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PRETREATMENT OF SEAWATER BY FLOCCULATION AND SETTLING FOR PARTICULATES REMOVAL

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SUMMARY

Seawater flocculation was studied in this investigation as an aid in preventing fouling of reverse osmosis (RO) membranes by particulates. The behavior of clays in seawater and their possible use in the pretreatment process was also investigated. Mediterranean seawater samples were found to have a salinity of about 36‰, pH of 7.9—8.2 and turbidity of 1.0—17.5 NTU (Nephelometric Turbidity Units). After 1—3 h of quiescent settling, 30—50% of the turbidity remained and then stabilized, pointing to a possible advantage of lagooning prior to further treatment.

Tests carried out with artificial seawater, as well as natural seawater, were carried out to study particle removal in general, and algae and clay in particular. Different conventional and polyelectrolytic flocculants were used in the experiments. The best clarification was found using alum and an anionic polymer in combination, resulting in 20—100 particles per ml and a turbidity of less than 1 NTU. It was also found that particle size distribution measurements may provide a better picture of the quality and mechanism of treatment.

INTRODUCTION

It has long been established that particulate matter can cause mechanical fouling in reverse osmosis membrane units by being caught in the membrane fibers or on its surface. As the water passes through, these substances are concentrated and a process similar to coagulation—flocculation takes place. Neutralization of the particles' charge and coagulation of additional matter may occur, while the trapped matter acts as a nucleus for polymerization or flocculation. As the rate of flow increases so does the rate of fouling since more nuclei are created and, thus, the rate of growth increases [1, 2].

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Despite the high salt content of seawater, particles of colloidal nature do not tend to coagulate and settle on their own. The main components of particulate matter that may be found in coastal water are microorganisms, detritus, quartz and clay minerals. Numerous studies have proven that there is enough surface-active organic matter to be adsorbed on the surface of the particles, thus affecting the predictions of the double-layer theory and allowing particles to remain discrete [3—7].

Usually filtration is used as a pretreatment for the removal of particulate matter from seawater. Different case reports of pilot plants and full scale plants in operation have been published [8—11], and most of them utilize either in-line (contact) coagulation or conventional clarification as a destabilization means prior to the filtration step. For either method preliminary testing of flocculants is highly recommended due to similar attachment mechanisms [12, 13].

The above articles point out the important role of flocculants in the pretreatment of seawater and, together with the existing need for the improvement of the design and economics of the systems involved, call for more systematic research in this area.

Our research was aimed at studying seawater flocculation by: (a) chemical, physical and biological characterization of seawater (in this case Mediterranean water) and particulates in relation to flocculation mechanisms; (b) study of clays and algal behaviour in a seawater chemical environment; and (c) study of seawater flocculation as a method for the removal of particulates or as a preparatory destabilizing step before filtration.

EXPERIMENTAL

The flocculation of algae and clays was first studied in artificial seawater. Water was prepared according to the analysis of salt content of real seawater made by Lyman and Fleming [21]. Clay (bentonite and kaolinite) suspensions were prepared by dissolving 2.5 g clay in 500 ml distilled water and then mixed at 25 rpm for 20 min, at 250 rpm for 1 min and 30 s sonication. The alga chosen was *Nannochlorus*, a non-flagellate spherical cell found free-floating in the water. The tested flocculants were aluminum sulphate (alum) and various polyelectrolytes. The tests were carried out in a jar test apparatus consisting of six paddles with 1 l beakers of sample. Each "jar" contained a different concentration of coagulant tested. The standard test involved 1 min, 100 rpm rapid mixing and 20 min, 25 rpm slow mixing, followed by quiescent settling. After 30′ of settling, turbidity and pH were measured and for certain tests particle size distribution was determined.

Such main characteristics of seawater and of particles as salinity, pH, alkalinity, total dissolved solids, suspended solids, turbidity, particle size distribution, algal count and identification were determined. Samples were taken from different beaches on the Mediterranean coastline. Analytical methods were those of Strickland and Parsons [14] and Standard Methods [15]. A HIAC/ROYCO particle size analyzer, model PC-320, was used to measure particle size distribution in the 4—300 μm range. This instrument was found to be very useful for this type of work [16]. In addition, scanning electron micrographs were made of the residuals of various samples filtrated through a 0.45 μm Millipore filter. Turbidity measurements took place using a HACH nephelometer.

The last stage of experimental work consisted of flocculation tests in the jar test apparatus with Mediterranean seawater using alum, ferric chloride and various polyelectrolytes.

RESULTS

Artificial seawater

Clays were tested with a double purpose: (1) to represent the inorganic (mineral) suspended solids component of seawater, and (2) to examine the possibility of using clay as a flocculant aid by increasing the number of particles present or as material for absorption, improving flocculation.

In the first stage, settling tests were carried out with different concentrations of clay in artificial seawater. Within a few hours most of the clay had settled and after 24 h the residual turbidity was less than 1 NTU for all concentrations of clay, pointing at very unstable conditions.

Flocculation tests with three concentrations of bentonite (10, 50 and 200 mg/l) were performed with different flocculants such as alum, cationic and anionic polymers and combinations of these. Fig. 1 shows flocculation curves for tests with alum alone. At about 25—35 mg/l of alum the turbidity removal reaches a maximum (60—85% removal, 0.75—1.75 NTU residual). A sharp peak, as is usually found for polyelectrolytes but not for alum in surface water, appears at the optimum alum dose, presenting a quick overdose phenomenon. Flocculation curves for similar tests performed with a combination of optimum alum doses and polyelectrolyte (Magnafloc LT 25) are presented in Fig. 2. Maximum turbidity removal was 77—95% with the typical phenomenon of a single peak for optimal polymer dosage. It can also be observed from the graphs that particle counts followed the turbidity results pretty closely.

The range of algae concentrations in seawater is usually $1.2–2.6 \times 10^3$ cells/ml [17, 18]. As mentioned above, *Nannochlorus* was used as the representative alga in these experiments. Concentrations of this alga of less than 10^3 cells/ml did not affect turbidity.

Fig. 3 shows the results of flocculation tests of artificial seawater containing $705–2 \times 10^5$ algal cells/ml with alum. The optimum alum concentration was similar (20 mg/l) over most of the algal concentration. The flocs were usually small and light. Overdosing occurred at slightly higher doses. Turbidity and particle size distribution were measured. Turbidity removal was relatively low (45—75%). Since there was no direct way to measure removal of algae it is hard to say what percentage of algae was removed. The use of 0.05 mg/l anionic polyelectrolyte (superfloc A110) with alum improved the turbidity removal (84%) and gave larger flocs.

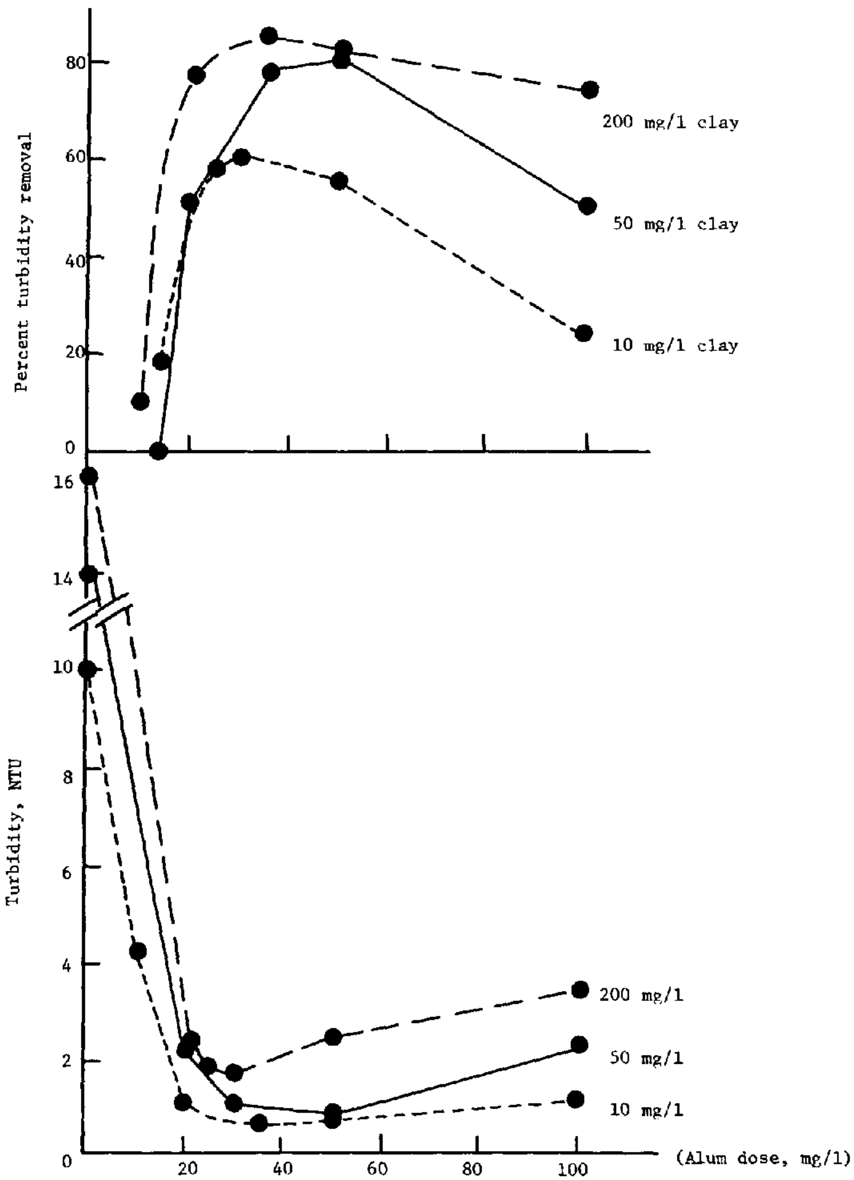


Fig. 1. Flocculation curves for tests with alum in artificial seawater containing varying concentrations of Kaolinite Ramon.

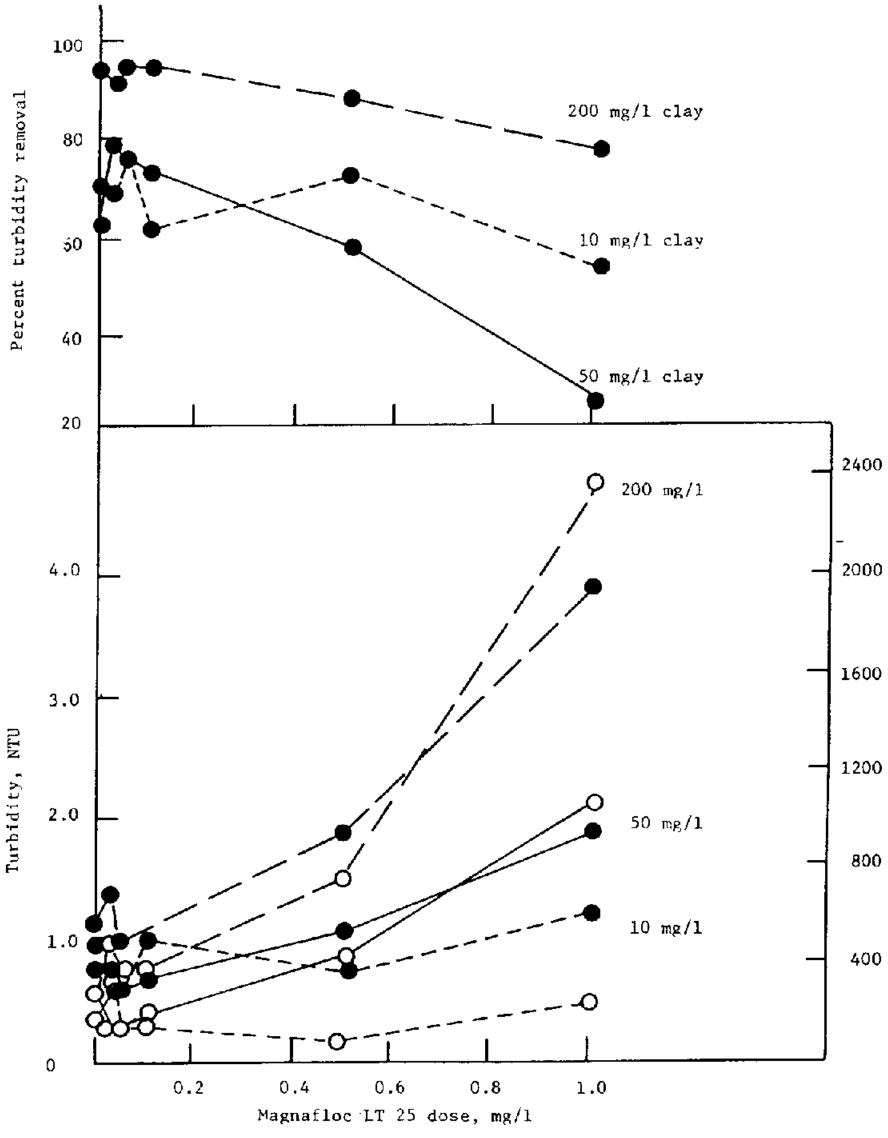


Fig. 2. Flocculation curves for tests with alum and Magnafloc LT 25 in artifical seawater containing Bentonite Ramon, ●, turbidity; ○, particle count.

Fig. 4 shows the flocculation curves when both algae and clay were added to artificial seawater. A larger plateau of good removal was obtained here as compared to algae alone. The optimum dose was 25—35 mg/l alum. The lowest final turbidities were for 10 mg/l clay, but they were higher for no

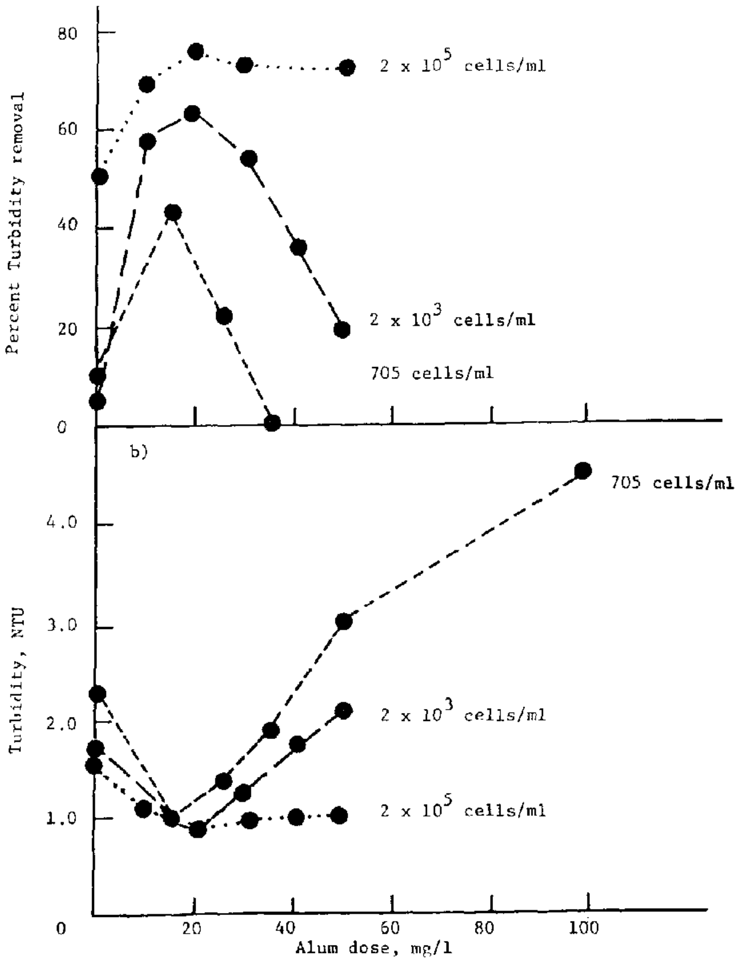


Fig. 3. Flocculation curves for tests with alum in artifical seawater containing different algae concentrations.

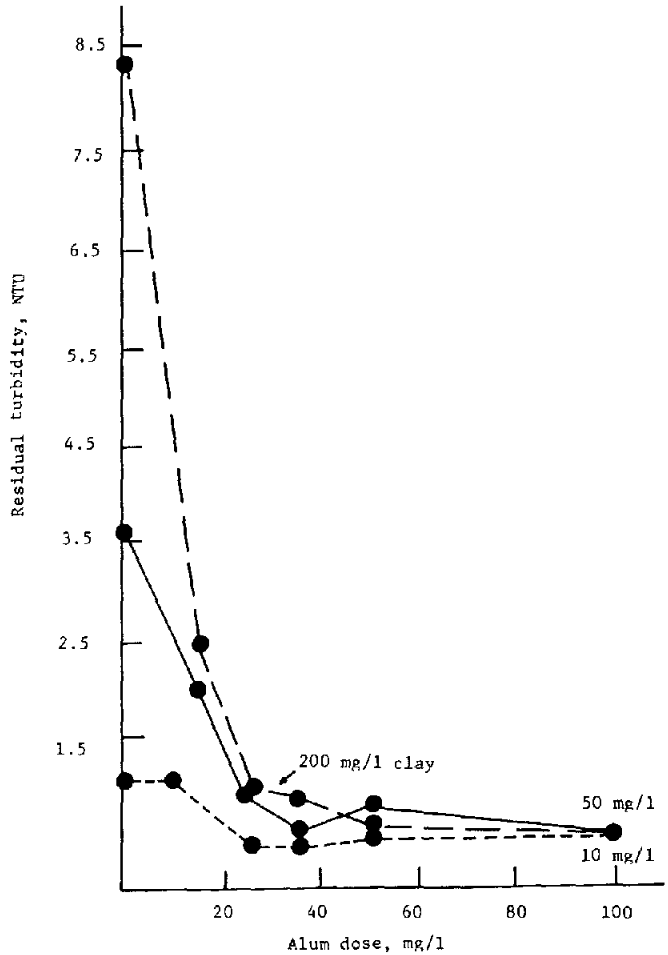


Fig. 4. Flocculation curves for tests with alum in artificial seawater containing 1 × 10^3 cells/ml and various clay concentrations.

clay addition (0.36 and 0.40 NTU as compared to 0.45 and 0.42 NTU for 10^3 and 10^5 cells/ml respectively).

Mediterranean seawater characteristics

Eleven samples of seawater were taken from a number of beaches. Table I shows the date and location of sampling and some of the quality parameters measured for each sample. As can be seen, salinity, as measured by titration with silver nitrate, ranged from 30.06—38.88‰, total suspended solids were 7.6—35.4 mg/l and turbidity 1.0—17.5 NTU. High turbidity was due to the presence of sand. pH was in the normal range for seawater (7.9—8.2) as was the number of algae, 62—2650 cells/ml. Total particle counts for 4—300 μm ranged from 1072—5292 particles/ml.

Algae identified included *Nannochlorous*, *Asterionella*, *Nitzchia* and *Chlamydomonas*. All these algae are also found in polluted estuaries and were present in most of the samples examined.

In addition, to characterize the particles in seawater in the range of less than 4 μm, electron micrographs were made using a scanning electron microscope (SEM). Particles in the colloidal size range of less than 1 μm and even as small as 0.1 μm were measured. These were usually crystallites, although some particles were of undefined shape. Matsumura et al. [19] indicated that the crystallites are likely aluminum silicate clay particles and perhaps algae.

A settling test was carried out for each sample in order to determine the amount of settleable solids. Fig. 5 shows tests for several samples of seawater. Turbidity was measured at varying intervals during a 48 h period. The samples started with a large range of turbidities: 1—12 NTU. After 1—3 h the turbidity dropped sharply (30—50%) and after 48 h only 12—50% of the initial turbidity remained (0.5—1.5 NTU). The significance of these results in planning pretreatment is that it may be useful to have a primary settling basin with 1—3 h residence time before flocculation or direct filtration.

Fig. 6 shows results for the settling of sample G (see Table I) to which several concentrations of clay were added (10, 150, and 200 mg/l) without any chemical addition. After 23 h of settling, the appropriate turbidities approached each other (1.7—2.4 NTU) and after 47 h they ranged from 1.0 to 1.5 NTU, while the sample that contained no clay had the lowest final turbidity. These results indicate that the addition of clay considerably improves the percentage sedimentation, as could be expected from flocculation kinetics, but does not improve the clarification of seawater by settling in absolute numbers.

Flocculation of natural seawater

Flocculation tests were carried out with alum and ferric chloride. Comstock [11] considered the latter more effective but the results found in this work do not indicate it clearly (one may bear in mind that iron itself is considered

TABLE I

SUMMARY OF RESULTS OF CHARACTERIZATION OF SEAWATER

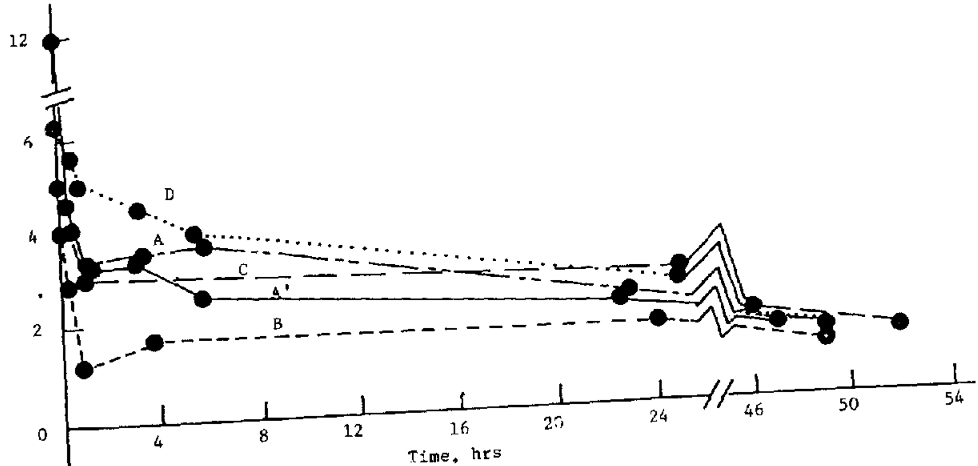
Sample	Date of sampling	Location of sampling	Salinity ‰ by titration	Salinity ‰ by density	TDS mg/l 180°C	pH	Turbidity NTU
A	14/12/82	Tel Aviv near the opera	37.49 (21.31)*	ND+	ND	8.2	11.5—17.[illegible]
B	15/1/83	Jaffa Port	35.59 (20.20)	ND	ND	7.9	4.9
C	23/2/83	Ashelon desalination plant	34.39 (19.5)	ND	27 760	8.2	8.0
D	10/3/83	Jaffa Port	30.06 (16.99)	ND	28 860	8.1	5.7
E**	4/6/83	Rishon Le — Zion Beach	35.04 (19.88)	ND	38 160	8.0	2.0
F**	18/6/83	Gordon Beach — Tel Aviv	37.87 (21.53)	37.1	36 870	ND	1.9
G	5/7/83	Ashkelon desalination plant	36.76 (20.88)	41.4	41 960	7.96	2.4—3.0
H**	9/7/83	Rishon Le — Zion Beach	34.28 (19.40)	41.0	43 810	8.26	1.0
I	21/8/83	Nof Yam Beach	36.14 (20.52)	39.4	27 590	8.2	2.1
J**	18/10/83	Rishon Le — Zion Beach	38.88 (21.33)	41.4	42 130	8.15	1.2

* Chlorinity by titration.
\+ ND — Not Done.
** Temperature taken at time of sampling for samples E, F, H and J was 27, 28, 28 and 25°C, respectively.

to be a fouling agent). Ferric chloride gave slightly larger flocs than alum but in both cases (when used as sole flocculants) the flocs were small, light and slow to settle. Fig. 7 shows, for example, flocculation curves for two seawater samples flocculated with aluminum sulfate and ferric chloride. Summarizing all the tests performed, the maximum turbidity removal was 40—80% depending on initial turbidity as well as clarification. For all samples the optimum alum dosage range was 30—50 mg/l and the $FeCl_3$ dosage

Total suspended solids mg/l	Volatile suspended solids mg/l	Particle count per ml (4—300 μm)	Total alkalinity per ml as $CaCO_3$	Algae cells per ml	Phosphorus mg/l	Optimal alum dose mg/l
9	4.4	ND	135	ND	ND	40
18.4	—	ND	133	ND	ND	30
41.5	6.8	4373	148	ND	ND	30
9.8	5.2	5292	145	ND	ND	40
7.6	2.9	2964	145	625	0.008	30
10.8	5.6	2677	ND	2650	0.029	30
9.6	4.6	2580	145	460	ND	35
ND	ND	1072	147	63	ND	30—35
35.4	8.7	1824	143	2000	ND	50
30.4	24.2	1420/1855	158	1100	ND	30

range 20—50 mg/l. Overdosing occurred rather close to the optimum dose, giving a small plateau, while conventional coagulants in surface water usually give a wider range of optimum turbidity removal. The lowest particle counts for treatment with alum were 42—237 particles/ml (up to 95% removal). pH decreased linearly with increasing coagulant doses (little more than 1 unit for 100 mg/l of coagulant). Ferric chloride was slightly more influential in this respect.



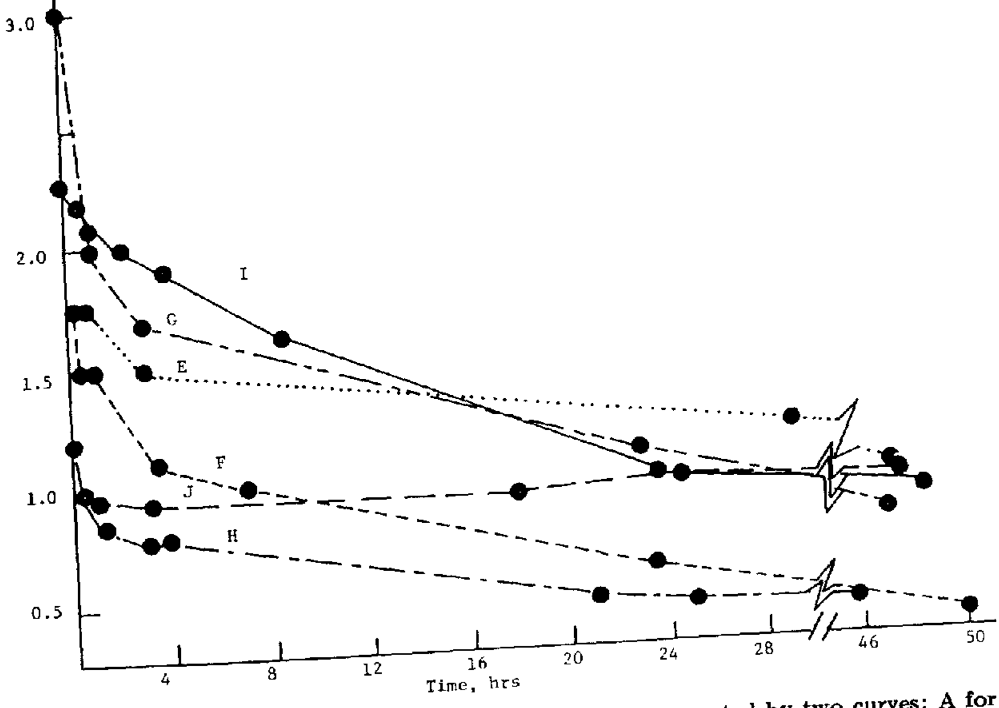


Fig. 5a. Settling tests for seawater samples A—D. A is represented by two curves: A for after mixing of sample and A′ for mixing and 15 min settling of sample before transfer to settling test.

Fig. 5b. Settling tests for seawater samples E—J.

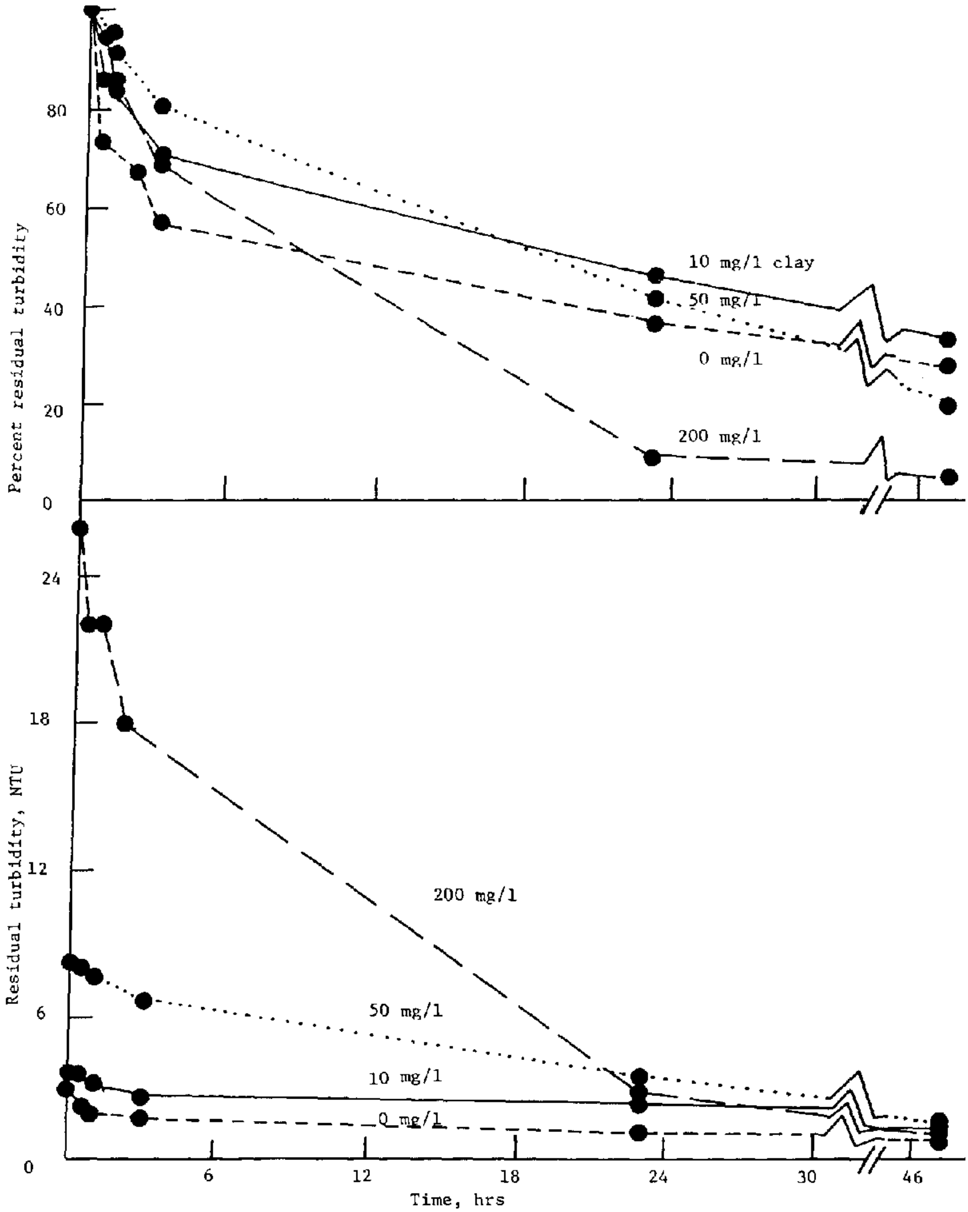


Fig. 6. Settling tests in seawater sample G, containing various concentrations of Bentonite Ramon.

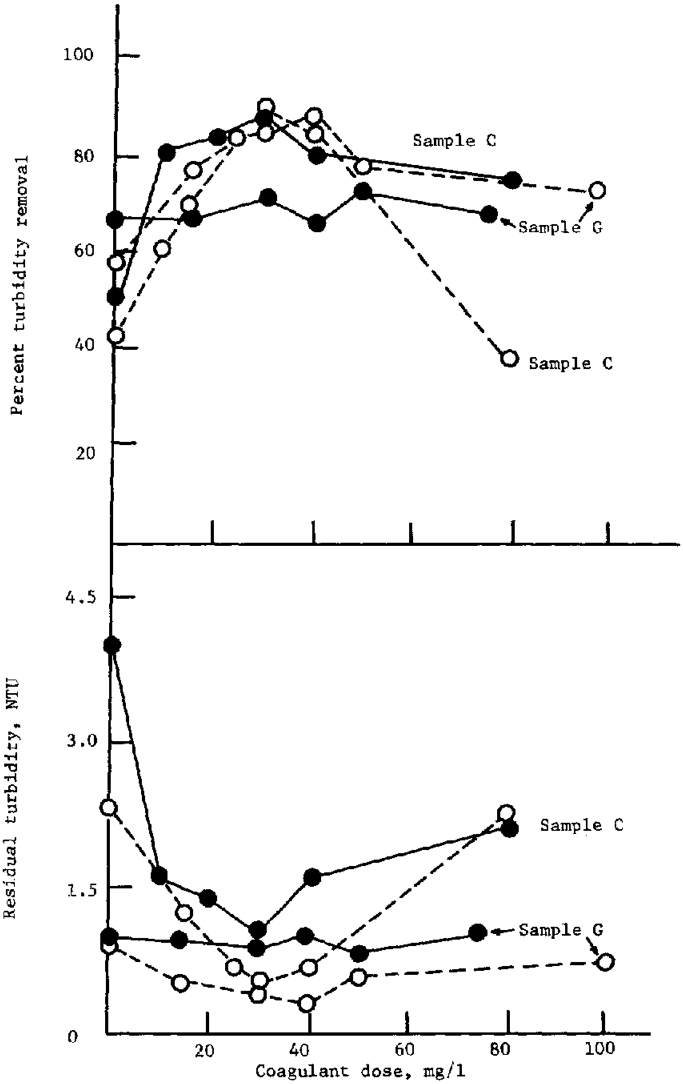


Fig. 7. Comparison of flocculation curves of Mediterranean seawater with conventional flocculants: aluminium sulfate and ferric chloride, ●, alum; ○, $FeCl_3$.

The best results for particle removal by flocculation were found when alum was used with an anionic polyelectrolyte. The flocs formed were larger, settled more quickly and formed a more compact precipitate than alum alone. The most effective polymers (out of 16 tested) were Magnafloc LT25 (0.05—0.1 mg/l) and Superfloc A1839 (0.01—0.05 mg/l). Superfloc A-110 (0.025—0.05 mg/l) was also effective (e.g. Fig. 8). All three flocculants are permitted for use in drinking water by the U.S. Health authorities. The presented experimental findings indicate a clear case for optimal polymer dosage, in accordance with previous works done with polyelectrolytes [12]. Although the improvement in turbidity due to addition of polyelectrolytes is small, compared to treatment with alum alone the improvement in the flocs properties is significant, and can be of great effect in actual plants.

Clay, in concentrations of up to 400 mg/l, was further tested for use as an aid in flocculation with alum. It was found that it did not significantly improve turbidity removal whereas a much larger precipitate was formed.

According to work done on sewage treatment by Narkis et al. [20] higher clay concentrations may be needed in order to obtain improved treatment. However, this creates the problem of massive sludge removal or storage.

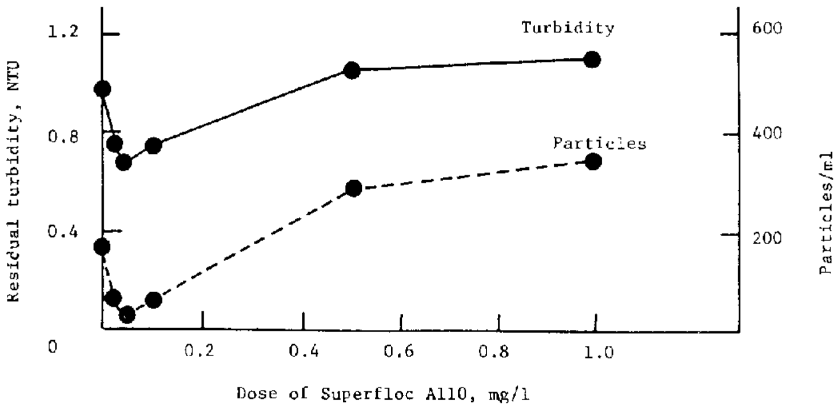


Fig. 8. Flocculation curve for seawater sample E after flocculation with 30 mg/l alum and various doses of Superfloc A110.

DISCUSSION

The best clarification by flocculation of seawater at different clay concentrations was found with alum and an anionic polymer. This combination gave larger, more stable flocs than those with aluminum alone. This suggests that the anionic polyelectrolyte is likely to act as a flocculating agent via chemical interaction and bridging.

Algae do not significantly contribute to the turbidity of seawater at usual concentrations nor are algae always counted one to one by a particle counter. This depends on the size of the algae and the detection limits of the particle counter. Percent turbidity removals of algae-containing seawater were lower than for clays. However, this may or may not reflect similar removal of algae. Since no simple and reliable method could be found to monitor algal concentrations, none was used. The addition of clay did not seem to improve the removal of algae. Alum with an anionic polyelectrolyte gave better treatment than alum alone.

Settling tests indicate that an initial clarifier in the pretreatment of seawater could help if it allowed for 1—3 h settling. Settling with the addition of clay in seawater was similar to that in artificial seawater but did not actually contribute to turbidity removal.

Aluminum sulfate as a coagulant gave better turbidity removal than ferric chloride. The flocculation of seawater does not seem to differ from that of fresh water except that overdosing occurs in a very close range to the point of maximum turbidity removal by conventional coagulants. Therefore frequent monitoring of coagulant dosing is necessary.

Flocculation tests were carried out both to test the use of flocculation as a pretreatment process and as preparatory work for contact flocculation—filtration tests. Although these processes differ, a similarity in the relation between removal efficiency, dose and strength of flocs formed was found by other investigators, showing that there are some common mechanisms in the two processes.

The use of polyelectrolytes as primary coagulants did not give good clarification. This may be due to the relatively low particle concentration, thus making collisions less frequent. However, alum with an anionic polymer gave the best treatment in the case of clays. Although turbidity removal values were not always higher than for alum alone, the flocs were larger and settled three times as quickly. The addition of clay as a settling aid did not improve treatment and merely increased the amount of precipitate (making it uneconomical as well).

CONCLUSIONS

1. Setting tests in seawater indicate that a sedimentation tank with 1—3 h residence time could give 50—70% turbidity removal. The use of clays as settling aids gives practically no advantage.

2. The best treatment by flocculation in the seawater tested was by aluminum sulfate dosages of 20—30 mg/l with an anionic polyelectrolyte flocculant aid at concentrations of 0.025—0.1 mg/l.

3. A combination of alum and an anionic polyelectrolyte gives the best clarification in artifical seawater containing clay — about 70—98% turbidity removal.

4. Algae do not affect the turbidity level at the concentrations most commonly found in seawater, i.e. less than 10^3 cells/ml. It is possible to remove them by 45—75% with flocculation using alum or alum and an anionic polymer.

5. A particle counter is useful for the evaluation of the flocculation process and shows that the percent removal of particles is greater than the turbidity removal in the range tested.

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