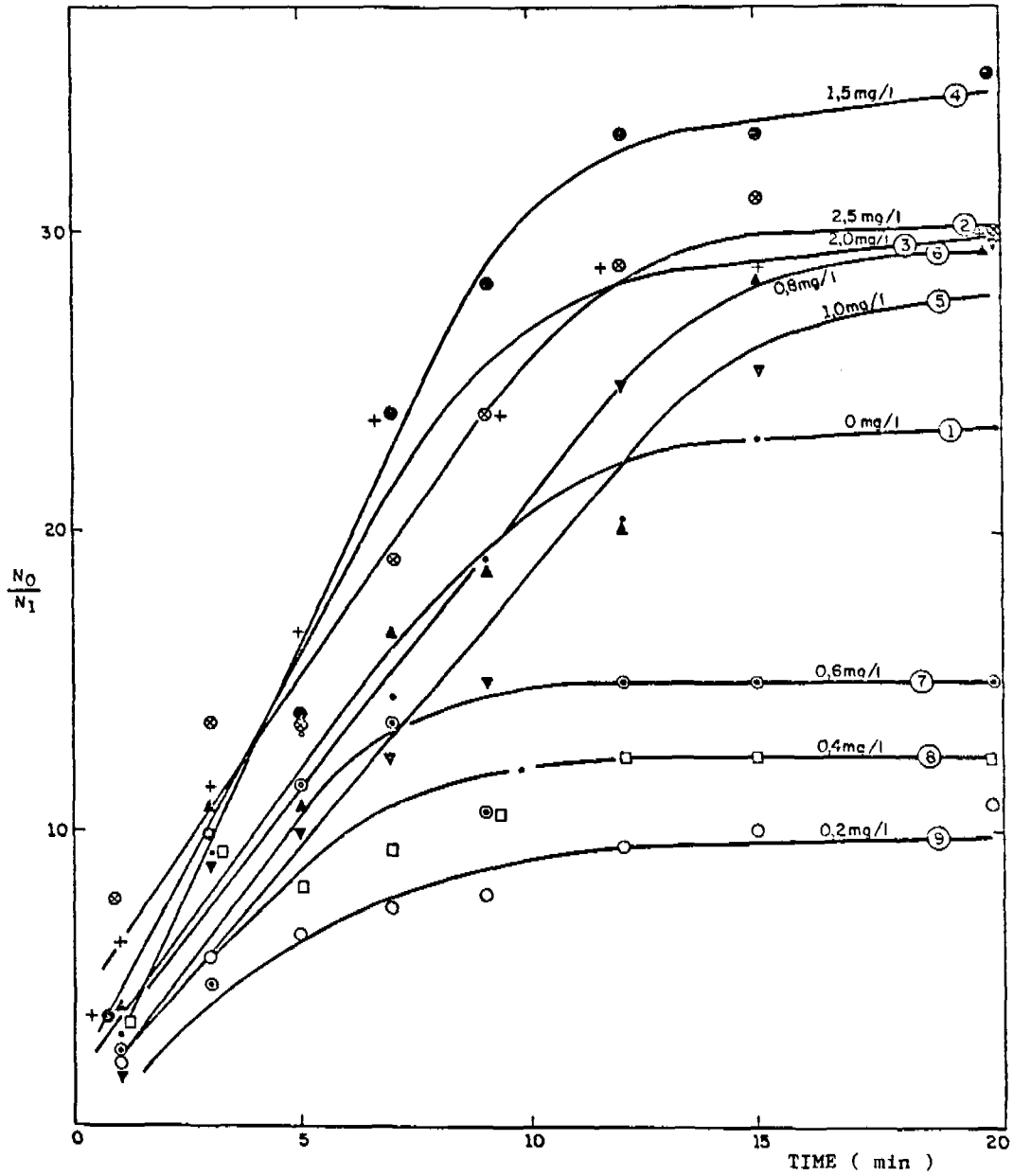


FIGURE 25 - EFFICIENCY OF FLOCCULATION AS FUNCTION OF SETTLING TIME WITH 20 γ g/l OF ALUM AND INCREASING DOSAGES OF BABOSAFLOC V

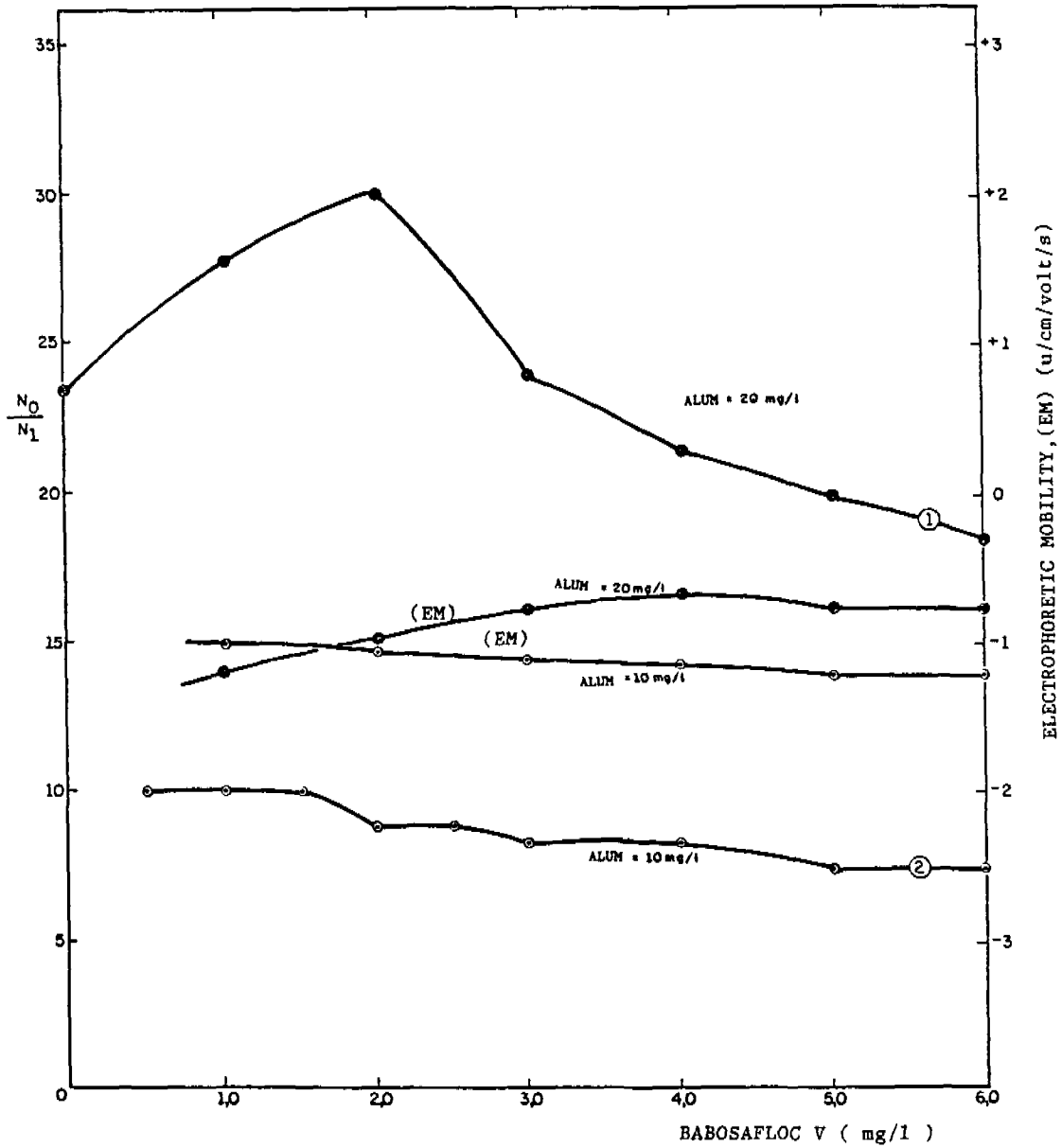


FIGURE 24 - ELECTROPHORETIC MOBILITY (EM) AND EFFICIENCY OF FLOCCULATION AS FUNCTION OF ALUM AND BABOSAFLOC V DOSAGES

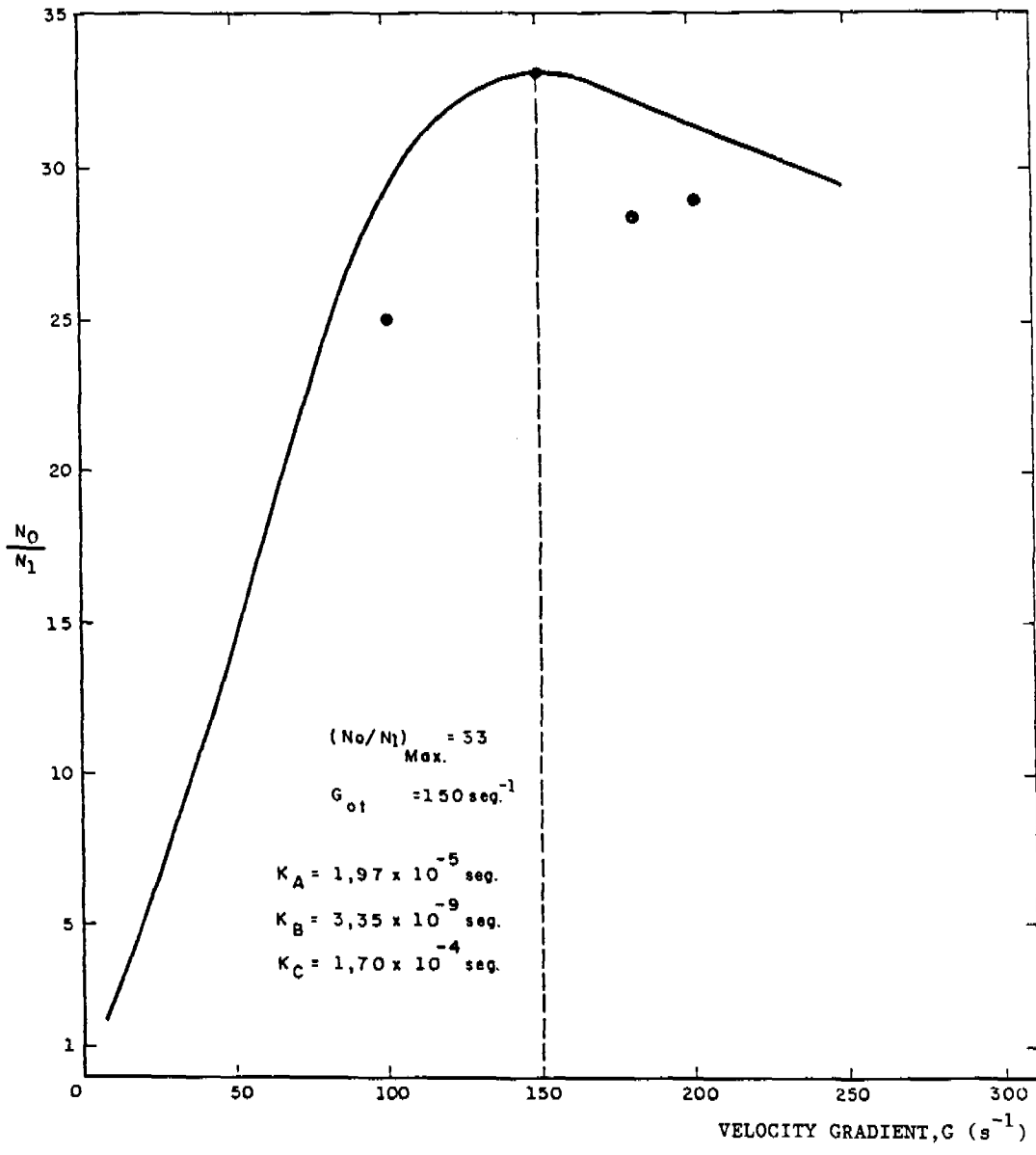


FIGURE 23 - EFFICIENCY OF FLOCCULATION X VELOCITY GRADIENT
 (ALUM = 20.0 mg/l ; CACTUSFLOC VI = 1.0 mg/l)

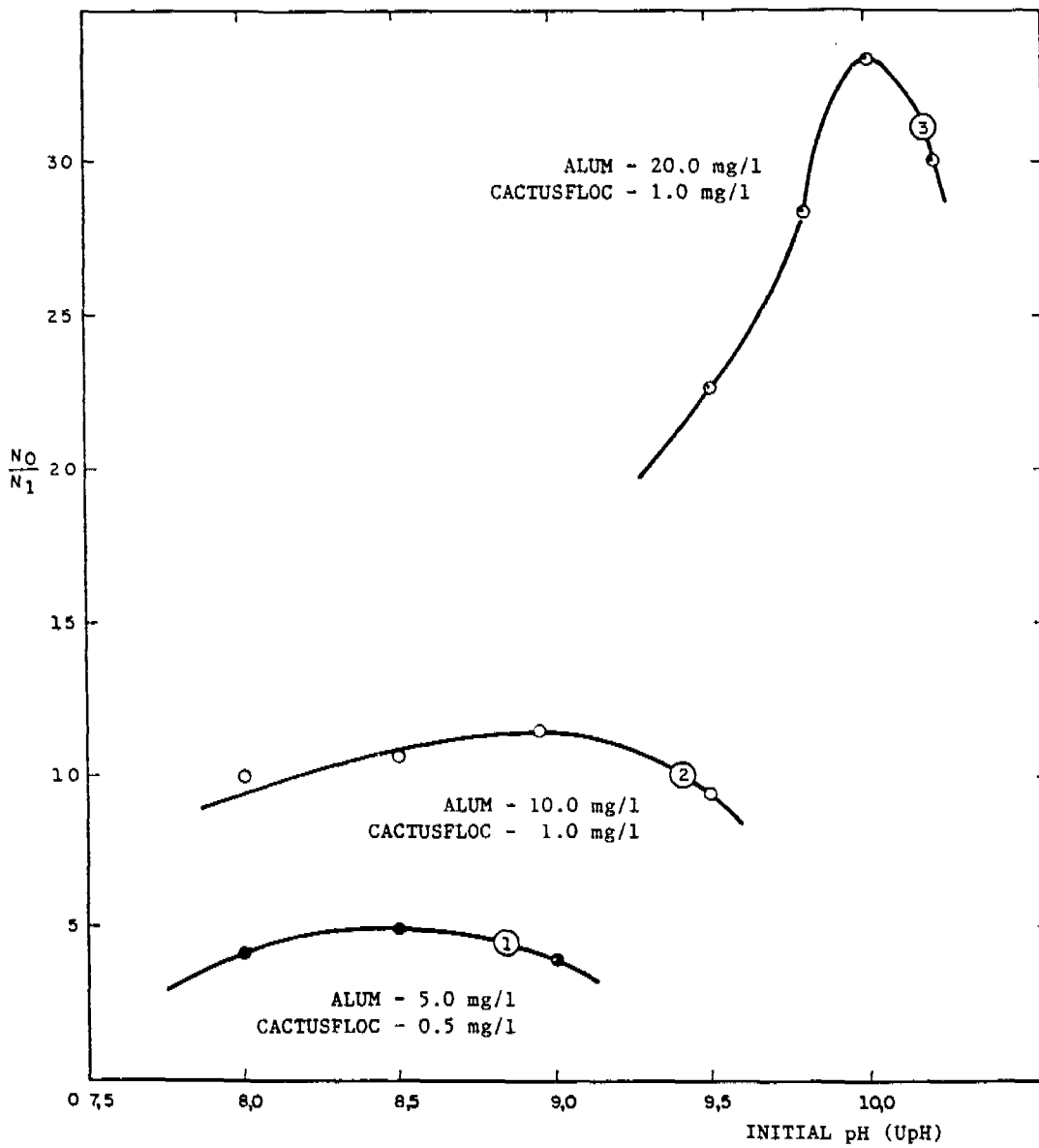


FIGURE 22 - EFFECT OF INITIAL pH ON THE FLOCCULATION EFFICIENCY OF CACTUSFLOC VI

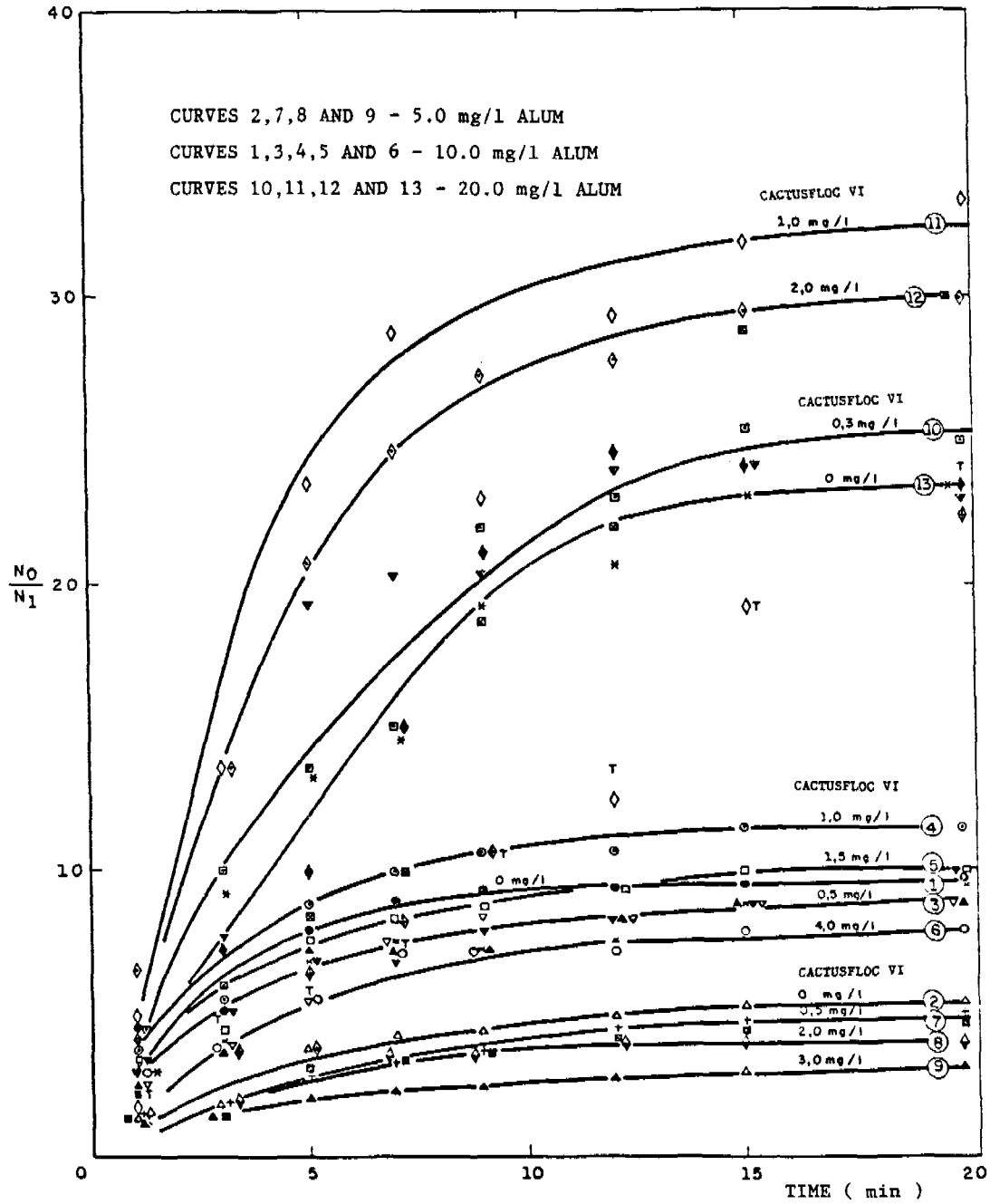


FIGURE 21 - EFFICIENCY OF FLOCCULATION AS FUNCTION OF
 ALUM AND CACTUSFLOC VI DOSAGES AND OF
 SETTLING TIME

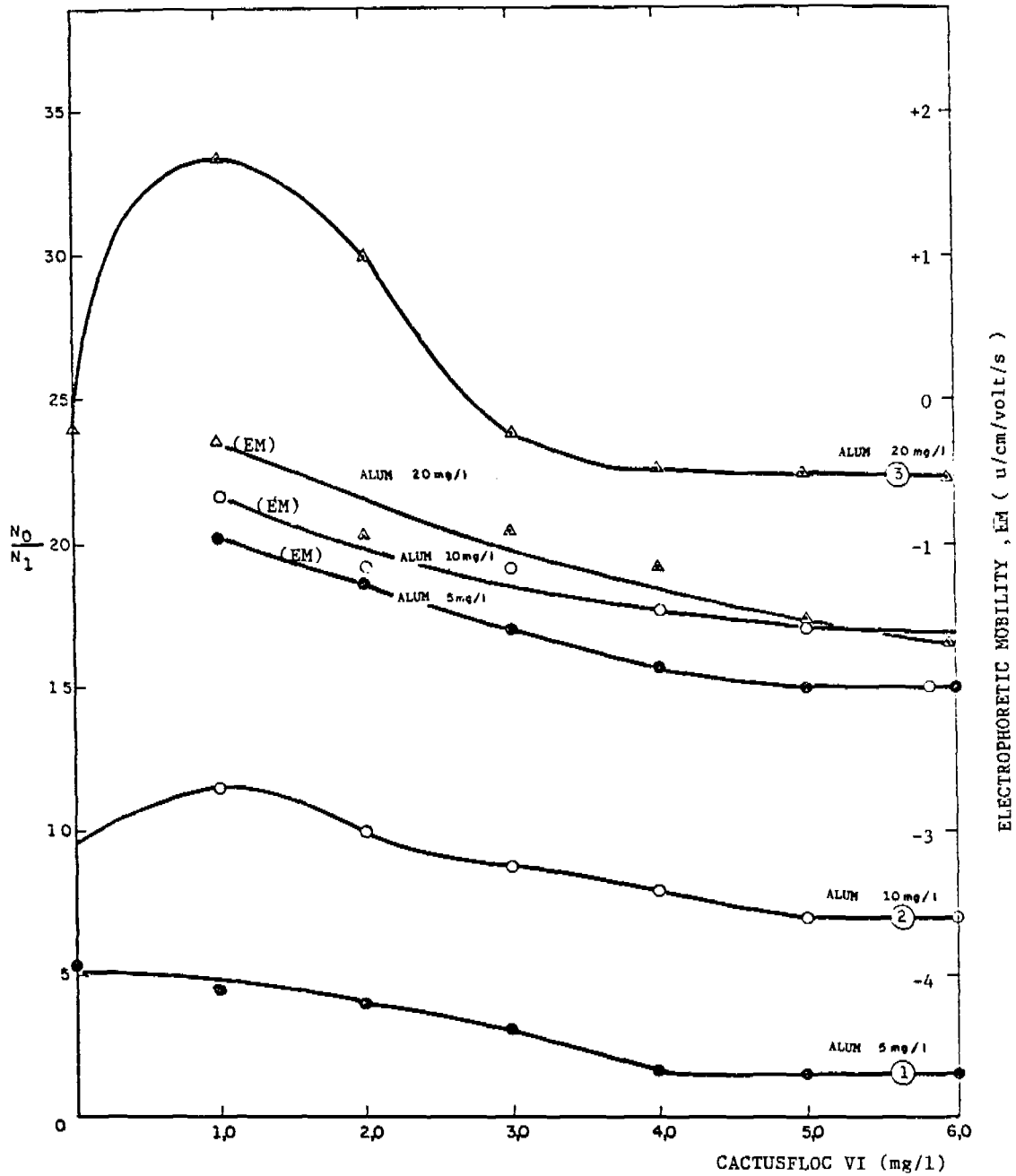


FIGURE 20 - ELECTROPHORETIC MOBILITY (EM) AND EFFICIENCY OF FLOCCULATION AS FUNCTION OF ALUM AND CACTUS - FLOC VI DOSAGES

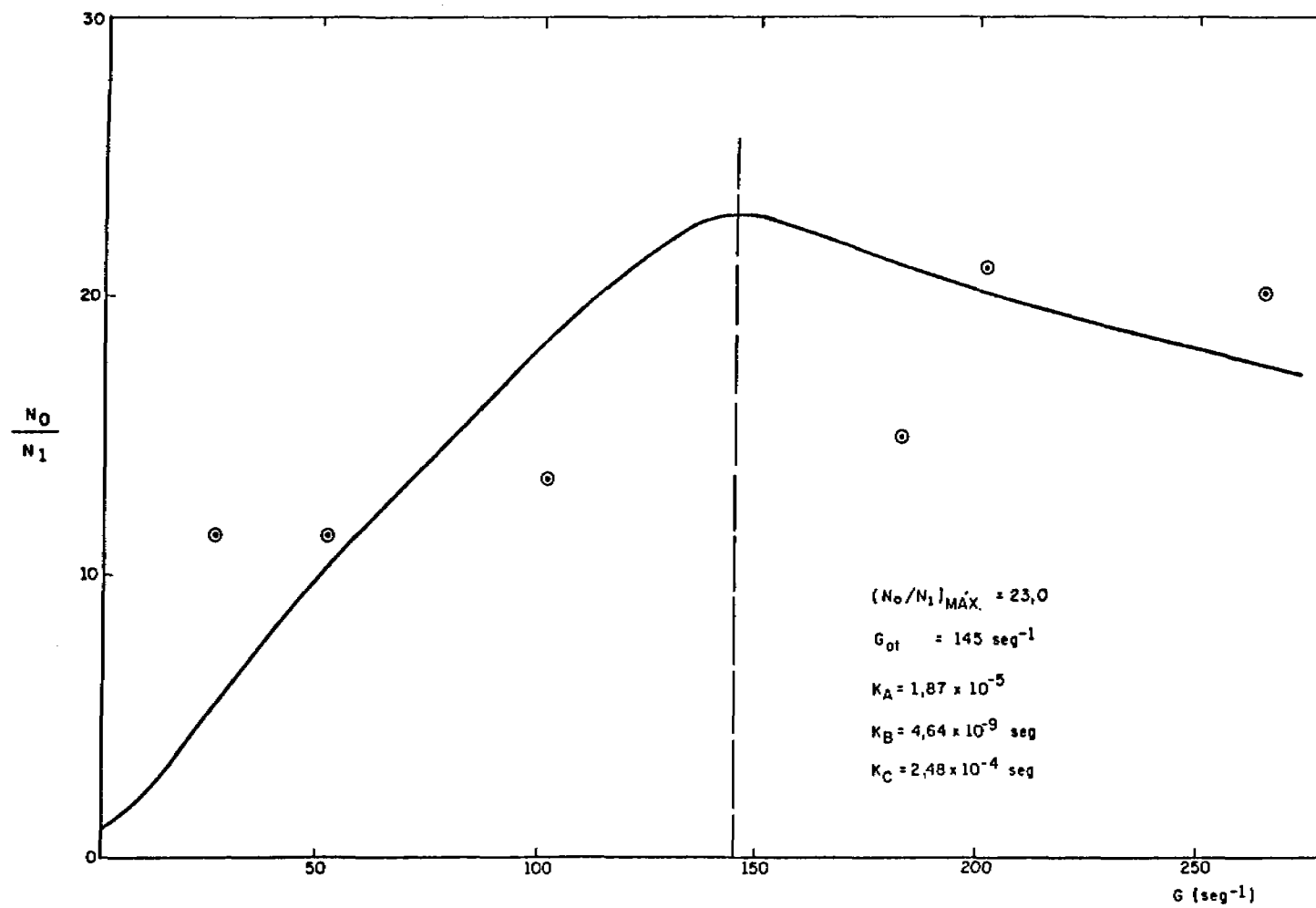


FIGURE 19 - EFFICIENCY OF FLOCCULATION X VELOCITY GRADIENT (ALUM = 20.0 mg/l)

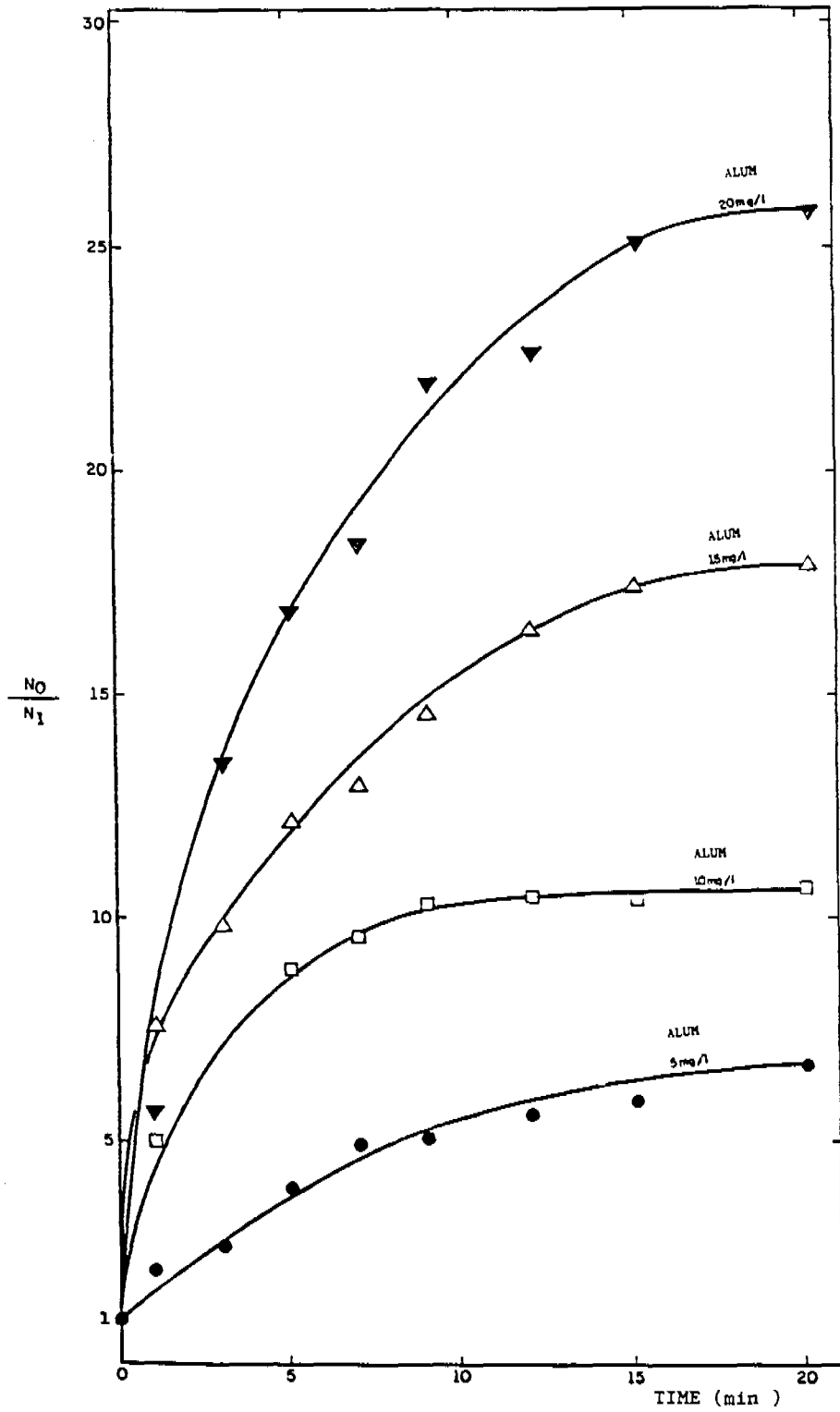


FIGURE 18 - FLOCCULATION EFFICIENCY AS FUNCTION OF ALUM DOSAGE AND SETTLING TIME

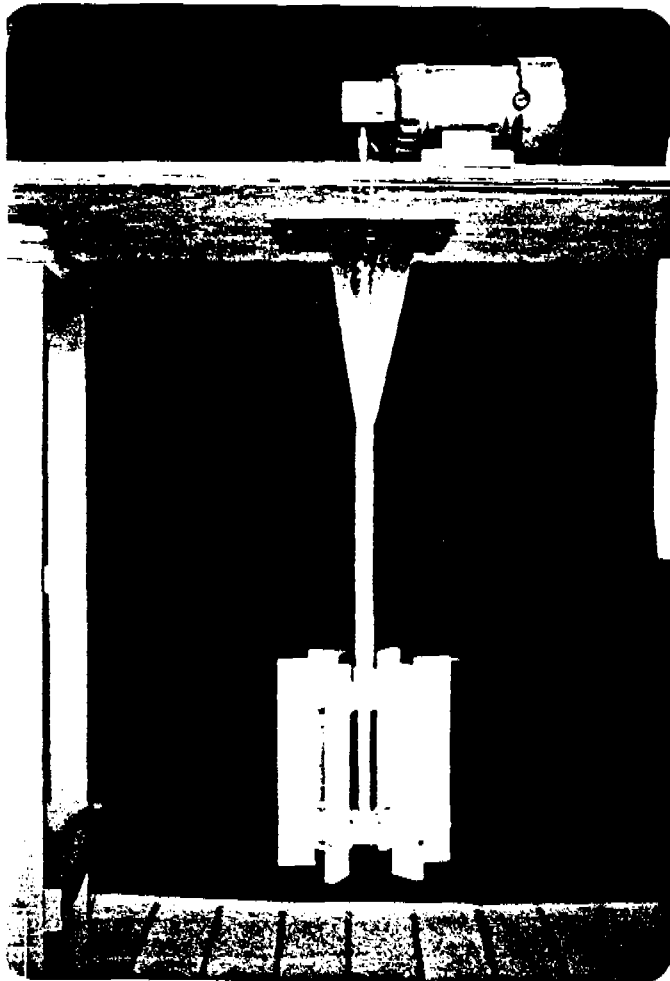


FIGURE 17 - TURBINE MIXER UTILIZED IN
THE FLOCCULATION UNITS

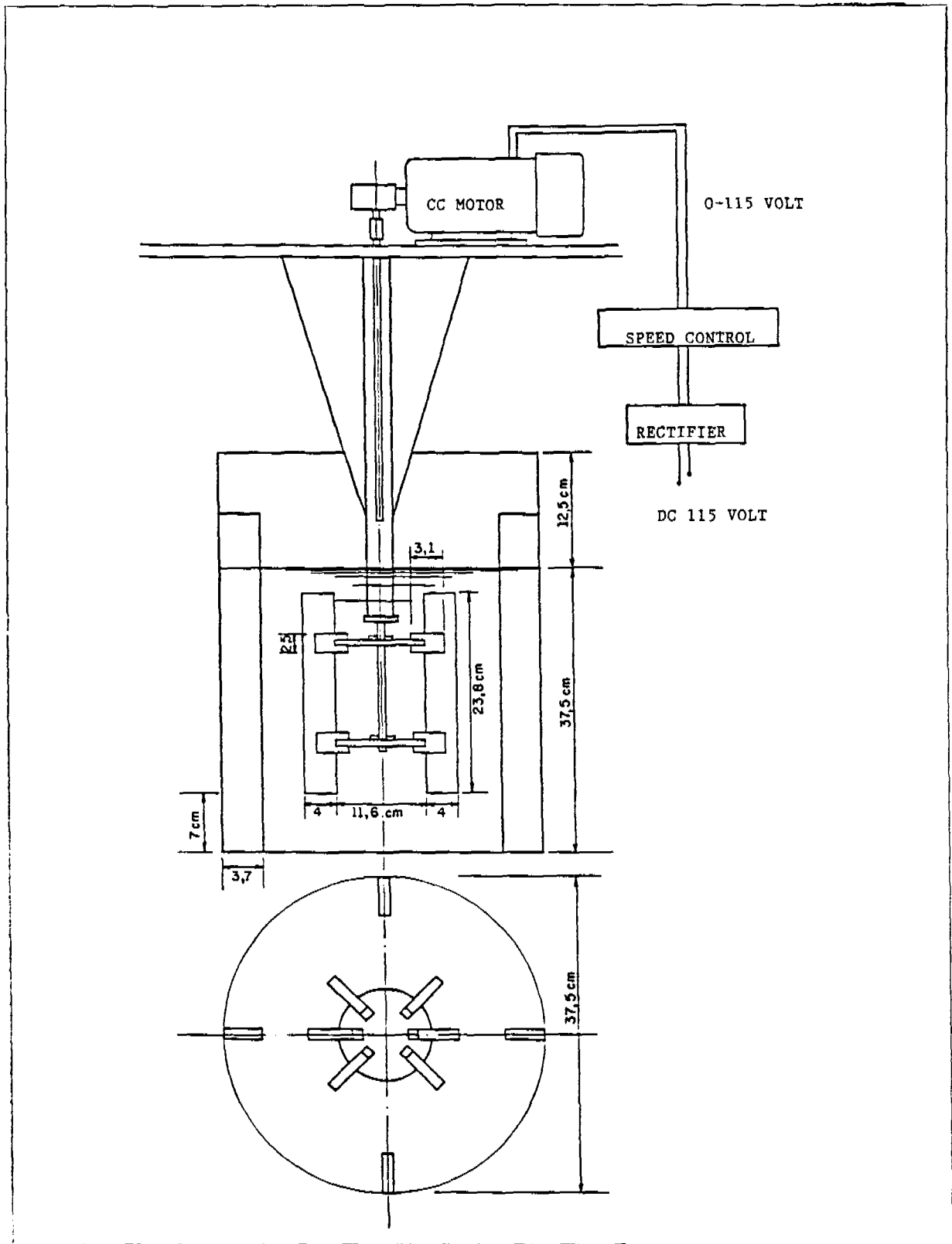


FIGURE 16 - CONTINUOUS FLOW STIRRING TANK REACTOR

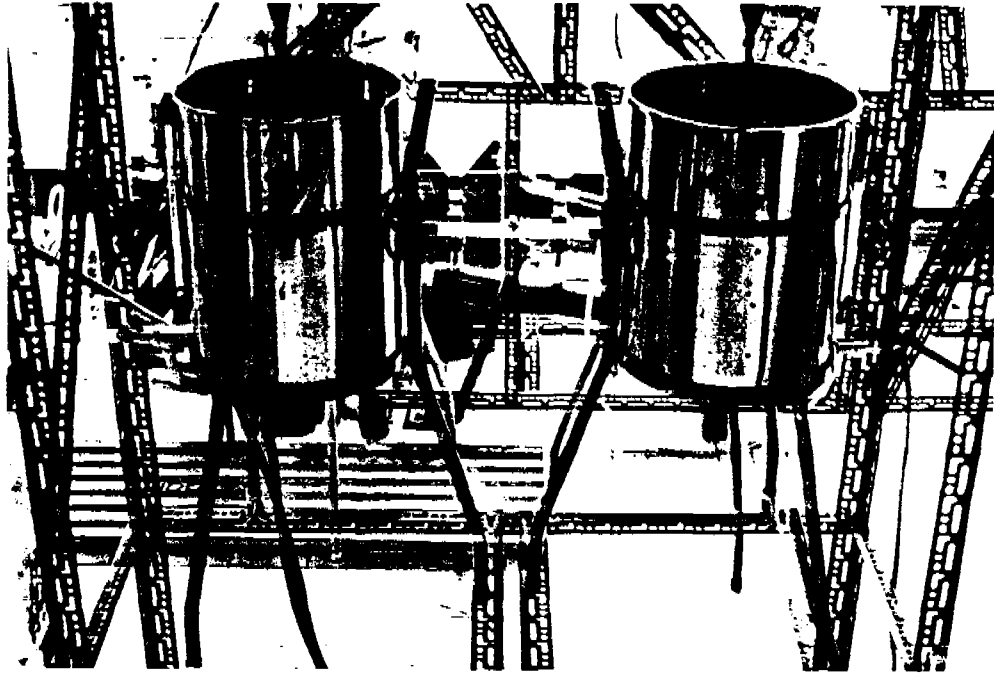


FIGURE 15 - FLOCCULATION UNIT WITH TWO CONTINUOUS
FLOW STIRRING TANK REACTORS IN SERIES

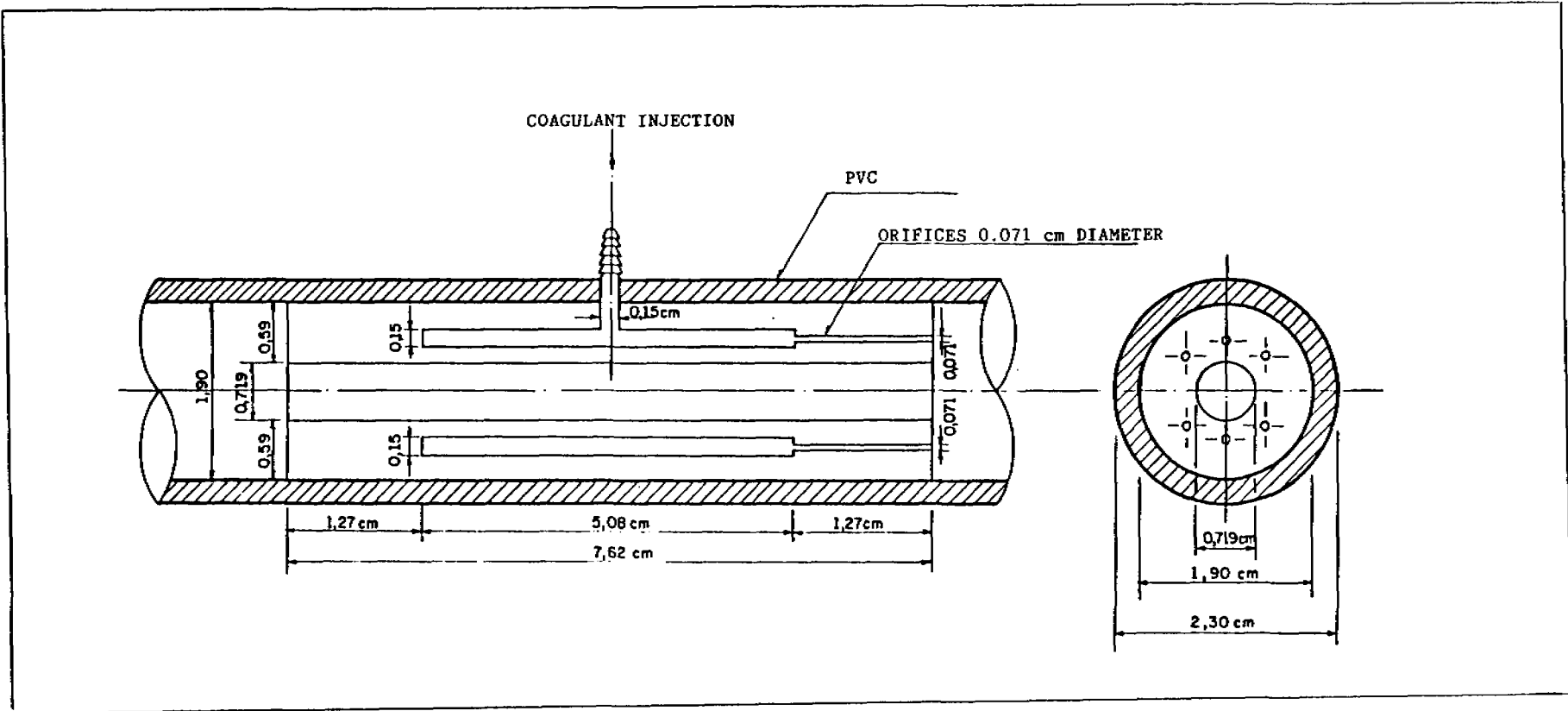


FIGURE 14 - INJECTOR UTILIZED FOR INTRODUCTION OF COAGULANT SOLUTIONS

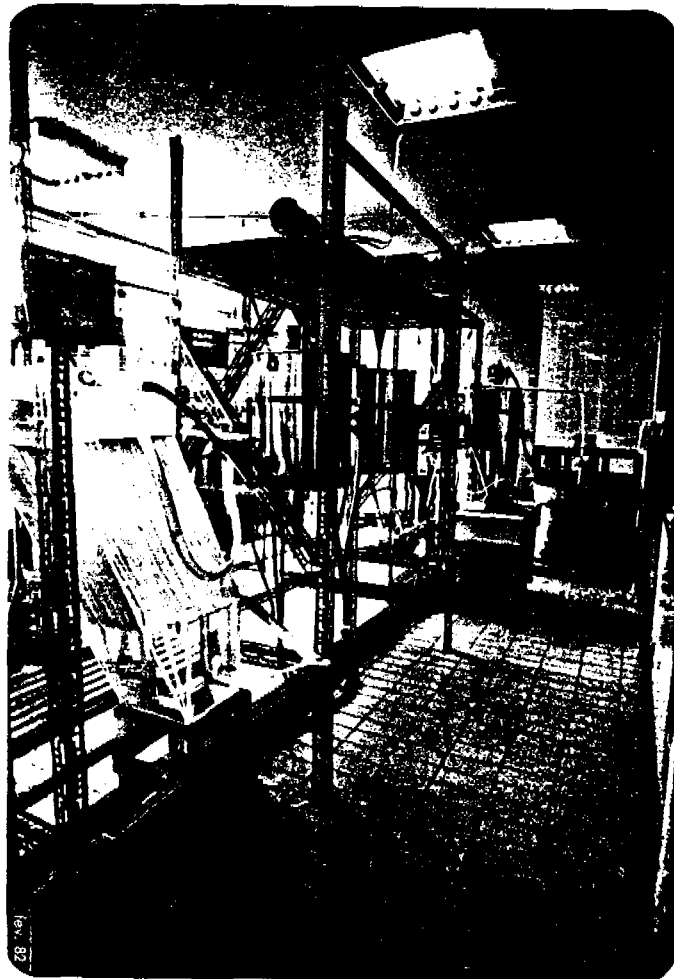


FIGURE 13 - VIEW OF THE PILOT PLANT

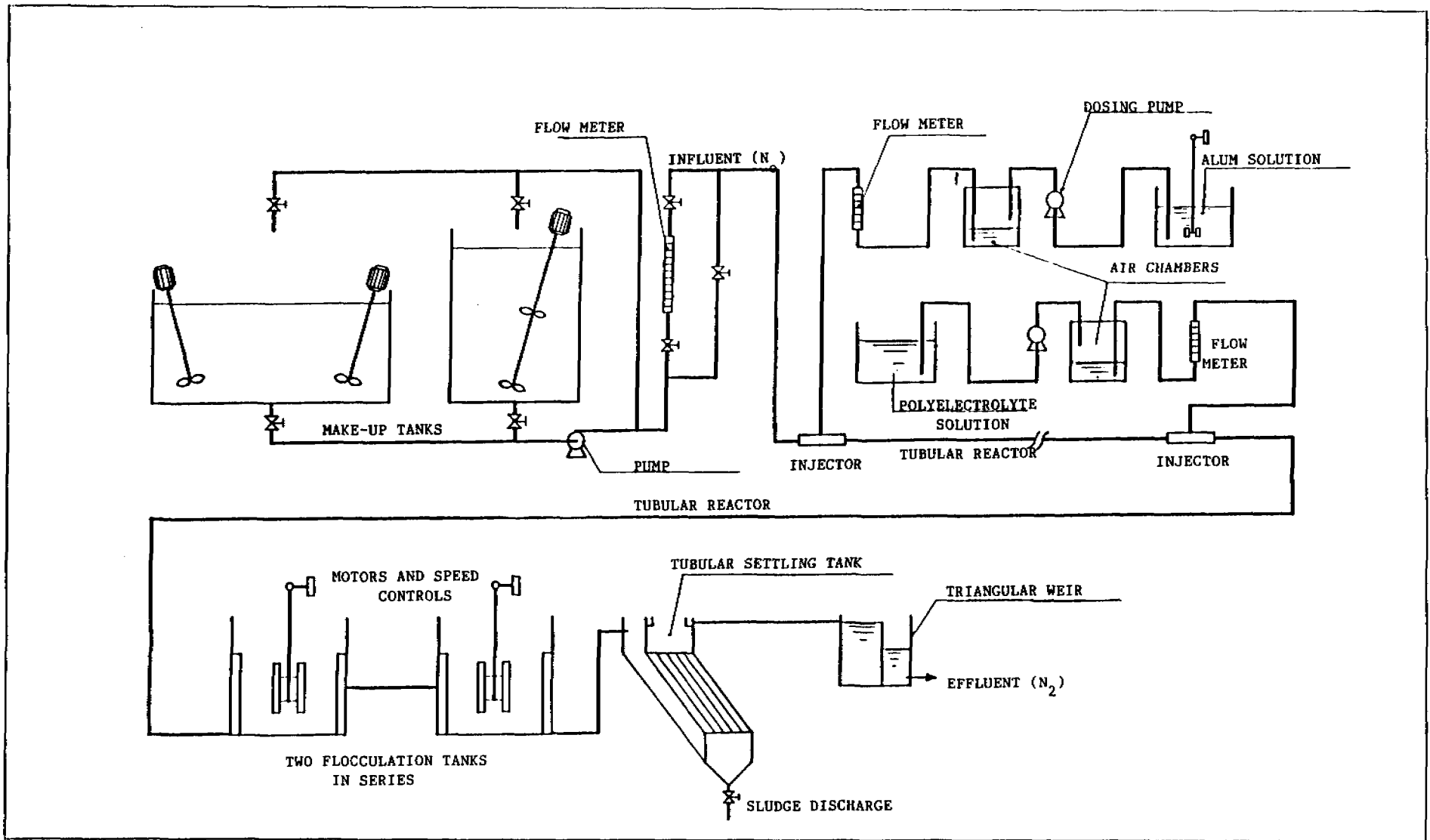


FIGURE 12 - PILOT PLANT:FLOW SHEET

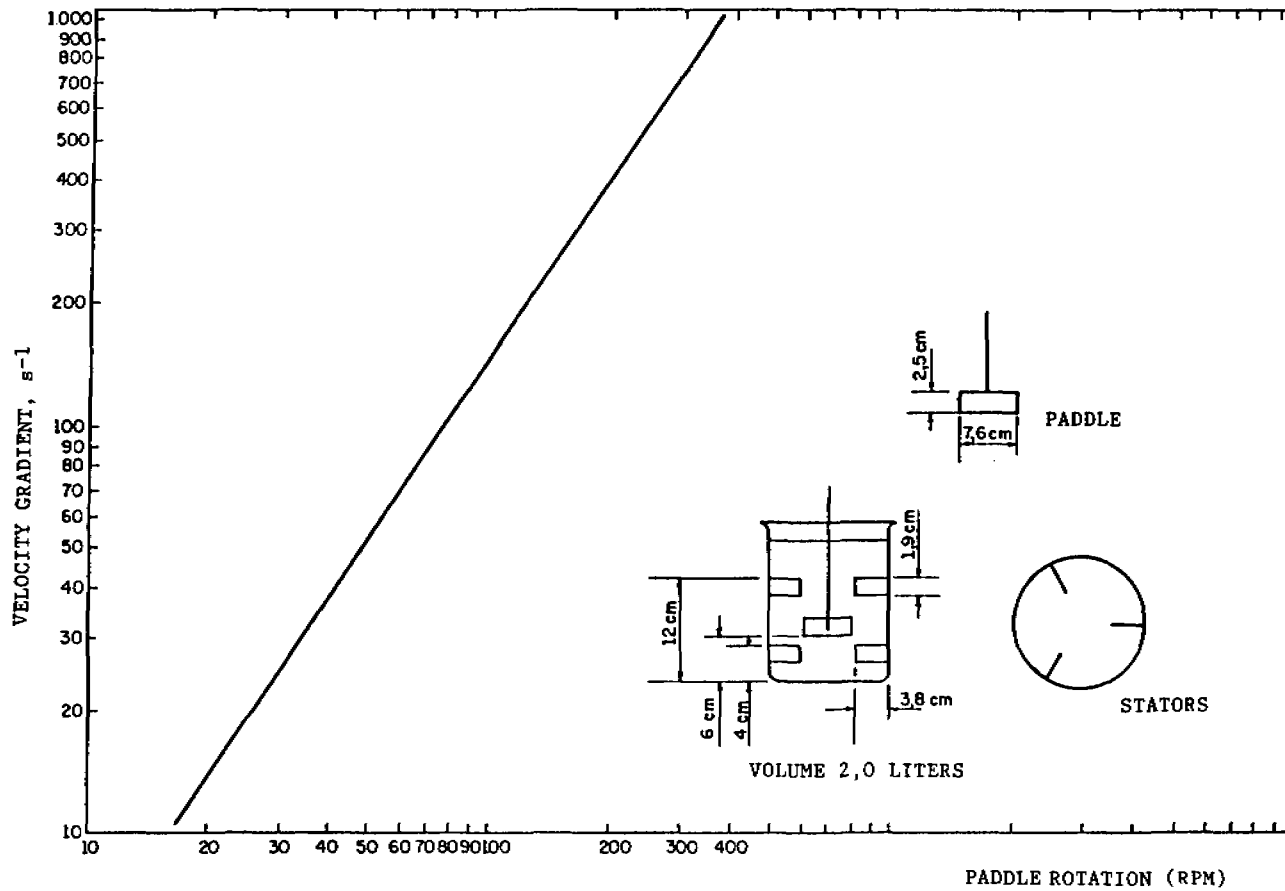


FIGURE 11 - MULTIPLE STIRRING APPARATUS - VELOCITY GRADIENT X PADDLE ROTATION

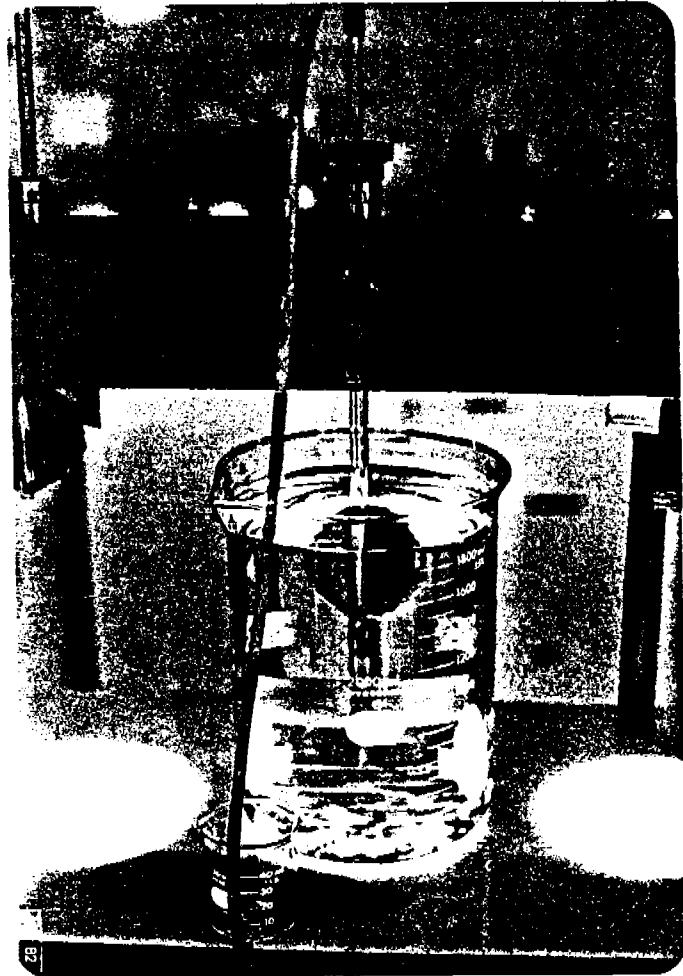


FIGURE 10 - MULTIPLE STIRRING APPARATUS WITH
FLOATING SAMPLE DEVICE AND BAFFLES

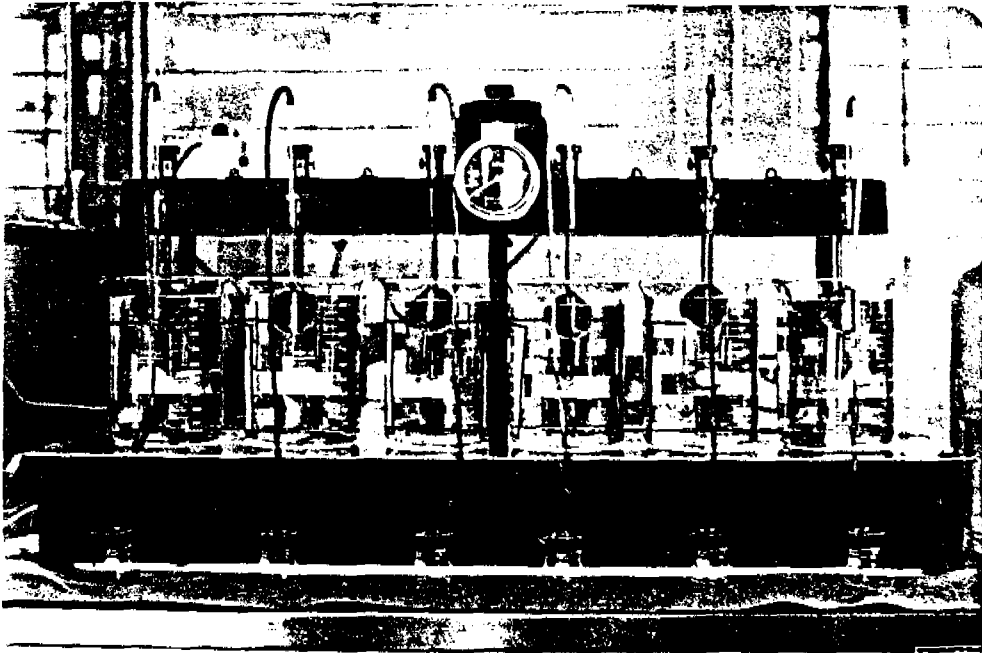
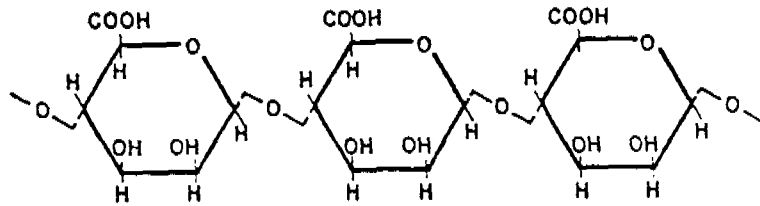
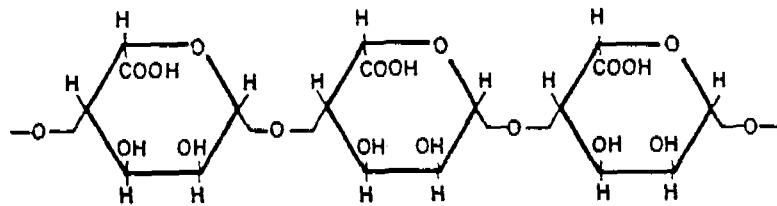


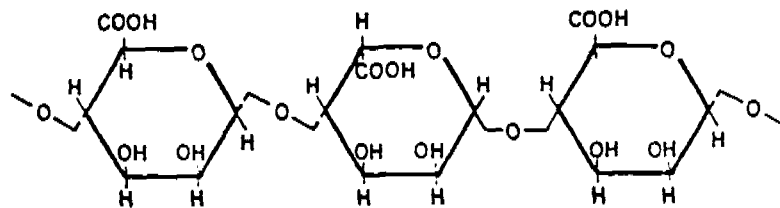
FIGURE 9 - MULTIPLE STIRRING APPARATUS UTILIZED
FOR THE STATIC EXPERIMENTS



ACID POLI-d-MANURONIC (STRUCTURE -M-M-M)



ACID POLI-L-GULORONIC (STRUCTURE -G-G-G-)



COPOLYMER MANURONIC-GULORONIC (STRUCTURE -M-G-M-)

FIGURE 8 - MONOMERS COMPONENT OF THE ALGINIC ACID