

# **EFFECT OF ACID DOSING OF SEAWATER FEED AHEAD OF SAND FILTER ON PHYTOPLANKTON DEGRADATION<sup>1</sup>**

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## **ABSTRACT**

In an RO pretreatment system sand-anthracite filters trap and concentrate suspended matter of organic and inorganic nature, including phytoplankton resulting in a seawater feed with lower turbidity. When seawater feed is acidified ahead of sand-anthracite filter the acid reacts with the trapped matter, mainly with the cellulosic cellular wall structure of the phytoplankton, degrading it to smaller sized particles and soluble glucose. The soluble glucose is not removed by the sand filter and thus it flows with the filtrate along with other acid degraded cellular products, e.g., lipids & proteins. The concentration of these degraded products found in the filtrate is dependant on the amount of the phytoplankton trapped on and within the sand filter. In one of the experiments, over 16 ppm glucose was found in the filtrate collected from an acidified feed enriched with phytoplankton. Passage of such a feed with a high ratio of glucose and other products resulting from acid degradation on RO membranes containing living microorganisms provides them with the necessary nutrients on which they feed and can rapidly multiply. This process leads to an increased formation of biotilm on the membrane and may give rise to membrane biofouling. Another disadvantage of dosing acid ahead of sand filter is that it leads to a rise in the feed acid demand. Acid is consumed in the neutralization of the organic and inorganic matter which otherwise i.e., without acidification would have coagulated and trapped in the sand filter without their degradation into soluble products. In one case the acid demand for a phytoplankton enriched feed was about 38% higher than that for a similarly treated normal seawater feed. Moreover, in an acidic medium the chlorine becomes more potent than in a neutral or alkaline medium, which contributes to the further destruction of the phytoplankton cells into smaller fragments and increases the chlorine demand. It is recommended to carry out this experiment, which was done using a small sized sand filter, on a pilot plant scale and if proved beneficial it should also be tried on a large size RO plant, e.g., SWCC Al-Birk SWRO Plant.

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## 1. INTRODUCTION

The pretreatment of feed water in desalination by Reverse Osmosis is a crucial factor for the process to run efficiently maintaining the designed salt rejection and flux within the lifetime of the membrane. By pretreatment it is meant that the feed water physical and chemical parameters are suitably adjusted to achieve the maximum efficiency from the process. The physical parameters involved are those which could be altered beneficially with or without the addition of chemicals. To avoid excessive use of costly chemicals and not to create an environmental problem the change in chemical parameters are brought about by suitably adding certain chemicals in the proper place at the proper time. In the RO process chlorination, coagulation-flocculation, antiscalant addition and finally acidification with sulfuric acid play very important roles.

In seawater besides heavier particles there are suspended particles. These may be of organic (alive or dead) or inorganic origin. To meet the feed water demand of the RO plant filtration of the seawater is carried out by passing it through a graded column of sand and anthracite. Filtration of seawater is a time consuming process, even more so when the quantities of treated feed water required are in thousands of m<sup>3</sup>/hr for a medium sized RO desalination facility. To have a reasonable rate of filtration the process of coagulation-flocculation is used ahead of filtration. Colloidal particles which are in the range of microns are coagulated, thereby there is an increase in their size, and filtration could be carried out at a faster pace. Flocculation is a step further wherein these coagulated particles aggregate into still larger particles. Floe formation helps to trap within them algae, bacteria and other microorganisms. The coagulation-flocculation process requires control of specific conditions, e.g., feed water temperature, no turbulence after coagulation and pH, etc, to be maintained for the effectiveness of the process. The filtrate itself would have lesser numbers of algae and bacteria.

The sand/anthracite filters tend to get clogged-up quickly when there is bacterial and phytoplankton build-up on the filter surface. To control the proliferation of bacteria and other living organisms on or within the sand/anthracite filters chlorine is normally dosed. This results in a decrease of microorganisms due to the biocidal activity of chlorine. The organisms are retained on the surface of the sand/anthracite filters either as spores or dead cells until the next backwash. Meanwhile, the dead cells lyse and their cellular products enter the feed stream. Their concentration in the feed is dependant on the concentration of the accumulated organic mass in the feed water itself.

Dosing of sulfuric acid prior to the filtration process causes hydrolysis of the cell walls of plant tissue, and their selective conversion into their constituent sugars. These degraded products and humic acids<sup>1</sup> when passing through the filter enter the RO system and provide the food for the microscopic living organisms that had survived the lethal attack of the disinfectant and established biofilm on membrane surfaces. The availability of food in the form of sugar from the acid degraded cell tissue gives rise to increased growth and multiplicity of the microorganism, eventually leading to a rapid rate of

membrane biofouling. This study examines the effect of acid addition to seawater feed ahead of the filtration process on the quantities of acid degraded biological products, e.g., sugars.

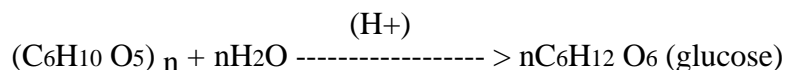
## 2. Phytoplankton

Phytoplankton are the grass of the oceans. They are the primary food source in the food chain of other living organisms found in the sea. They live by the photosynthetic activity trapping with the help of their chlorophyll pigments carbon dioxide together with other nutrients mainly nitrate and phosphate, in presence of sunlight to formulate the cell building blocks and also the food necessary to sustain them. The chief products found within their bodies bound to cell walls are composed mainly of cellulose<sup>2</sup>, other carbohydrates, proteins and fats. Small unicellular algae contain upto 10-60% of their dry weight as proteins and 4-80% of their dry weight as lipids<sup>3</sup>. Under favorable conditions they are capable of remarkably rapid growth, sometimes producing its own weight of new organic material within 24 hours, a rate greater than that achievable by land plants<sup>2</sup>. Eventually as a result of respiration and excretion, death and decomposition, organic materials become broken down and are returned to the water as simpler substances, e.g., humic acids. These degraded products are again utilized by bacteria and other microorganisms as a food source<sup>2</sup>.

Cell wall of algae are variable in composition and structure, e.g., cell walls of the Rhodophyta, Chlorophyta, Phaeophyta and Xanthophyceae contain a greater variety of fibrous and matrix carbohydrate although cellulose is usually present. Cellulosic microfibrils form the framework of the cell wall of most green plants including algae and some fungi. Cellulose is a polysaccharide consisting of long straight unbranching chains of B-D-glucose residues joined by 1,4 links. In phytoplankton the principal sugar in cellulose has been shown to be glucose<sup>4</sup>.

## 3. Degradation of Cell Wall (Cellulose) in Presence of Acid

Dosing of sulfuric acid causes hydrolysis of the cell walls, and their selective conversion into smaller constituent sugars. Depending on the source of the cellulose<sup>5</sup> in the plant tissue it is converted into glucose, mannose or xylose. In presence of acid the cellulosic wall in phytoplankton is degraded to glucose:



Hydrolysis occurs rapidly converting hemicelluloses into simple sugars within matter of minutes or even seconds. Strong acids, 70-72% sulfuric acid, even dilute acids, 052% sulfuric acid cause hydrolysis of cellulose to simple sugars<sup>5</sup>.

In general, addition of acid may improve the coagulation-filtration process resulting in an improved feed quality. In certain cases, however, addition of acid prior to filtration may increase the solubility of certain colloids leading to membrane colloidal fouling. However, this rarely is the case.

#### **4. Determination of Sugars in Acid Degraded Phytoplankton**

The sugar was determined using the standard method as described in "A Practical Handbook of Seawater Analysis" by J. D. H. Strickland & T. R. Parsons<sup>6</sup>. Phenol and sulfuric acid are added directly to seawater and after a period of an hour the extinction of the resulting color is read in a spectrophotometer at 490 nm, slit width 1.0 nm and using a 5 cm cell. The color so formed is stable for 24 hours and the sensitivity of the procedure is between 0.10 to 20 mg/lit. Calibration curves were obtained by preparing standards from pure glucose in the range 0.5 to 5.0 ppm.

#### **5. Experimental Work**

To examine the effect of feed acidification with & without phytoplankton in seawater on pH, glucose and lipid content of the filtrate, a total of five different experiments were made. Nonchlorinated seawater was collected from the Jubail plants intake basin between 0730 to 0930 hrs on different days. Seawater was filtered through different media, e.g., glass fiber GA 200, sand/anthracite column. Phytoplankton net was used to concentrate the phytoplankton required in the experiments.

In experiments number one & two, to ensure that there is no acid consumed by the clean filtering media, blank runs were performed on a sand/anthracite column and a glass fiber GA 200 filter paper [Table 1](#) and [Table 2](#). In experiment number three, concentration of Algae and other suspended matter was made by first passing 50 liters of seawater (pH 8.2) through a sand/anthracite column. One liter of the seawater filtrate (pH 8.2) was acidified to pH 6.25 and passed through the same column (run # 1, [Table 3](#)). The filtrate (pH 7.27) was again acidified to pH 6.37 and passed again through the same column to yield filtrate with pH of 7.26 (run # 2). The process of collecting, acidifying, and passing of filtrate through the filter column was repeated for twenty times ([Table 3](#)).

In experiment number four, two buffer solutions, one liter each, pH 8.3 & pH 5.8 were prepared in distilled water. A total of 50 liters of unchlorinated seawater, (pH 8.2) was filtered through a GA 200 glass fiber filter paper. The trapped phytoplankton on the surface of the glass fiber filter paper was treated first with a liter of the high pH buffer (8.3). The process was repeated 4 times, after which the low pH buffer (5.80) was passed through the same glass fiber filter paper containing the trapped phytoplankton. The same filtrate was passed repeatedly without observing any change in the filtrate pH of 9.14 [Table 4](#)).

In the fifth experiment phytoplankton was collected using a phytoplankton net and concentrated by centrifugation. Concentration was achieved using a refrigerated centrifuge model Europa 24 M capable of attaining a g value of 49,640 'g'. An accumulated suspension of phytoplankton and seawater sample was centrifuged at, 14000 rpm corresponding to approximately 34748 'g', 25°C for about 45 minutes. The supernatant seawater was filtered through GA 200, its total alkalinity, glucose & lipid levels were determined. The compacted residue obtained from the centrifuge, approximately 2.5 ml, was diluted to 100 ml using the filtered supernatant. The residue could not be dispersed evenly through the filtered supernatant. However, after waiting for 15 minutes, 25 ml of sample was pipetted out, of whatever was dispersed, and diluted with 25 ml of distilled water (Table 5). Acid consumption and glucose content was determined for the filtrate from seawater feed with and without phytoplankton addition.

## 6. Results and Discussion

Table 3 shows the changes in the pH of filtrate of an acidified seawater when it is passed through sand-anthracite filter with phytoplankton trapped on and in the filter. The pH of the seawater filtrate increases from a range of 4.22 to 6.37 for the unfiltered acidified seawater to a pH range of 6.62 to 7.27 for the filtrate. This peculiar behavior, i.e., rise in pH of the filtrate collected after acid addition to seawater sample containing phytoplankton results partially from the neutralization of the acid by seawater alkalinity and partially due to the reaction with cellulose in the phytoplankton. This is illustrated in Table 5. A liter of seawater filtrate void of phytoplankton requires 26 ml of 0.1 N sulfuric acid to bring the pH down from 8.2 to 4.5. By comparison, 36 ml of 0.1 N sulfuric acid is required to bring the pH of 1 liter of seawater containing phytoplankton to the same level, i.e., pH 4.5. This indicates that the additional acid of 10 ml required to lower the pH to 4.5 is consumed in the conversion of cellulose in phytoplankton to sugars. The glucose present in the acidified seawater filtrate results from the conversion of the cellulose in organic matter, e.g., nanoplankton, etc, and its concentration is much lower in the seawater filtrate than in the filtrate of seawater enriched with phytoplankton.

No significant conversion of cellulose to sugar is noticed when the feed pH was raised to 8.58 (Table 4A) where the glucose level in the filtrate remains low 0.34 ppm. The sugar level, however, rose to 3.6 ppm from 0.34 ppm when the seawater feed pH was lowered to 5.8 instead of 8.3 (compare Table 4A & 4B). As mentioned earlier cellulose is degraded by acid to glucose, the suspended matter concentrated on the surface of the glass fiber filter is rich in phytoplankton whose cell wall is composed of cellulose.

The alkalinity of supernatant seawater without addition of phytoplankton collected by centrifugation was 130 ppm as CaCO<sub>3</sub>. The glucose content was 6.6 ppm, while the acid consumption to bring the pH to 4.5 was 26 ml of 0.1 N sulfuric acid per liter of supernatant. This latter number was raised to 36 ml of 0.1 N sulfuric acid per liter of supernatant (an increase of 38%) when phytoplankton was added to the supernatant. At the same time glucose level also increased (by 142%) from 6.6 ppm for the acidified supernatant without

addition of phytoplankton to > 16 ppm for the acidified supernatant containing phytoplankton ( Table 5). The results prove that the increases in both acid consumption and glucose production are due to the interaction of acid with the phytoplankton's cellular structure, mainly the cellulose part. In summary, in all cases in which acid was added to phytoplankton collected from seawater (Tables 1 to 5), besides the increase in acid consumption, an increase in glucose levels were observed.

By analogy to above results, in the RO process, when the pH = 8.2 of seawater containing plankton cells is made acidic to pH = 6 prior to the filtration process, certain changes may occur. First and foremost, the cells of dead or living microorganisms, their cellular products, are likely to be destroyed by the acid addition producing sugar along with other degradation products. Most of the large coagulated bioparticles are removed from the feed stream by the sand filter. Sugars and other low molecular weight compounds which are produced by acid decomposition of cell and cellulose walls, however, because of their small size and solubility are likely to pass through the sand filter and into the RO system. The quantities of the cellular products mainly sugar, humic acid, proteins, lipids etc, entering the RO system is proportional to the quantity of microorganisms trapped & killed due to unfavorable pH conditions on the surface of the sand filter. The more the microorganisms trapped, the more would be the cellular products entering the system, until the next backwash. This arrangement, of introducing soluble cellular products into the feed acts as an excellent source of nutrient to the bacteria and other microorganism which may be present inside the RO modules. They feed and multiply quickly resulting in an increase in the rate of biofouling of the RO membrane, and the lowering of their performance. On the otherhand, addition of acid after the filtration process is not expected to increase the sugar and other fine biodegradation products resulting from the acid interaction with the phytoplankton. The filter is likely to capture most of the phytoplankton, leaving only a few to pass through. This case, i.e., addition of acid after the filtration process, is expected to cause less membrane biofouling.

Incidentally, Al-Birk plant is the only RO plant operated by SWCC in which acid is dosed prior to sand filter. Rate of acid dosing at Al-Birk plant is 97 mg/L, higher by 51%, when compared to the other RO plants - Umm Lujj, Hagl & Duba, though all are located on the shores of the Red Sea. Part of the excess acid dosed at Al-Birk plant could be attributed to the acid consumed in the degradation of cellulose from the cell walls of algae and the dissolution of colloidal particles trapped on the surface of sand filter. The water soluble algal degradation products, i.e., glucose, lipids and proteins, could compound the loss of plant productivity, by acting as feed to the bacteria that have escaped the disinfection process and already attached to the membrane as part of a biofilm. This may partially explain the biofouling observed at this plant.

An additional advantage to dosing acid after the filtration step is the lowering of the chlorine potency in immobilizing/degrading/killing bacteria & phytoplankton. This becomes obvious after studying Fig. 1 and Fig. 2 which show respectively how the chlorine species at different pH range and their comparative potency with time at different

chlorine species concentration in water. In an acidified seawater feed to an RO plant where the pH is normally in the range of 6 to 6.5 the dominant chlorine disinfectant species is hypochlorous acid (HOCl), while in a nonacidified seawater feed (pH 8.2), the dominant species is hypochlorite ion  $\text{OCl}^-$  (Figure 18). It is evident from Figure 29 that the germicidal activity of HOCl is much greater than that of  $\text{OCl}^-$  which in turn is greater than that of chloramine. This leads to the one obvious conclusion that chlorine is a much more effective disinfectant in acidic medium than in an alkaline medium and, therefore, the immobilizing/degrading/killing of microorganisms is much greater in an acidic medium than in alkaline medium. Due to this greater killing of microorganisms by chlorine in acidified feed than in nonacidified feed the chlorine demand is expected to be much greater in the former case than in the latter where a large number of microorganisms are trapped and degraded in the filter.

Once the unacidified but chlorinated seawater passes through the sand filter which removes most of the coagulated bacteria & phytoplankton it still has a residual amount of chlorine in the feed stream which exists as  $\text{OCl}^-$  ion. On acidification of this filtrate after the sand filter HOCl becomes the dominant species which ensures an efficient kill of whatever organisms that have escaped the sand filter.

From this discussion it can be concluded that acid addition ahead of the filtration process not only increases the acid demand but also the chlorine demand. It also results in more biodegraded products in the feed flowing to the membrane. To lower both acid and chlorine demand and also to minimize the biodegraded product in the pretreated feed to the membrane it is best to dose the acid after the sand filters and not before them.

## 7. Conclusion

In the RO pretreatment process both the biodegradation of microorganisms and the dissolution of colloids, could be minimized if the acid is dosed after sand filter. A minimum of the trapped living microorganisms will die and disintegrate upstream of the sand filter if the pH is maintained at 8.2. A substantial reduction in the acid and chlorine consumption also can be achieved if the acid dosing is carried out downstream of the sand filters.

## 8. Recommendation & Further Study

It is recommended to carry out further studies on a pilot plant scale to determine the effect of acid addition before and after sand filters on nutrient concentration in the filtrate. Also on the number of colony forming units (CFU) and type of microorganisms in the feed stream to RO membranes as well as on the membrane itself.

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**TABLE 1**  
**Effect of Filtration (sand-anthracite) on pH of**  
**Filtrate Seawater Feed Acidified to pH 6.47**

Time (mins)	Filtrate pH after reaction with sand-anthracite
0	6.47
2	6.51
3	6.53
5	6.57
6	6.59
7	6.61
8	6.63
10	6.64
11	6.65
13	6.66

**TABLE 2**  
**Effect of Filtration Using Glass Fiber Filter GA 200 on**  
**pH of Filtrate Seawater Feed Acidified to pH 3.5**

Time (mins)	Filtrate pH after reaction with Glass Fiber Filter GA 200
0	3.5
2	3.54
3	3.57
5	3.59
6	3.61
7	3.62
8	3.64
10	3.64
11	3.65
13	3.67
14	3.68
16	3.88

**TABLE 3**

**Effect of Phytoplankton on the pH of Filtrate Collected by Passing Acidified (pH 4.22 to 6.37) Seawater Feed Through Sand-Anthracite Filter Containing Phytoplankton Trapped on and in the Filter Media**

**(One liter of seawater was repeatedly acidified in each of the 20 runs as shown below passed over phytoplankton trapped on and in anthracite/sand filter).**

Run	Seawater feed pH	Filtrate pH	Run	Seawater feed pH	Filtrate pH
1	6.25	7.27	11	4.7	6.7
2	6.37	7.26	12	6.15	6.621
3	5.78	7.26	13	5.57	6.8
4	5.86	7.0	14	4.68	6.73
5	5.76	6.94	15	4.36	6.66
6	5.32	6.8	16	4.22	6.63
7	5.61	6.67	17	5.34	6.67
8	5.75	6.66	18	5.66	6.83
9	5.69	6.66	19	4.61	6.8
10	5.18	6.72	20	5.75	6.81

**TABLE 4**

**Effect of Feed Acidity on Changes in pH, Glucose and Lipid Content of Filtrate Collected by Passing Buffered Solution Through GA 200 Glass Fiber Filter Paper Containing Concentrated Phytoplankton Mass Collected by Fine Filtration of Seawater.**

**A. By passing of one liter per run of buffer pH 8.3 prepared in distilled water**

RUN	Feed pH	Filtrate		
		pH	Glucose ppm	Lipids units
1	8.58	8.58		
2	8.58	8.58	0.34	ND
3	8.58	8.58		
4	8.58	8.58	0.43	ND

**TABLE 4 (contd)**

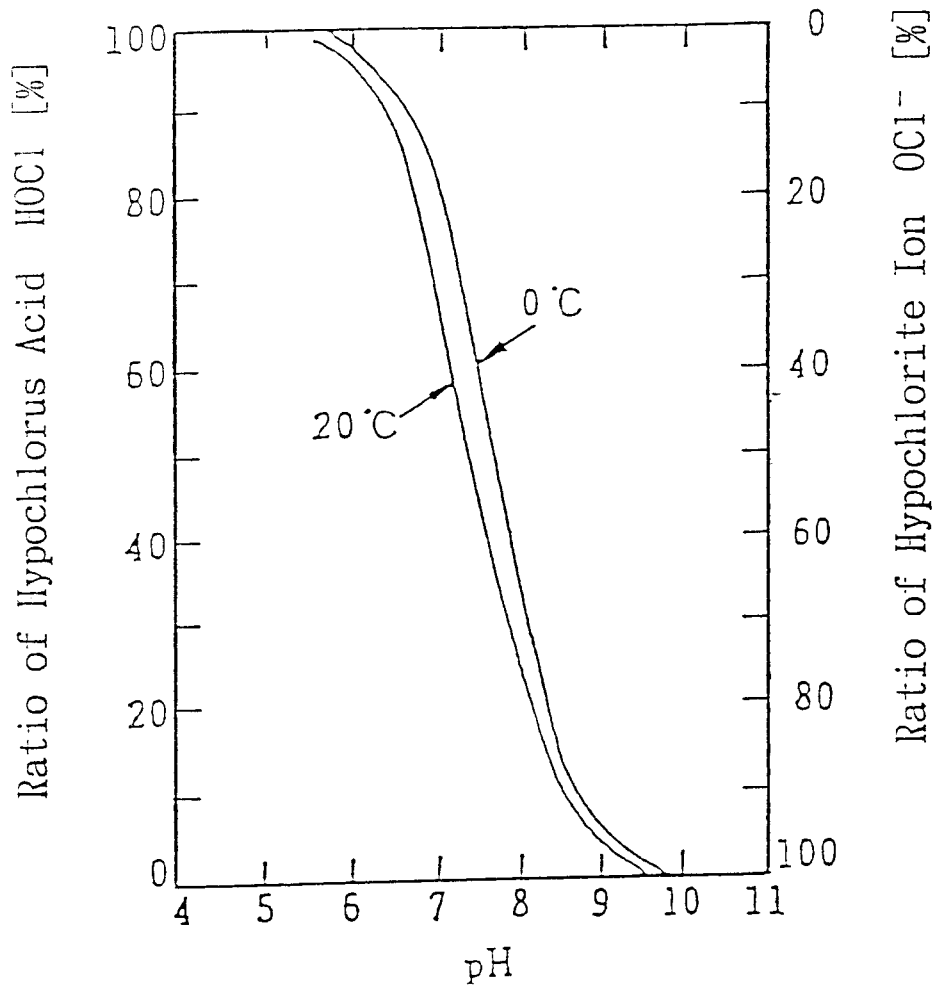
**B. By passing one liter for the first run of buffer pH 5.8 prepared in distilled water, run numbers 2, 3, & 4 were made by repeatedly using the filtrate from run 1**

RUN	Feed	Filtrate		
	pH	pH	Glucose ppm	Lipids units
1	5.80	9.14	3.6	1.0
2	9.14	9.14		
3	9.14	9.14		
4	9.14	9.14	3.62	1.0

**TABLE 5**  
**Acid Consumption & Glucose Content of Centrifuged Seawater Samples Acidified to pH 4.5 With & Without the Addition of Phytoplankton**

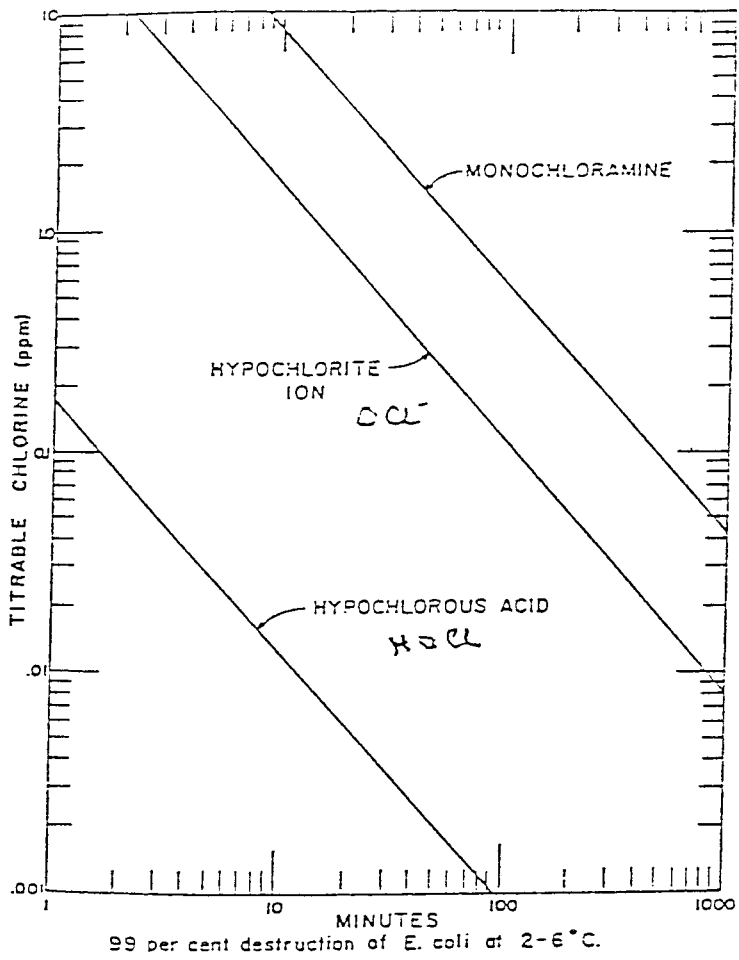
Sample	Acid Consumption (0.1N H <sub>2</sub> SO <sub>4</sub> ml/Lit)	Glucose (ppm)
Seawater supernatant without phytoplankton enrichment	26	6.6
Seawater supernatant with phytoplankton enrichment	36	> 16.0

FIGURE 1



Relationship of ratio of hypochlorous acid and hypochlorite ion for various pH<sup>10</sup>

FIGURE 2



Comparison of germicidal efficiency of hypochlorous acid, hypochlorite ion, monochloroamine<sup>9</sup>