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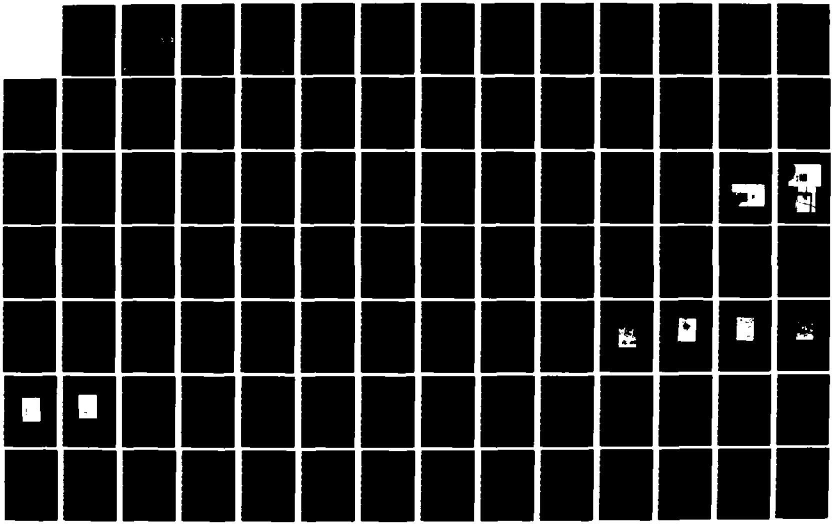

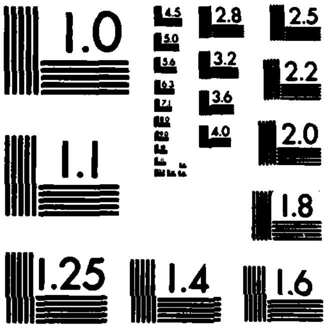

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ABSTRACT

A new test to predict the fouling potential of a reverse osmosis (RO) feedwater was developed. The Permanganate Demand Test is based on both of the accepted equations used to describe the solvent and solute flow through the membrane. It characterizes the reduction in solvent flow by an increase in the osmotic pressure at the membrane.

The Silt Density Index (SDI) is a membrane test that has come into widespread use to predict the fouling potential of a feedwater. RO processes can be expected to operate successfully over a long period of time without significant reduction in permeate flux if the SDI values are between 2 and 5.3, on a scale of 1 to 6.67. The study of the SDI was conducted as a step-off point to a subsequent study of fouling, and the development of the Permanganate Demand Test.

The SDI was found to be sensitive to suspended particles large enough to be measured as turbidity, but insensitive to dissolved metal concentrations. The concentration of humic acid in the feedwater, that would result in acceptable SDI values, was

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found to be between 0.5 and 1.0 mg/l.

The fouling potential of humic acid feedwater solutions to a RO membrane was studied, as humic substances account for over 90% of the organics in natural waters. The rate of fouling was found to be directly related to the concentration of humics in the feedwater.

The Permanganate Demand Test was developed to characterize the concentration of humics by a simple procedure that could be performed in a few hours by plant operation personnel. Since the test successfully represents the humic concentration, and the concentration of humics relates to the rate of fouling, a predictive equation could be developed. This equation predicts the permeate flux decline from the permanganate demand of the feedwater.

The test was performed on a saline feedwater containing iron, which was reported as a major cause of fouling in the literature. The iron, in the form of ferrous ammonium sulfate, did not have a permanganate demand, and no fouling occurred in a month long trial.

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be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

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James K. McDonough

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A REPLACEMENT FOR THE SILT DENSITY INDEX; PERMANGANATE DEMAND TO PREDICT REVERSE OSMOSIS MEMBRANE FOULING

A dissertation submitted to the

Department of Civil and Environmental Engineering

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1983

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M.S. The University of Cincinnati 1974

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Introduction

Reverse osmosis is a pressure driven separation process in which the feed stream is separated, by opposing osmotic pressure through a semi-permeable membrane; into the product stream. the permeate, and a stream of higher concentration than the feed stream, the concentrate.

The process has found widespread acceptance in desalination, water reclamation, and the production of water of exceptional quality. Designers are attracted to the simplicity of design, low energy requirements, and the potential of high recovery that reverse osmosis offers. However, the process is not without drawbacks.

Perhaps the most challenging of the problems associated with the use of reverse osmosis technology is fouling. Fouling is the reduction of permeate flow with time, caused by constituents in the feed, or changes in membrane structure. This phenomena introduces a degree of uncertainty to a planner as to the usable life expectancy of the membrane and the need for pretreatment.

Unfortunately, the relationship between fouling and the normal characterizations of the feedwater, i.e. hardness, turbidity, suspended or dissolved solids, has never been quantified or hardly explored. Currently, the results of a simple filtration test, the Silt Density Index (SDI), have been used to determine if the process can be reasonably operated for an extended period of time without fouling. The SDI cannot predict the expected lifespan of the membrane, nor can it react linearly with the potential fouling agents.

The purpose of this research, in light of this, was to: (1) Determine the relationship between fouling and concentration of a common foulant. (2) Develop a simple test which could characterize a feedwater's potential to foul. (3) Develop a predictive equation by which designers may assertain, with a reasonable degree of accuracy, an estimation of a membrane's useful life from the performance of a predictive test.

I. The Nature of Reverse Osmosis Membrane Fouling

A. Review of the Literature

1. Introduction

Schippers and Verdow (1) state that the fouling of the reverse osmosis membrane is one of the most challenging of the technological problems associated with the use of the process. Allard (2) reported that experience with the process has gradually weakened the general image, propagated primarily for publicity reasons, that an RO plant was a "black box". RO performance is linked to a thorough knowledge of the physical-chemical quality of the water to be treated.

2. Principles of Reverse Osmosis Operation

Wong (3) listed four different basic designs which have been evaluated for possible use in RO separations.

(1) Plate and Frame (PF). The PF design developed by Keilin et.al.(4), with membranes developed by Loeb at UCLA, and marketed by Aerojet-General, has the product water flowing through stages of circular discs toward a porous supporting structure.

(2) Tubular Design. This design allows the concentrate to flow axially along a hollow tube. The separation

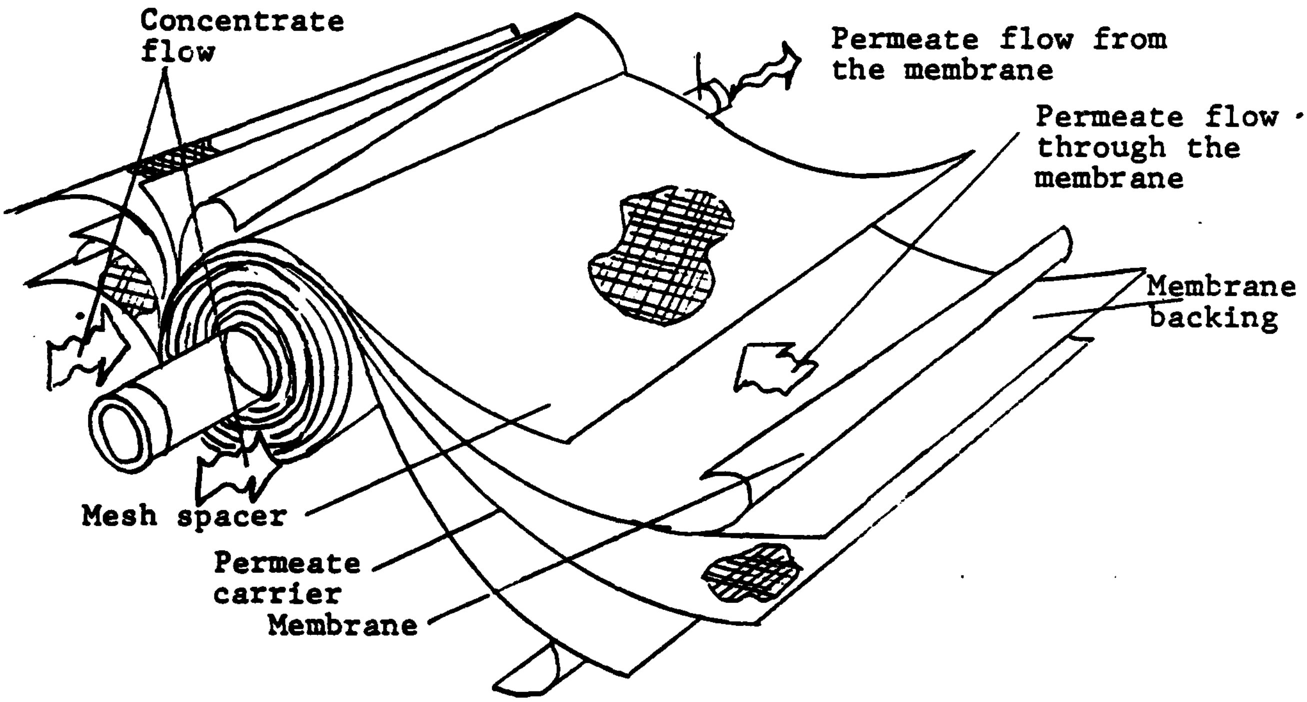
of the feed occurs as the permeate flows transversely through the membrane and the porous support structure.

(3) Hollow Fine Fiber. This design, developed by the Dow, Dupont, and Monsanto Corporations, utilizes a large number of hollow fibers from 25 to 250 microns in diameter. The concentrate flows axially along the fibers, with each individual fiber affecting the separation, the permeate being removed in a counter-current fashion from the direction of flow of the concentrate.

(4) Spiral Wound Module Configuration. The spiral wound concept allows the permeate to spiral along an impermeable barrier toward a center collection septum as shown in figure 1.1. This particular design makes high density membrane packing possible, along with decreased pressure requirements, normally 150 to 225 psi.

3. Reverse Osmosis Membrane Development

Porter (5) noted that the most important advance in reverse osmosis technology was the development of the asymmetrical cellulose acetate membrane by Reid and Breton in 1957, and the "anisotropic" membrane by Loeb and Sourirajan at UCLA from 1958 to 1961. This membrane had an asymmetric structure, consisting of a figure 1.1 Spiral Wound Reverse Osmosis Membrane



0.2 to o.5 micron thick, dense layer, supported by a 50 to 100 micron thick, porous substructure. The substructure has pores 0.1 to 1.0 micron in diameter, while the dense layer has pores with a diameter estimated at 10 Å.

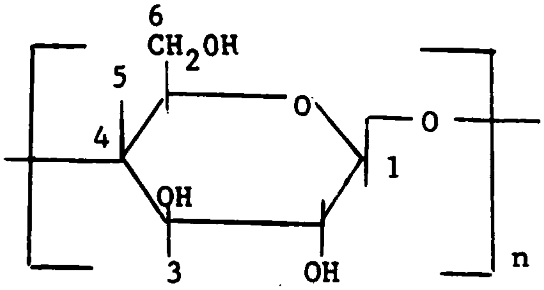
Solute passage through a membrane is governed not only by diffusion, but also by the dissolution of the solute into the membrane. The extent of dissolution depends on the degree of hydrogen bonding between the solute and the membrane. As hydrogen bonding increases, more solute enters the membrane and there is more solute available for diffusion (98).

The transport of solvent (water) through the membrane is quite sensitive to the configuration of the monomer units comprising the polymer chain. The ratio of primary to secondary hydroxyl groups has a strong influence on desalination performance (99).

Membrane failure is known to result from acid or base catalyzed hydrolysis which results in polymer de-acetylation (92).

Research is ongoing toward the development of membrane materials with improved rejection characteristics. Osmonics (6) offers a choice of materials, including polysulfone, polyethylenimine, polyamide, and polyfurane. Osmonic membranes are integrally bonded to a synthetic backing material, giving added strength and simplifying the orientation of the membrane.

The basic structure of cellulose is shown below (100). Polymers are formed by substituting esters or ethers for the hydrogen atoms on the hydroxyl groups associated with the 2.3, and 6 positions on the ring. (acetate, $O-\underset{O}{C}-CH_3$)



4. Reverse Osmosis Membrane Phenomena

Lonsdale et.al.(7) showed that the pure water (permeate) flux through the membrane, J_w, over a moderate pressure range, obeys the relationship:

$$J_w = A\ (\Delta P - \Delta\pi) \qquad \text{eq. 1.1}$$

where A is a constant, the coefficient of permeability, ΔP is the hydraulic pressure drop, and $\Delta\pi$ is the osmotic pressure drop across the membrane. Furthermore, in the absence of solute leakage, the salt flux, J_s, is given by:

$$J_s = B (C_f - C_p) \qquad \text{eq. 1.2}$$

where B is a constant, C_f is the feed solute concentration, and C_p is the permeate solute concentration.

Michaels (8) expands the constant A in equation 1.1 to:

$$\frac{\bar{C}_1 \bar{D}_1 \bar{V}_1}{tRT} \qquad \text{eq. 1.3}$$

where:

$\bar{C}_1$ = Mean concentration of solvent in the membrane

$\bar{D}_1$ = Diffusivity of solvent in the membrane

$\bar{V}_1$ = Partial molar volume of water in solution

and the constant B in equation 1.2 to:

$$\frac{K_2 D_2}{t} \qquad \text{eq. 1.4}$$

where:

K_2 = Solute distribution coefficient between membrane and solution

D_2 = Solute diffusivity in membrane

t = Membrane thickness

The simplified transport relationships for solvent and solute flowing through the pores of a membrane, where rejection is determined by the molecular dimensions of the solute and the pore size distribution. are:

For the solvent:

$$J_1 = \frac{K_1 P}{nt} \qquad \text{eq. 1.5}$$

Where n = solvent viscosity

For the solute:

$$J_2 = \sigma J_1 C_1 \qquad \text{eq. 1.6}$$

where the quantity σ represents the fraction of solvent flowing through pores large enough to accomodate the solute molecule.

These early mechanisms do not account for the phenomena which causes changes in the flux or changes in the rejection characteristics of the membrane. Membrane compaction, concentration polarization, and membrane fouling are phenomena which have been associated with permeate flux decline.

Podall (9) defined membrane compaction as the gradual and irreversible decline in permeate flux caused by the creep of the membrane substructure, reducing porosity, due to the application of high pressure.

Porter (5) indicated that the composite RO membrane, such as the Osmonics SEPA cellulose acetate, is apparently much more resistant to compaction than the Loeb-Sourirajan membrane, which has the skin and substructure fabricated in one operation (10).

Before steady state occurs, the convective flow of components in the feed stream being rejected by the membrane accumulate on the membrane surface at a greater rate than those which diffuse into the concentrate stream. Matthiasson (11) called this phenomenon concentration polarization.

Semi-empirical analyses of concentration polarization in turbulent flow (12,13,14,15) show that the concentrate velocity is the principal independent variable affecting the ratio of salt concentration at the membrane-solution interface to the concentration of the turbulent feed.

Sheppard (16) observed that salt rejection for a fouled membrane was less than for the clean membrane.

When the concentrate flow was fully turbulent, the fouled membrane gave better rejection than when concentrate flow was laminar. The flux through the fouled membrane was always less than the flux through the clean membrane.

Membrane fouling will always occur during the operation of pressure-driven membrane processes (17).

The major limiting factor in using pressure-driven membrane processes, and in particular, hyperfiltration (reverse osmosis) for industrial, agricultural, and municipal applications, is membrane fouling (18).

Membrane foulants reported in the literature can be categorized according to whether they form a gel layer or that the permeate flux decline is caused by plugging of the membrane's pores. Organics, such as humic substances, biological slimes, and macromolecules like proteins have been seen to cause the buildup of a gel layer on the membrane. Less compressible species, including precipitates such as $CaSO_4$, $CaCO_3$, $Mg(OH)_2$, $Fe(OH)_3$, and other metal hydroxides may form a porous layer on the membrane. The reduction in flux due to these species is thought to occur because the pores of the membrane become blocked as the foulants come out of solution.

Burztynsky (20) indicated that the principal causative agent in the membrane fouling from municipal wastewater is finely dispersed solids, and that dissolved organics are of lesser importance. The presence of ions which may precipitate on the membrane did not appear to be critical to the fouling process.

Goodall (21) stated that turbulence alone was seldom sufficient to prevent fouling. Salts, such as calcium carbonate, come out of solution easily. Other materials that foul membranes are iron and colloids. Ferrous ions, in the presence of dissolved oxygen, are oxidized to the ferric state, forming a gelatinous precipitate.

Winfield (22) concluded that membrane fouling from secondary sewage is caused by a negatively charged colloidal layer. The major factor controlling the rate of fouling is the dissolved organic concentration of the liquid feed.

Fang (23) reported that fouling often resulted from the precipitation and gel formation of organic and inorganic substances on the membrane surface. The organic slimy layer is attributed to humic and

and fulvic substances and biological growth, whereas the inorganic precipitation is caused by calcium carbonate, ferric hydroxide, and amorphous silica.

Doelle (24) expected that calcium sulfate would be a serious fouling problem whenever a high yield reverse osmosis system, using sulfuric acid for pH control, is shut down.

Shuvall (25) stated that the most hazardous fouling constituents of domestic sewage are:

1. Biological activity
2. Suspended solids
3. Dissolved organics

The exact contribution of each of these constituents is not known.

Brunnelle (26) stated that the colloidal particles of surface water, principally silica clays, fouled reverse osmosis membranes regularly. The most important factors influencing the stability of the colloids, and possibly the fouling rate, depend on the dissolved salt concentration of the surrounding solution.

Ogegaard and Kootatep (27) studied the effect of suspended solids on fouling. They concluded that the maximum suspended solids concentration in raw water that did not affect product water flux was about 100 mg/l of bentonite clay at 145 psig. The product water decreased by 50% during three to four hours of operation in the presence of about 130 mg/l.

Industrial Water Engineering (28) related that a two-fold increase in the iron concentration resulted in a major fouling problem.

Argo (29) maintained that good pH control was essential to minimize membrane hydrolysis and precipitation of scale forming or membrane fouling minerals. The hydrolysis rate of the membrane is at a minimum at the pH value of 4.7. and increases with both increasing and decreasing pH.

Potts et. al. (30), in an excellent review of membrane fouling, considered dissolved organics, together with colloidal matter, as the most serious foulants. Theories on the mechanism of this type of fouling are in their infancy. The simplest explanation is that, due to their low mobility, colloids retrodiffuse from the membrane surface more slowly than small ionic series. Complicating this, is the question whether fouling is only a surface phenomena, or whether pores plug as well.

Senstrom et.al. (31) obtained the highest rate of fouling from uncoagulated wastewater (flux decline coefficient = 0.243), with a TSS of 20 to 30 mg/l, and a turbidity of 10 to 20 NTU. Coagulation with alum and ferric chloride reduced the coefficient to 0.146.

Macro-molecules and biological slime probably represent the category of fouling agents which tend to be the most difficult to remove from the membrane. Turbulence, abrasion by mechanical means, and pH treatments have been partially successful in preventing fouling.

Ridgeway et.al.(32), studying microbial fouling of membranes used in advanced wastewater treatment, postulated that inorganic fouling did not appear to be a major factor in flux decline. A multilayered biofilm, 20 microns thick, composed of bacteria firmly secured within the biofilm matrix by extracellular fibrilar secretions, was seen.

Ultrafiltration and reverse osmosis have been used successfully in the cheese processing industry even though membrane fouling by macromolecules occurs.

Lim et.al.(33) expressed the change in flux, J in terms of resistances caused by the membrane, R_m, concentration polarization, R_p, and fouling, R_f.

$$J = (K (\Delta P - \Delta \pi)/ (R_m + R_p + R_f)) \quad \text{eq. 1.7}$$

where K is the coefficient of permeability.

Membranes, used to concentrate cottage cheese whey, fouled with material which was predominantly protein; material with such low diffusion coefficients that the molecules did not diffuse away from the membrane. As the velocity of the feedwater across the membrane was lowered, the more significant R_f became as compared to R_m and R_p.

Muller (34) reported that demineralization and pH adjustments were significant factors affecting R_f and R_p.

5. RO Fouling Models. (Correlating Flux Decline)

The flux decline associated with fouling remains a complex phenomena which discourages attempts to model it mechanistically (35). Several researchers (36,37,38,39) have used geometric regression, first reported by Merten (40), to model flux decline with time.

$$F_t = KT^m \quad \text{eq. 1.8}$$

where: F_t = flux at time T

K = constant

m = flux decline index

and;

$$J_t = J_o ((t/t_o))^{-n} \qquad \text{eq. 1.9}$$

where:

J_t = membrane flux, at time t

J_o = membrane flux, time initially

n = flux decline index

The exponent n has been related to both the velocity of the concentrate (38), and the nature of the feed (37,39).

Fane (35) related that the flux appears to approach a minimum, which presumably corresponds to the maximum cake resistance due to compaction and growth.

Cheryan and Merin (41,42) used a similar model to characterize the fouling of cheese whey. The equation was developed based on the assumption that the flux decline is a function of the cumulative permeate volume.

$$J_t = J_o V^{-b} \qquad \text{eq. 1.10}$$

where V is the cumulative volume.

In the integrated form:

$$V = \left((b + 1)\, e^{\ln J_o} \right)^{\frac{1}{b+1}} * t^{\frac{1}{b+1}} \qquad \text{eq. 1.11}$$

Their data indicated that fouling occurs in two stages, an initial rapid drop in flux, followed by a more gradual decline. The first stage was interpreted as the result of the membrane resistance and the resistance of the concentration polarization layer. The more gradual decline was interpreted as the result of fouling.

The standard filtration equation has been a popular model to adapt to a model to describe reverse osmosis fouling. As developed by Porter (5):
The basic filtration equation is given as:

$$J = \frac{P}{R_c + R_m} \qquad \text{eq. 1.12}$$

The resistance of the cake, R_c becomes the resistance of the fouling layer.

$$R_c = \frac{\alpha w V}{A} (\Delta P)^{s} \mu \qquad \text{eq. 1.13}$$

Then:

$$\frac{1}{J} = \frac{\alpha w\ V\ (\Delta P)^{s-1}\mu}{A} + \frac{R_m}{\Delta P} \qquad \text{eq. 1.14}$$

Thus the flux declines as the throughput increases. Also, a linear relationship between the flux and feed concentration is represented.

Where: α = constant dependent on properties of fouling layer
w = concentration (wt/vol)
V = volume of filtrate
P = pressure drop across the membrane
s = compressibility factor of the layer

Belfort and Marx (18) noted that there are three problems in applying the standard filtration approach to reverse osmosis fouling; the effect of the concentrate, a varying suspended solids feed concentration, and differences in pressure.

$$\frac{1}{J} = \left(\frac{\alpha w \mu}{P_c S}\right) V + \left(\frac{\mu}{P_m - \sigma \Delta\pi}\right)(1 + \beta V^n) \qquad \text{eq. 1.15}$$

Where: P_c = pressure across cake
P_m = pressure across membrane
σ = Staverman reflection coefficient
β = membrane constant

μ = viscosity of filtrate

n = 1 during the initial transient period

n = 0 during the steady-state period

Michaels (44) presented the gel-polarization model based on the steady state mass transfer conditions which must exist within the polarized boundary layer.

$$Jc - D\frac{dc}{dx} = 0 \qquad \text{eq. 1.16}$$

Where: c = local solute concentration

D = local solute diffusivity in solution

x = normal distance from the membrane surface

Integrating:

$$J = K \ln \frac{C_g}{C_b} \qquad \text{eq. 1.17}$$

Where: C_g = solute concentration at the gel layer

C_b = solute concentration in bulk feed

K = film mass transfer coefficient

The model has been modified by several authors to include the effect of osmotic pressure (45,46,47), diffusional effects (48), and lateral migration (49).

Other fouling models besides the filtration and gel polarization models have been proposed.

Carter (50) considered the fouling layer of iron hydroxide. Its removal from the membrane depended on the shear stress, not on the flux rate or ferric concentration.

Gutman (51) proceeded from Carter's work (50) and proposed the equation for the net rate of fouling:

$$\frac{dm}{dt} = r_d - r_e \qquad \text{eq. 1.18}$$

where $\frac{dm}{dt}$ is the net rate of fouling, r_d is the rate of deposition, and r_e is the rate of re-entrainment. Re-entrainment is thought to be due to turbulence bursts from the fouling layer, sweeping down and removing small particles from the membrane.

Extensive reviews of fouling models were presented recently by Belfort (52) and Matthiasson (11).

B. Reverse Osmosis Fouling Study

1. Introduction

The concluding sections deal with a study of the formation of a fouling layer on a spiral wound reverse osmosis membrane by organic and inorganic compounds, a characterization of the feed, and an analysis of the effects of the fouling layer on permeate flux and rejection efficiency.

2. Experimental Protocol

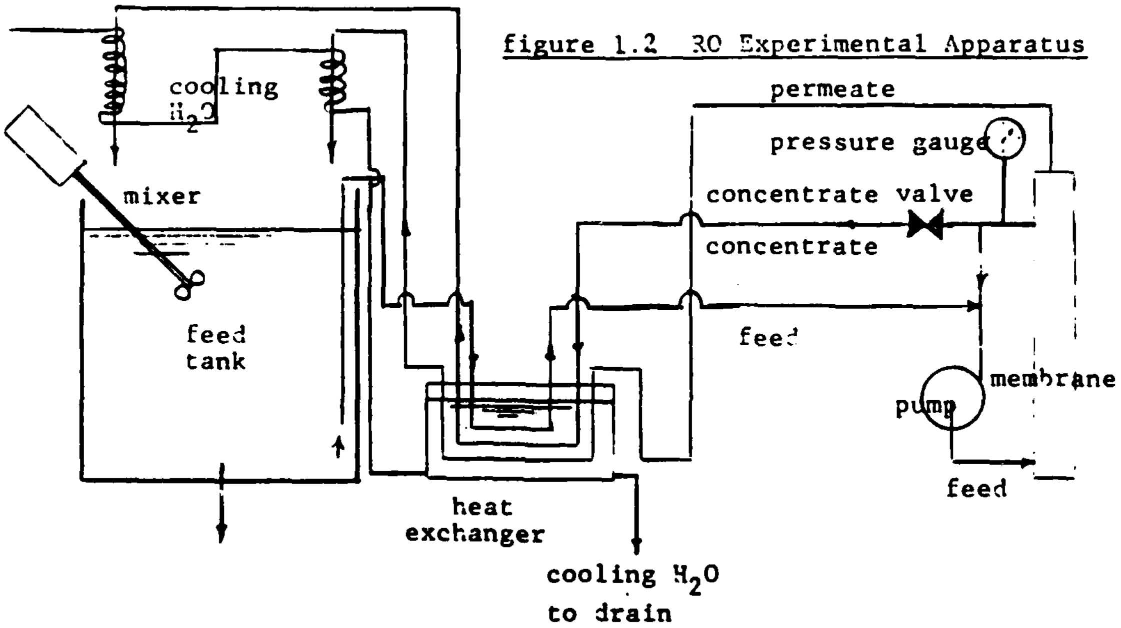
a. Experimental Apparatus

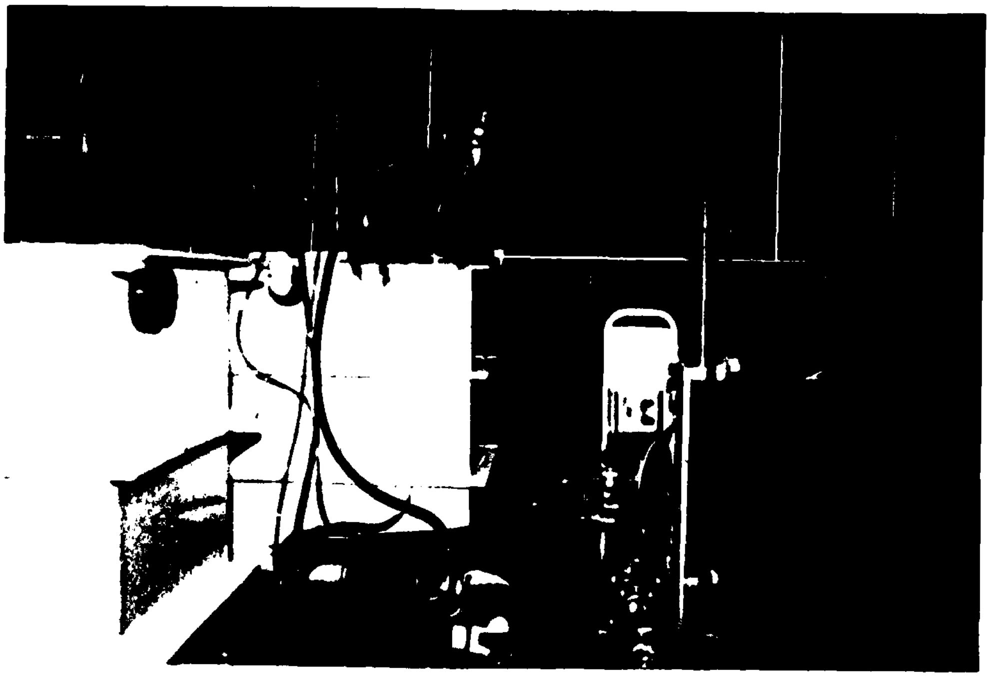
The reverse osmosis machine which was originally purchased for this research was an Osmonics OSMO 1919-SB, fitted with a SEPA 97E cellulose acetate membrane module. The general specifications of the machine are: (6)

Prefilter: 100 mesh screen
Pump: Rotary vane, Procon
Motor: 1/4 hp, 115 volt a.c., drip proof
Salt rejection: 90-98% of total dissolved solids
Size: 4.6 gal/hr (17 liters/hr) pure water rate
Membrane area: 19 ft^2

The machine was modified after several unsuccessful trials by replacing the Procon pump with a Tonka 18 stage centrifugal pump. The Procon pump was unable to maintain the required pressure. The Tonka pump performed admirally throughout the series of trials. The pressure was maintained at 190 psi. The trials were terminated when pressures dropped below this level. The experimental apparatus is pictured in figure 1.2.

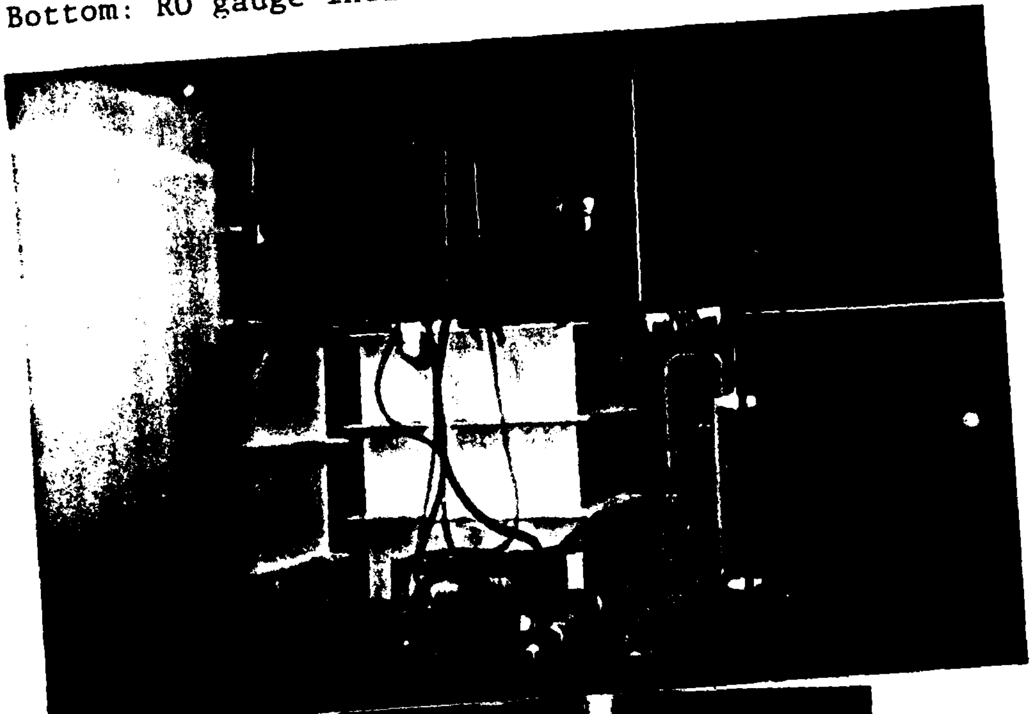
figure 1.2 RO Experimental Apparatus

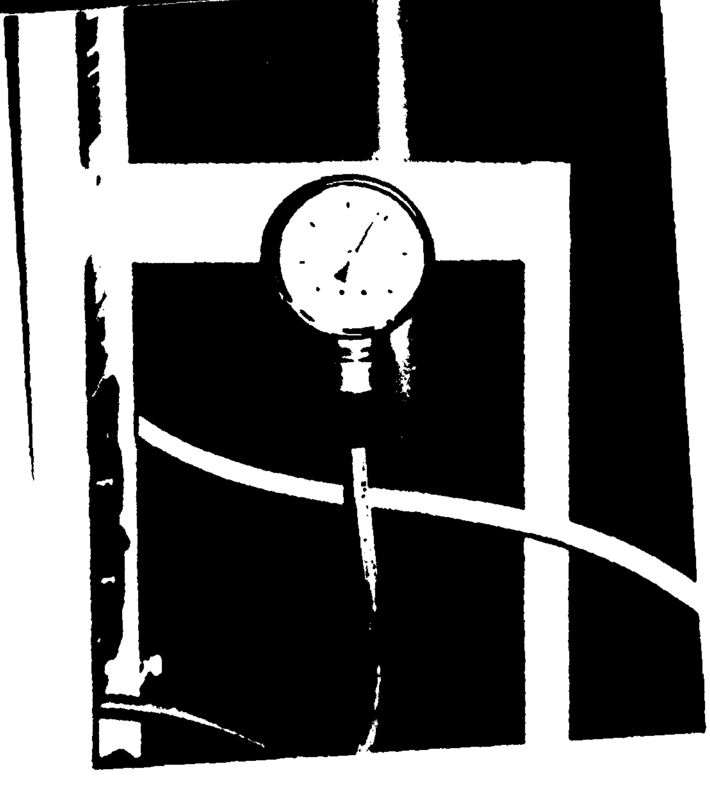




View of the experimental apparatus showing the feed tanks, heat exchanger system, mixer, and RO machine.

figure 1.2 (cont.) Top: View from another angle
Bottom: RO gauge indicating operating pressure of 190 psi.





The test solution flowed by siphon to the RO pump from a 100 gallon plastic feed tank, filled to the 80 gallon (300 liter) level. The feed line was 5/8" plastic garden hose. The concentrate line was 1/2", the permeate line was 3/8" plastic tubing. The concentrate and permeate tubes were spliced to allow for the use of glass tubing in the heat exchanger. A simple heat exchange system was constructed, as feed tank temperatures could reach unacceptably high temperatures without some sort of temperature control.

The heat exchange system consisted of three standard laboratory glass condensers; one mounted to accept the permeate, two in series to accept the concentrate line. Tap water from the condensers flowed into a 5 gallon plexiglass tank, through which all three lines from the machine passed.

A Lightnin 1/3 hp mixer was mounted straddling the top of the tank to provide rapid mixing of the solutions.

b. Experimental Procedure

(1) Preparation of Humic Acid Solutions

Humic acid solutions were prepared by dissolving comercially prepared extract, Aldrich Chemical Company, humic acid, sodium salt, tech., catalog # HI,675-2, in laboratory pure water (LPW). LPW was available from the distilled water taps, however the water was actually tap water which had been processed by another RO unit located in the rooftop penthouse. The humic preparations were not without residue. Thus, approximate weights were measured out, dissolved in five liters of LPW and allowed to mix overnight. The humic solution was then decanted from the flask and transfered into the feed tank, already partially filled with LPW. Additional LPW was added until the tank contained 300 liters. 300 grams (1000 mg/l) of sodium chloride crystals were added. The complete solution was mixed and allowed to stand overnight before reverse osmosis operation commenced.

The final tank solution concentration was determined by its comparison to prepared standards.

(2) Preparation of the Calibration Curve for Humic Acid Concentrations

1.00 gram of humic acid extract was carefully weighed and dissolved in 1.0 liter of RO permeate water of pH 7.0. This solution was mixed by a magnetic stirrer, and 50 mls pipetted volumetrically into a 500 ml flask, building a humic solution of 100 mg/l. Appropriate amounts were transfered, and absorbances measured at 426 nm with a B & L Spec 505, later a Coleman Model 124 scanning spectrophotometer. Typical calibration curve is shown in figure 1.3, and as the plot of the concentration vs. absorbance data in table 1.1.

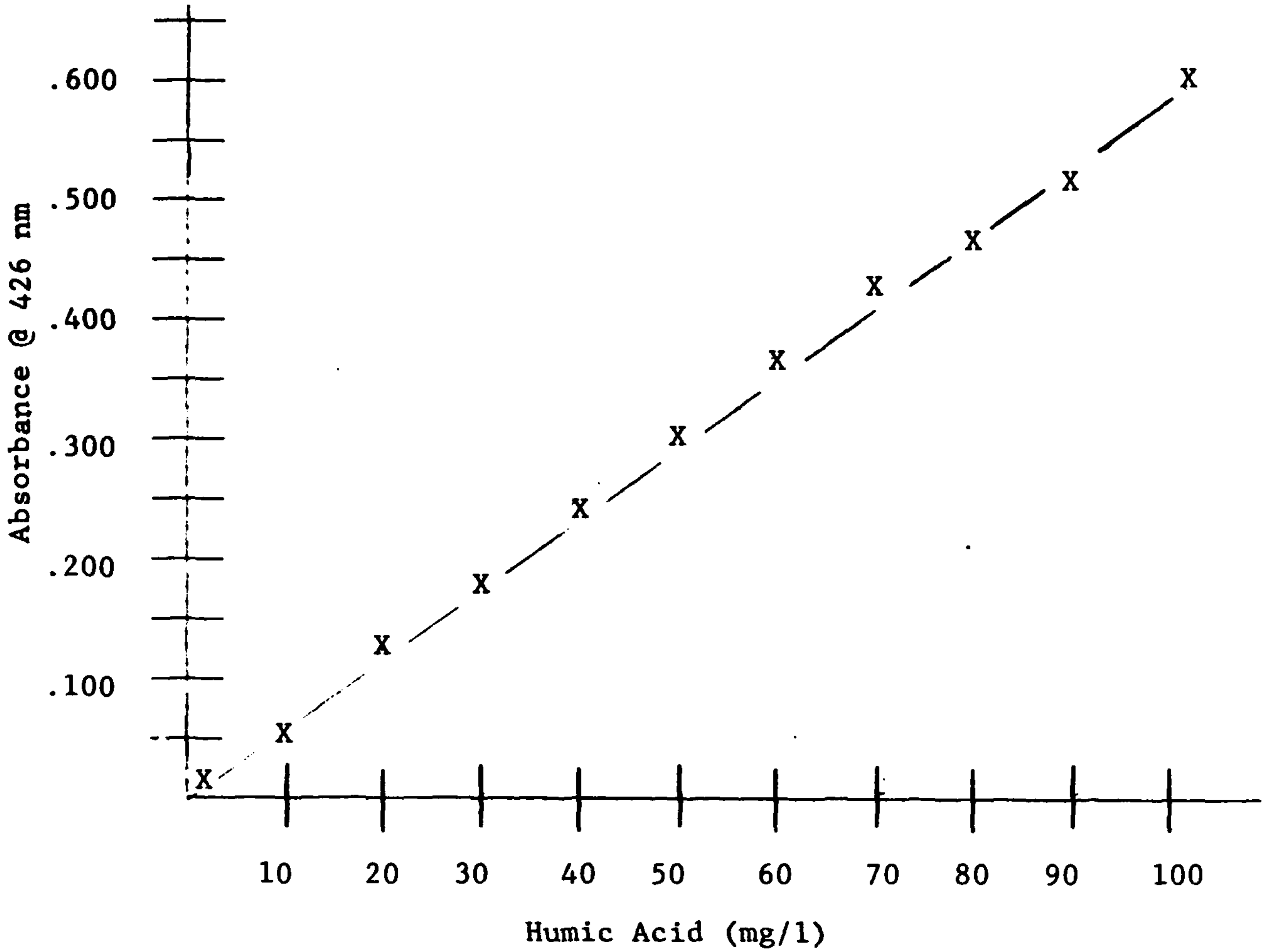
table 1.1 Calibration Curve Abs. vs. Humic Conc.

mg/1 humics	absorbance	pH
1.0	.005	7.0
5.0	.030	6.8
10.0	.060	6.8
20.0	.120	6.8
30.0	.180	6.8
40.0	.242	7.2
50.0	.310	7.2
60.0	.370	7.2
70.0	.430	7.3
80.0	.490	7.4
90.0	.550	7.5
100.0	.610	7.5

Humic acid extract prepared in this manner obeys Beer's Law, with correlation coefficients of .9999 to concentrations of 100 mg/1, .998 to 300 mg/1, with a maximum readible concentration of ~500 mg/1.

Figure 1.3 The Absorbance at 426 nm of Humic Acid

Typical Calibration Curve



(3) Operation of the RO for the Fouling Study

The reverse osmosis machine ran continuously throughout each individual concentration trial. The machine's pressure was adjusted to operate at 190 psig, except when the membrane was being flushed.

The membrane was flushed for 10 minutes, six times a week, by opening the concentrate valve which increased the concentrate flow from 0.36 to 1.32 gpm and reduced the operating pressure to 150 psig.

The parameters of absorbance, turbidity, conductivity, and pH were taken at the same interval. The permeate and concentrate flow, pressure, and feed tank temperature, were recorded also.

Between tests, the membrane was cleaned with either Osmonics CS detergent, or a cleaning solution developed for this research. The Osmonics CS detergent was used in accordance with the manufacturer's instructions, (2-4 oz. per gallon, minimum three gallons of cleaning solution). The solution was fed into the machine from a five gallon carbouy and recycled through the machine at 190 psig for two minutes, then through the machine at 150 psig for 15 minutes. The machine was shut off and allowed to stand overnight, then flushed with LPW for the remainder of the day.

The cleaning solution developed for this research consisted of one part pyridine and one part 0.1 EDTA per 100 parts water. The cleaning procedure was similar to that described before, except that the solution was only allowed to stand in the machine for one hour before flushing with LPW.

Two membranes were used during this experiment. The initial membrane was changed after salt rejection efficiency dropped below 80%.

Five concentrations of humic acid, 0, 30, 60, 100, and 225 mg/1 were tested over the period 25 October 82 to 25 April 83.

Trials were terminated whenever the pump was unable to maintain the set operating pressure of 190 psig.

c. Feedwater Parameters

(1) Osmotic Pressure

Osmotic pressure was measured with a Westcor Vapor Pressure Osmometer Model 5130. The meter is calibrated to read in the units, millimole/kg. The readings were converted to psi by the Van Hoff equation (53).

The results are given at 77°F (25°C).

table 1.2 Vapor Osmometry of Humic Solutions

Humic conc. (mg/l)	Osmotic pressure mmole/kg	 psia
30	24	8.63
60	17	6.11
100	33.5	12.04
225	26	9.35

Although osmotic pressure should vary with humic concentration, the results may be explained by the postulate that, at these low concentrations, the humics cause changes in the osmotic pressure which are insignificant in relation to the salt concentration and the sensitivity of the meter.

(2) Viscosity

The results of the viscosity measurements are given in table 1.3

table 1.3 Density and Viscosity of Humic Solutions

Humic onc. (mg/l)	Density (g/ml)	Viscosity (mp)
0	.995	6.56
30	.997	6.56
60	.995	6.59
100	.997	6.62
225	.998	6.56

Humic acid solution viscosities were measured with an Oswalt viscometer. The procedure is essentially that described by Daniels, et.al. (54). The passage of humic solutions through the viscometer was compared with that of liquids of known viscosity; LPW, acetone, 2-propanol, and methanol. The test was performed in a waterbath at 40°C. A volume of 10 mls was used. The densities were measured by weighing known volumes.

(3) Temperature

Permeate flux through the membrane is dependent on feedwater temperature. The method used for correcting for variations in feedwater temperature was an equation by Hittman (55).

$$J_c = J_f * (1 + 0.0166\ (T_f - T_s)) \quad \text{eq. 1.19}$$

$T_s = 77^{o}F$

T_f = feedwater temperature

J_c = temperature corrected water flux (gal/ft^2-day)

J_f = water flux, measured (gal/ft^2-day)

(4) Hardness

Hardness was determined for the feed tank solutions by the EDTA method, Standard Methods (56). Results are presented in table 1.4.

table 1.4 Total Hardness of Tank Solutions

Sample	Total Hardness (as $CaCO_3$,mg/l)
LPW	3.5
Feed, 30 mg/l humics	55.4
" 60 " "	24.8
" 100 " "	19.1
Permeate "	3.5

The hardness was reduced to the levels of the LPW in the permeate of the RO processing the humic solutions.

(5) Conductivity, Turbidity, pH

Conductivity was measured with a YSI model 31 conductivity bridge. Salt rejection by the membrane was calculated by the equation:

$$\% \text{ rejection} = \frac{(C_f + C_c)/2 - C_p}{(C_f + C_c)/2} * 100 \qquad \text{eq. } 1.20$$

Where:

C_f = conductivity (mho) pf feed

C_c = conductivity of concentrate

C_p = conductivity of permeate

Turbidity was measured with a Turner Designs Nephelometer. The instrument was calibrated with a Hach Chemical Co. 40 NTU standard.

The hydrogen ion concentration (pH) was measured with a Sargeant model LS pH meter. The instrument was calibrated with prepared standards of pH values of 4.0, 7.0, and 10.0.

The three parameters of pH, turbidity, conductivity and percent salt rejection are tabulated in Appendix I for the humic acid trials.

d. Measurement of Permeate Humic Acid Concentrations

Osmonics Co. claims that the SEPA-97 membrane will reject 99.9+% of the organic molecules over a molecular weight of 200. Since humics are large organic molecules, almost total rejection should be expected. The measurement of humics in the permeate presented an analytical problem. For example, the humic acid concentration in the permeate from a feed concentration of 30 mg/1 would be in the range of 30 μg/1. This is far below the sensitivities of both the usual spectrophotometric or direct injection gas chromatograph (56,57,58).

Rook (60) reported that humics, in the form of fulvic acids, combine with chlorine to form halogenated hydrocarbons, termed haloforms.

Bellar and Lichtenberg (59) considered both the head space and purge methods available for chromatographic analysis; developed the purge and trap method for the evaluation of chlorinated hydrocarbons in the μg/l range.

The basis for the method, which was developed to solve the analytical problem, is the measurement of the halogens formed after chlorine is reacted with the feed and permeate. The haloform, chloroform ($CHCl_3$) was selected to be representative, as it is normally formed in the greatest quantity of any haloform in a reaction of humics and chlorine. Assuming that the chlorine is present in excess, the recovery of humic acid for the reverse osmosis system can be calculated by comparing the concentration of chloroform formed in the permeate with the concentration of chloroform formed in the feed.

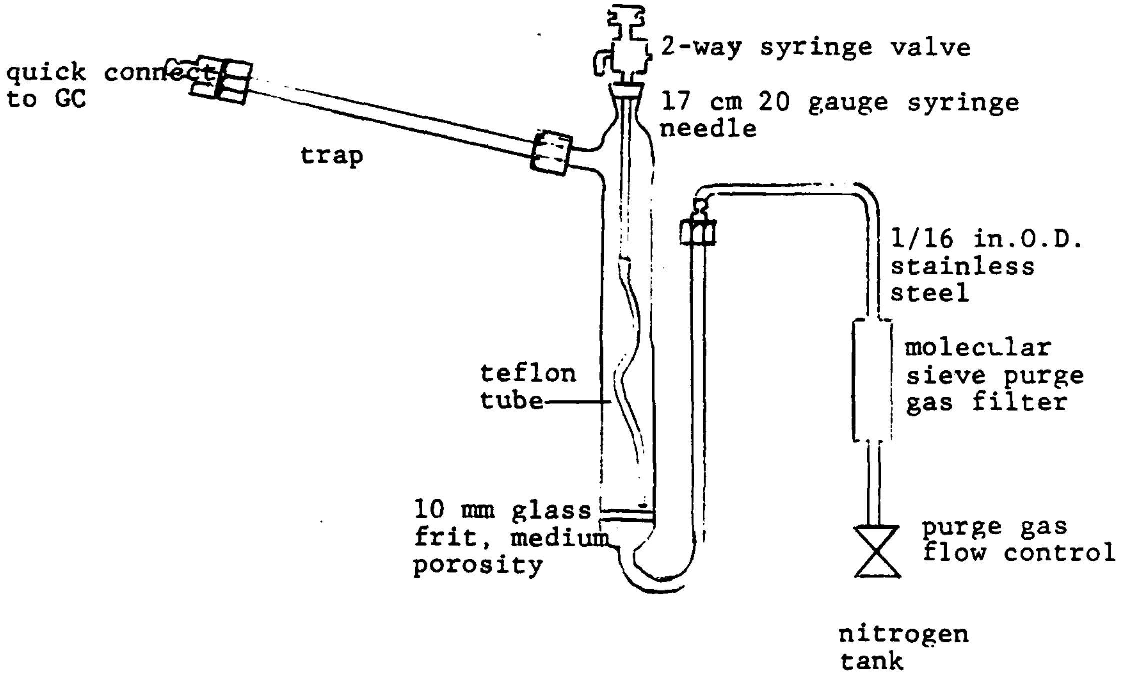
e. Procedure for Determination of Humic Acid Recovery

Samples for the determination were collected weekly during the period between January and March 83 as the 30 mg/l humic acid fouling trial was being conducted. The membrane had been installed new at the beginning of the trial.

Samples were collected in a liter Greenberg impinger from the feed tank and the permeate stream. The samples were purged with nitrogen for one hour to remove any volatile haloforms that might have been contained in the make-up LPW for the feed tank. Samples were split into 500 ml glass bottles with screw top enclosures. One bottle, of each of the feed and permeate, was injected with 1.0 ml of chlorine solution (Chlorox, 5.25% NaOCl equal to 36.3 mg/ml free available chlorine). The pH of the feed and permeate was approximately 7.0. The chlorine was allowed to react in the bottles, at room temperature, for three days. The bottles were brown glass and fitted with teflon septums. No head space was allowed in the bottles.

Five mls of chlorinated permeate, unchlorinated permeate, and unchlorinated feed samples were withdrawn from the bottles with a syringe and transfered to the purge and trap apparatus. The purge and trap apparatus consists of three separate pieces, the purging device, trap and desorber. The apparatus is pictured in figure 1.3.

Figure 1.4 Purge and Trap Apparatus



The purgeable haloforms were driven from the samples by the application of 40 ml/min nitrogen for 11.0 minutes. After the 11 minute purge time, the trap was attached to the chromatograph and desorbed. The desorption into the GC was accomplished by attaching nitrogen to the trap and backflushing it, while rapidly heating the trap to $180^{\circ}C$ for four minutes. A temperature program was initiated which increased the temperature of the detection column from $40^{\circ}C$ to $190^{\circ}C$ at a rate of $8^{\circ}C/min$.

Five microliters of chlorinated feed were injected directly (purge and trap apparatus not used) into the gas chromatograph.

A Perkin Elmer 900 gas chromatograph, fitted with a Tracor 700 Electrolytic Conductivity Detector and Varian CDS 111 Graphics Integrator, were used to detect and quantify the chloroform.

The column was six feet, 1/8" dia. porous polymer packing, 60/80 mesh chromatographic grade Tenax GC.

The trap materials were: activated charcoal, silica gel, Tenax, and OV-1.

The method of analysis, Method 601 - Purgeable

Halocarbon is contained in the Federal Register (60).

The concentration of chloroform was determined by either comparing the peak heights or integrated area of the peaks with those of known quantities of standard.

Typical chromatograms are shown in Appendix XII.

Table 1.5 summarizes the results of the 30 mg/l humic trial, comparing humic recovery, degree of fouling, and the salt rejection of the membrane.

table 1.5 Humic Acid Recovery

Date	% Flux Decline	% Salt Rej.	% Humic Rec
18 Feb	0.0	93	89.4
24 "	21.5	95	99.5
3 Mar	25.4	95	98.0
17 "	25.3	94	99.1
31 "	28.5	95	97.5
7 Apr	30.3	94	93.8

The percent flux decline was calculated as that percentage the flux had declined from the second day of the trial to the day the sample was taken.

The percent salt rejection was calculated using equation 1.20.

The percent humic acid recovery was calculated by the equation:

$$\% \text{ Humic Rec.} = \frac{(C_f - C_p)}{C_f} * 100 \quad \text{eq. 1.21}$$

where: C_f = chloroform concentration of chlorinated feed (mg/1)

C_p = chloroform concentration of chlorinated permeate (mg/1)

The results of the study which generated table 1.5 is included as Appendix II.

f. The Effect of Humic Acid Concentration on Permeate Flux Decline

The results of the preceding sections supplement the results of this section, as they further describe the nature of the RO feed stream.

Even though reverse osmosis treatment is a potential process for the removal of humus from water (27), a general lack of information exists in the literature relating the effect of the concentration of humic material on permeate flux decline. Personal correspondence with the author (96) restated their uncertainty to conclude that there exists a strong correlation between the feed concentration of humic acid and the rate of reverse osmosis membrane fouling.

Winfield (61) found a clear correlation (correlation coefficient .989) in a linear regression of the amount of dissolved organic material. as measured by its absorption at 275 nm, and the flux decline index.

Both studies (27,61), unfortunately, were performed on waters (river water, secondary sewage) which contain a complex matrix of components, several of which could influence the rate of fouling.

(1) Investigation of Flux Decline and Concentration

A series of experiments were performed to investigate the relationship between the concentration of humic acid in the feedwater and the fouling rate of a spiral wound reverse osmosis membrane. The study varied the concentration of humic acid in the feed, while controling parameters of temperature, pH, concentrate flow and particle size.

Regression analysis was performed on the relationships of permeate flux and time, and instantaneous flux with the accumulated processed volume, to determine the regression equation which best describes the experimental results.

Table 1.6 presents the regression analysis of the permeate flux decline and time. The independent variable (x) was time (days). The dependent variable (y) was the permeate flux (gal/ft^2-day). The regression models selected were the straight line, $y = ax + b$ (linear regression), the equation $y = ae^{bx}$ (exponential regression), the equation $y = ax^b$ (geometric regression), and the linear model, $y = a/(b + cx)$.

Table 1.7 presents the regression analysis of instantaneous permeate flux (flux at the time of sampling) and the accumulated volume (total throughput at the time of sampling) in a similar fashion. The geometric regression of these parameters has been used to model the flux decline phenomena (41,42,eq. 1.9)

The value of (a) represents the flux at time equal zero (pure water permeation flux). The value (b), or slope, has been termed the flux decline index or coefficient (40,37,31) in models using geometric regression to represent the phenomena of permeate flux decline with time. The correlation coefficient indicates the "goodness of fit" of the experimental data to the models. The fit of the data to the model is better as the value of the coefficient approaches 1.0.

The regressions were computed by the program, "Basic Equations by Laura", on an Apple Computer.

The data for the regression analyses are contained in Appendix III.

table 1.6

Regression Analysis of Fouling Data

Permeate Flux vs. Time

	Regression Equations			
Humics concentration	$y = a + bx$	ae^{bx}	ax^{b}	$\frac{a}{b + cx}$
0 mg/l (gal-day^{-1}-ft$^{2^{-1}}$) (gal-ft$^{2^{-1}}$ day^{-1})	a = 6.42	6.42	6.47	——
	b = -.015	-.0024	-.015	——
correlation coefficient	= .408	.408	.426	.397
30 mg/l	a = 7.56	7.53	8.96	——
	b = -.0378	-.0054	-.105	——
correlation coefficient	= .715	.729	.857	.787
60 mg/l	a = 6.06	6.03	7.70	——
	b = -.0603	-.01029	-.114	——
correlation coefficient	= .934	.890	.887	.935

a = y intercept, the flux at time equal to zero

b = slope, termed the flux decline index

table 1.6 (cont.)

Humic concentration	$y = a + bx$	ae^{bx}	ax^{b}	$\frac{a}{b + cx}$
100 mg/l	a = 6.90	6.95	8.86	——
	b = -.0522	-.00768	-.1584	——
correlation coefficient	= .984	.967	.858	.964
225 mg/l	a = 7.00	7.05	7.03	——
	b = -.1924	-.0315	-.105	——
correlation coefficient	= .910	.900	.863	.876

table 1.7

Regression Analysis of Fouling Data

Instantaneous Flux vs. Accumulated Volume

Humic concentration	$y = a + bx$	ae^{bx}	ax^{b}
0 mg/1 (gal/ft^2-day)	a = 6.45	6.45	7.42
(1/ft^2-day)	b = $-.1776 \times 10^{-3}$	$-.273 \times 10^{-4}$	-.0251
correlation coefficient	= .48	.47	.66
30 mg/1	a = 7.53	7.52	16.05
	b = $-.314 \times 10^{-3}$	$-.459 \times 10^{-4}$	-.1146
correlation coefficient	= .74	.76	.84
60 mg/1	a = 6.17	6.25	12.63
	b = $-.786 \times 10^{-3}$	$-.154 \times 10^{-3}$	-.130
correlation coefficient	= .93	.93	.87

a = instantaneous flux at initial volume processed

b = slope

table 1.7 (cont.)

Humic concentration	$y = a + bx$	ae^{bx}	ax^{b}
100 mg/1	$a = 7.08$	7.26	19.73
	$b = -.498 \times 10^{-3}$	$-.917 \times 10^{-4}$	-.165
correlation coefficient	= .98	.96	.90
225 mg/1	$a = 7.04$	7.096	12.00
	$b = -.165 \times 10^{-2}$	$-.271 \times 10^{-3}$	-.109
correlation coefficient	= .91	.90	.83

(2) Electron Microscopy of the Humic Fouling Layer

A sample of the membrane was removed after the completion of the fouling trial and taken to the USEPA Health Effects Research Laboratory, Cincinnati for analysis.

An ETEC scanning electron microscope (SEM) with an energy dispersive x-ray spectrometer (EDS) was used to picture the fouling layer and provide elemental analysis of the fouling deposits. (Procedure in 97)

As shown by microscopy, the fouling deposits were most evident on the spacers, and that a layer of non-specifically shaped substances were covering the membrane. Photographs are presented in figure 1.4 which show the membrane and membrane spacer at magnifications of 10 to 1900 times.

Figure 1.5 shows the results of the EDS by photographing the screen. The lengths of the bars of the graph represents the relative concentrations of elements found on the membrane and spacer.

Sulfur, silica, chlorine, and calcium were found. Larger concentrations of all elements were recorded at the spacer than on the membrane itself, with iron as the most abundant.

figure 1.4 Electron Scanning Microscopy of the Fouling Layer of Humic Acid

10X RO SPACER

10X Membrane and Spacer

Humic acid accumulations appear as light areas of the spacer.

figure 1.4 (cont.)

280X RO SPACER

280X Fouling on the RO spacers

A closer look at the accumulations seen on the preceding photograph.

figure 1.4 (cont.)

1000X RO SHEET

1000X Showing fouling on the membrane itself.

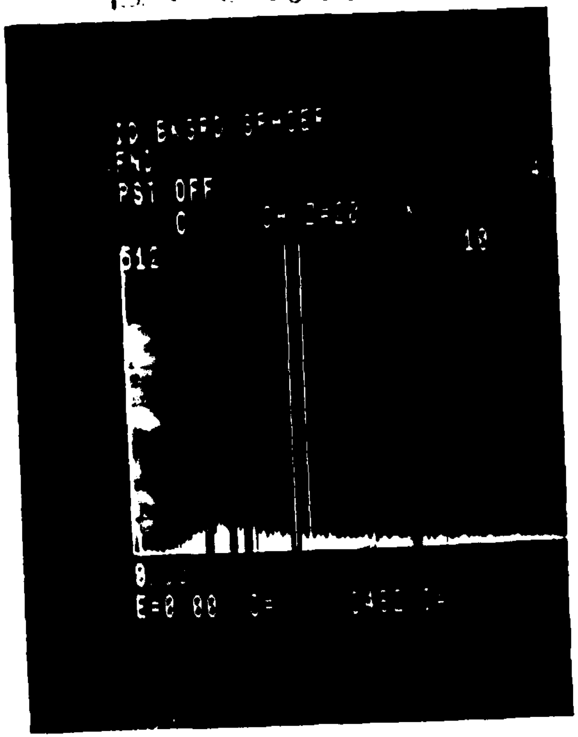
figure 1.4 (cont.)

1900X RO SHEET

1900X Showing a closer look at the foulants on the membrane.

figure 1.5 Energy Dispersive X-Ray Spectrometry of Fouling Layer of Humic Acid

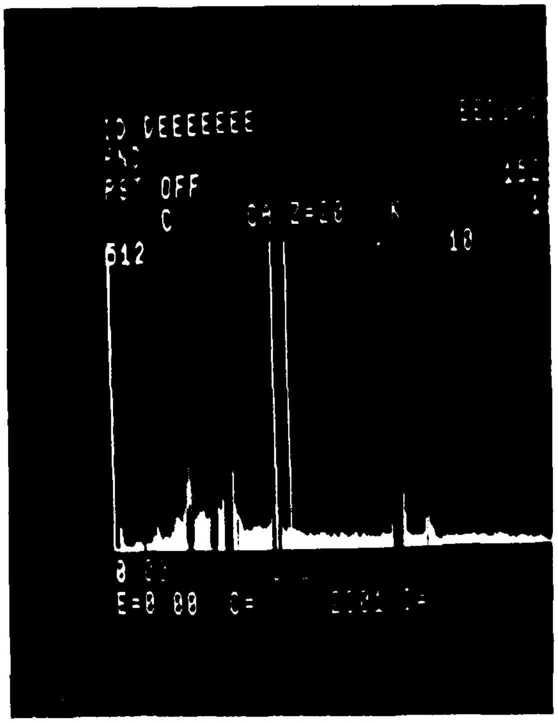
BACKGROUND



AREA ADJACENT TO DEPOSIT

Area of membrane adjacent to the deposit on the spacer. Results show little or no quantities of Fe, Si, S, Cl, and Ca.

figure 1.5 (cont.)



Deposit on RO Spacer

Analysis of accumulation on the RO spacer, showing higher concentrations of Fe,Si, S, Cl, and Ca.

g. The Effect of Ferrous Ammonium Sulfate on Permeate Flux Decline

A study was conducted to determine the effect, postulated by Goodall (21) that ferrous ions, in the presence of oxygen or chlorides, are oxidized to the ferric valence state, and form a gelatinous precipitate on the membrane that causes fouling.

The experimental apparatus (RO, membrane, tankage, etc.) was the same as that which was used for the humic fouling study. The procedure was similar, however, there were some differences. Ferrous ammonium sulfate was added to the 300 liter tank directly. The tank's contents, containing 1000 mg/l NaCl and 20 mg/l Fe, as ferrous ammonium sulfate, were mixed until complete dissolution resulted.

Ferrous ammonium sulfate was selected to provide the iron (II) species, as it is one of the few soluble ferrous compounds and has been used as a primary standard.

The membrane was flushed as before, however, the mixer was turned on to reconstitute the tank's contents. A bright orange colored concentrate initially was flushed from the membrane and, over the period of the 10 minute flush, the color changed to match the feed solution. A sample of the feed solution was taken at this time. Samples of the permeate and the concentrate were taken 30 minutes later.

Iron concentrations were determined daily, five days a week, using the phenanthroline method (69).

Other parameters recorded were: turbidity, pH conductivity, (Appendix XI), pressure, temperature, and concentrate and permeate flow (Appendix X).

The pH of the tank was adjusted to a pH of 7, daily. However, as the RO processed the tank solution, the pH decreased to a minimum of 4.7. As the membrane was flushed, the pH increased to near the 7.0 value. The membrane may have been accumulating a ferric hydroxide species.

The regressions described in section I.f(1) were carried out on the flux decline and time, and the instantaneous flux and accumulated volume relationships. The analysis is contained in table 1.8.

table 1.8

Regression Analysis of Fouling Data

20 mg/1 Fe - Permeate Flux vs. Time

Conc. Fe	$y = a + bx$	ae^{bx}	ax^{b*}	$\frac{a}{b + cx}$
20 mg/1 $(\text{gal-day}^{-1}\text{-ft}^{2^{-1}})$	a = 5.80	5.81	5.79	—
$(\text{gal-ft}^{2^{-1}})$	b = +.0179	+.00289	+.0198	—
correlation coefficient	= .73	.73	.50	.73

Instantaneous Flux vs. Accumulated Volume

Conc. Fe	$y = a + bx$	ae^{bx}	ax^{b}
20 mg/1 $(\text{gal-day}^{-1}\text{-ft}^{2^{-1}})$	a = 5.79	5.80	5.18
$(\text{1-ft}^{2^{-1}}\text{-day}^{-1})$	b = $+.177 \times 10^{-3}$	$+.286 \times 10^{-4}$	+.0224
correlation coefficient	= .75	.75	.52

a = flux at initial time or volume

b = slope, *flux decline index

h. Summary of the Results of Section I.

1. The relationship between permeate flux decline and time best followed zero order kinetics, for the fouling of a spiral wound reverse osmosis membrane by humic acid.

2. The relationship between the instantaneous permeate flux and the accumulated permeate volume best followed zero order kinetics, as well.

3. "The goodness of fit" to this linear relationship was better for more concentrated humic acid solutions.

4. The slopes of the regression between permeate flux and time varied linearly with the concentration of the humics.

5. A feed solution of 20 mg/l Fe, as ferrous ammonium sulfate, did not cause a decrease in permeate flux over time, or accumulated volume. A slight increase in flux, and a corresponding decrease in salt rejection, did result.

6. Humic acid feed solutions did result in a decline of permeate flux over time, however, salt rejection did stay constant throughout the trial. (An exception seemed to

be the 60 mg/l trial, when rejection did fall off substantially, as the membrane neared the end of its useful lifetime. (The ability for rejecting salt was lost.)

7. Evidence of fouling deposits remained on the spacers and the membrane even after flushing by the turbulent action of the concentrate. The major element found in the deposits of humic material was iron.

8. A method for the determination of minute quantities of humic acid in the permeate was demonstrated. The humic acid recovery seemed to correlate with the salt rejection of the membrane.

II. The Characterization of a Feedwater's Potential to Foul

A. Review of the Literature

Results of the preceding sections indicate that a linear relationship exists between the rate at which a membrane fouls and the concentration of a foulant in the feedwater. It should therefore be possible to develop a test to assess a feedwater's potential to foul based on this relationship.

The Silt Density Index (SDI) is a membrane test which has come into widespread use for the prediction of a feedwater's potential to foul a reverse osmosis membrane (65). In another version, the test is called the Plugging Factor (PF). Both tests measure the plugging of a cellulose triacetate membrane of 0.45 micron pore size, by colloidal material.

Silt Density Index: The determination of the SDI is based on the measurement of the speed at which a membrane filter becomes plugged at a pressure of 30 psig.

Procedure: The time, t_1 is determined; the time required to filter an initial 500 mls of feedwater through the membrane. Feedwater is then passed through continuously for 5, 10, or 15 minutes, depending on the quality of the water. The time, t_2 is the time required to filter a second 500 mls after continuous filtration.

$$\mathrm{SDI} = \frac{(1 - t_1/t_2) * 100}{T} \qquad \text{eq. 2.1}$$

where T is the time of continuous filtration. That time is reduced to 5 or 10 minutes if the term ($1 - t_1/t_2$) is greater than 75.

Plugging Factor (PF) Expressed as a percentage, the Plugging Factor is:

$$\mathrm{PF} = 100 * (1 - t_1/t_2) \qquad \text{eq. 2.2}$$

Comstock (62) concluded that the mechanism responsible for the plugging of the membrane filter is one of blocking filtration.

Matsuura (63) showed, by way of x-ray studies, that there is no clear correlation between the amount of metals on the membrane filter and the SDI. The change in permeability was presumed to be influenced by organic substances.

Green and Belfort (17) reported that there were six tests to evaluate feedwater quality for reverse osmosis. These include the test procedure by Taniguchi (64).

two instruments (manual and automatic) developed by Permasep Permeator Corp. and the instrument developed by Kaiser (65).

Brunnelle (66) correlated SDI values with zeta potentials as they related to RO fouling. The zeta potential, a measure of the electrical charge of the diffuse layer of the colloidal, can be approximated by the use of a zeta meter.

The Modified Fouling Index was developed because the current methods (SDI) for determining the fouling characteristics of feedwaters did not respond linearly with the concentration of colloidal and suspended matter. The authors (67) conceded that their modified Index did not faithfully simulate the action of the concentrate across the membrane.

A Microfouling Index was developed that uses Alcian Blue, a cationic dye which combines with slime and polyanionic material; the amount of residual dye is measured by a spectrophotometer at 580 or 610 nm (95).

B. Investigation of the Silt Density Index

An investigation of the SDI to determine the responsiveness of the test to changes in the concentration of organics, colloids, and dissolved chemicals, was carried out. The value of the SDI was assessed quantitatively by measuring parameters characterizing RO fouling, i.e. turbidity and total silica for colloidal contributions, calcium, magnesium, and iron, for chemical precipitation, and total organic carbon for organics, before and after passage through the membrane filter.

1. Experimental Protocol

a. Experimental Apparatus

A 25 gallon plexiglass tank served as both a flocculation and settling basin. The structure was V-shaped, having an overall length of 49 inches (124.5 cm), a width of 12 inches (30.5 cm), and depth at the V of 16 inches (40.5 cm).

A Phipps Bird Stirrer was suspended into the tank so that its six stirrers extended to a depth of 8 inches in the filled tank. Clarified effluent was withdrawn from a tube which floated, suspended by a wooden block.

A Neptune Dynapump transfered effluent from the tank up to the sand column.

A plexiglass column, 3 inches in diameter, filled with 24 inches of 35 mesh sand, simulated a rapid sand filter.

A Welsbach T-816 ozone generator with a minimum ozone generating capacity of 6.6 gm/hr was used.

b. Analytical Apparatus

A Sargeant Model LS was used to measure pH and calibrated with standard solutions at 4.0, 7.0, and 10.0 before each run.

A Perkin Elmer Model 373 Atomic Absorption unit was used to analyze calcium, iron, and magnesium. The unit was standardized with standards prepared by Scientific Products Co.

A Baush and Lomb Spectronic 20 was used to determine the concentrations of ozone and silica.

Total organic carbon in the samples was measured by a Beckman Model 915 Total Carbon Analyzer.

c. Experimental Procedure

Water samples were collected from a small unnamed stream which feeds into Winton Woods Lake, Hamilton County, Ohio. The water was transported to the laboratory in two carbouys. At the lab, 95 liters of the sample were transfered into the flocculation tank. The water was allowed to settle for 24 hours. After this time, 2000 mls of water were withdrawn from the top of the tank, and pumped through the sand column into a graduated cylinder. The pH of the water was adjusted from its natural value of 7.8 to 6.5. by dropwise addition of 0.1 HCl. The SDI test was performed at that time. The results of the SDI and the analysis of of the chemical parameters served as the baseline by which the effects of the following treatments were compared. Apparatus for the SDI is shown as figure 2.1.

Ozonation of the raw water: An additional 2500 mls were pumped through the sand column and the pH was adjusted to 6.5 as before. The water was transfered into an 18 liter glass bottle, into which ozone was bubbled in through a fritted glass diffuser. An air-ozone mixture at 8.0 psig and a flow rate of 5.0 slpm was administered for a period of 5 minutes. The ozone residual in the water was measured spectrophotometrically using buffered potassium iodide (68).

Alum addition: A solution of aluminum sulfate was prepared to achieve the desired concentration in the tank (10-30 mg/1), by weighing out the required amount and dissolving it in 30 mls of LPW. The tank's paddle stirrer was placed in operation at 100 rpm and

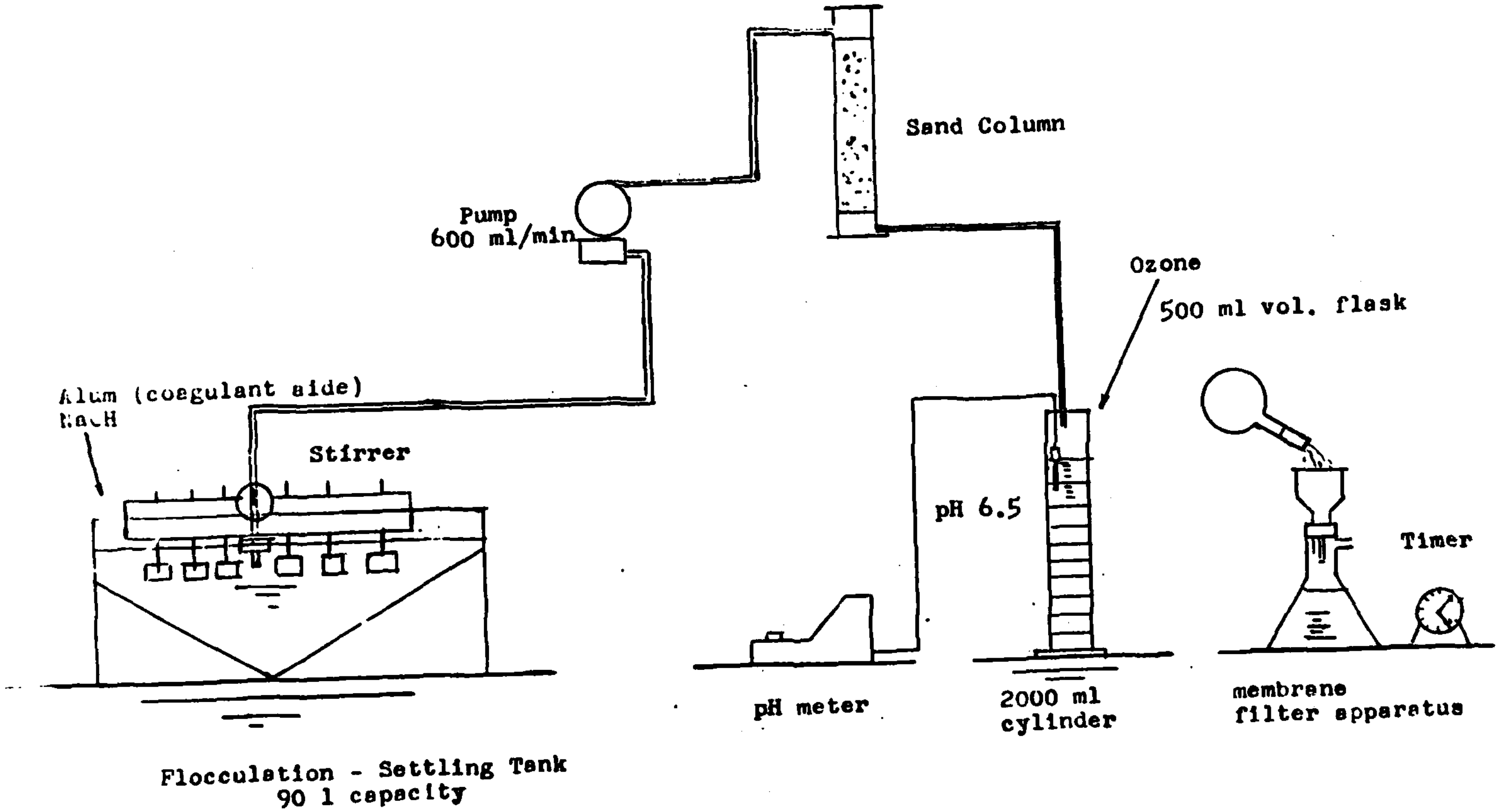


Figure 2.1

Apparatus for the Determination of the Silt Density Index the alum was poured in. The duration of the fast mix was 5 minutes, after which the stirrer was slowed to 20 rpm for 30 minutes to allow for floc formation. The stirrer was stopped and the water allowed to settle overnight. A sample was withdrawn from the tank, passed through the sand column, pH adjusted to 6.5, and the SDI performed.

NaOH addition: With the water already withdrawn for the alum treatment, it was possible to treat the remaining water further by the addition of 500 ml of 0.1 N NaOH. This raised the pH in the tank above 10.0 to affect calcium and magnesium precipitation. The same flocculation regime was followed, as described before. The usual analysis and sample taking was performed after 24 hours of quiescence.

Ozonation of the alum and NaOH treated water: An additional 2500 ml sample was adjusted and ozonated under the same conditions, to affect any organics which might have been present after the turbidity was reduced by the alum, and the inorganics reduced by the sodium hydroxide.

Table 2.1 represents the results of the studies. The following key was used to report the data:

Sample #	Description
1	Sand filtered water
2	Sand filtered,membrane filtered water
3	Alum treated,sand filtered water
4	Alum treated,sand,membrane filtered water
5	NaOH,alum treated,sand filtered water
6	NaOH,alum,sand,and membrane filtered water
7	Ozonated,sand filtered water
8	Ozonated,sand filtered,membrane filtered water
9	Ozonated,alum,NaOH,sand filtered water
10	Ozonated,alum,NaOH,sand,membrane filtered water

In essence, the odd numbered samples represent water which did not pass through the membrane filter, the even numbered samples did. Therefore, the difference in the values of samples #1 and #2. for example, indicates what was presumably retained by the filter. A significant difference would mean that the membrane, and possibly the SDI, was responsive to that particular parameter. Sample #1 is merely sand filtered water, and the samples # 3,5, and 9 represent the addition of alum, NaOH and ozone respectively. Sample #7 represents ozonated sand filtered water. Then the difference in the values of the SDI, for example, between samples #1 and #3, indicates if alum addition was effective in reducing the SDI.

table 2.1

Effect of Treatments on the SDI

Run #1 9 Sept 1981

Sample Number	SDI	Turbidity	Silica	TC	TIC	TOC	AA		
							Fe	Mg	Ca
1	20.0	2.3	2.6	32.8	18.2	14.6	<.1	7.6	25.5
2	-	2.0	2.2	30.8	18.0	12.8	<.1	4.6	19.5
3	16.1	2.3	2.9	35.7	15.7	20.0	<.1	7.3	35.9
4	-	.5	2.6	31.5	15.7	15.8	<.1	8.3	33.3
5	15.8	2.3	2.0	30.8	18.2	12.6	<.1	.10	1.5
6	-	.4	2.0	30.6	9.8	20.8	<.1	.05	1.8
7	14.6	1.1	2.0	28.7	15.7	13.0	<.1	6.5	26.8
8	-	.4	2.5	27.4	18.2	9.2	<.1	5.0	27.8
9	15.3	2.2	1.2	34.4	17.0	17.4	<.1	.10	2.2
10	-	.4	1.1	32.0	10.8	21.2	<.1	.06	.8

#1 = sand filtered water
#2 = sand filtered,membrane filtered water
#3 = alum treated,sand filtered water
#4 = alum treated,sand,membrane filtered water
#5 = NaOH,alum treated,sand filtered water
#6 = NaOH.alum.sand, and membrane filtered water
#7 = Ozonated, sand filtered water
#8 = Ozonated,sand filtered, membrane filtered water
#9 = Ozonated,alum,NaOH,sand filtered water
#10 = Ozonated,alum,NaOH,sand,membrane filtered water

table 2.1 (cont.)

Effect of Treatments on the SDI

Run #2 21 Sept 1981

Sample Number	SDI	Turbidity	Silica	TC	TIC	TOC	AA Fe	AA Mg	AA Ca
1	19.35	.80	3.3	44.3	30.6	13.6	.01	17.3	37.6
2		.20	2.8	37.9	30.6	7.3	.00	17.6	30.7
3	19.80	.83	3.2	39.8	34.1	5.7	.02	27.4	36.8
4		.50	2.9	31.5	22.9	8.6	.01	17.3	37.9
5	18.10	.66	2.5	20.1	13.0	7.6	.01	8.2	18.2
6		.27	2.1	15.0	6.5	8.5	.00	3.7	16.7
7	18.45	1.00	2.6	37.2	24.5	12.7	.02	7.5	20.1
8		.11	2.6	36.6	25.8	10.8	.01	17.0	32.2
9	17.32	.39	2.4	23.3	12.0	11.3	.00	6.5	9.4
10		.13	2.3	19.5	13.6	5.9	.04	6.5	12.3

table 2.1 (cont.)

Effect of Treatments on the SDI

Run #3 5 Oct 1981

							AA		
Sample Number	SDI	Turbidity	Silica	TC	TIC	TOC	Fe	Mg	Ca
1	19.01	2.4	0.12	19.7	15.3	4.4	.16	12.7	26.3
2		1.6	0.00	25.7	13.3	12.4	.30	8.6	32.0
3	18.01	1.6	0.12	25.5	15.6	9.9	.08	14.3	31.4
4		1.0	0.00	23.4	11.9	11.5	.06	13.9	30.9
5	15.7	2.3	0.18	15.8	11.4	4.4	.05	1.9	9.4
6		1.3	0.18	17.9	11.9	6.0	.06	2.3	9.4
7	12.95	1.2	0.12	22.5	12.0	10.5	.20	13.0	30.4
8		1.2	0.12	19.2	12.5	6.7	.06	13.1	25.4
9	15.80	1.6	0.12	16.9	8.6	8.3	.06	1.0	5.7
10		1.0	0.12	17.9	9.8	8.1	.16	1.5	4.1

Sample #7 ozone residual = 2.12 mg/l

Sample #9 ozone residual = 1.30 mg/l

table 2.1 (cont.)

Effect of Treatments on the SDI

Run #4 · 19 Oct 1981

Sample Number	SDI	Turbidity	Silica	TC	TIC	TOC	AA		
							Fe	Mg	Ca
1	20.0	3.9	2.42	37.4	27.4	10.0	.04	9.4	19.6
2	-	0.2	2.24	35.8	26.3	9.5	.01	8.8	18.2
3	20.0	2.5	2.06	40.5	27.0	13.5	.04	10.8	28.8
4	-	0.2	2.06	31.1	23.4	7.7	.05	9.6	21.8
5	16.7	0.7	1.74	27.6	18.0	9.6	.07	3.6	2.4
6	-	0.2	1.42	27.6	15.6	12.0	.02	5.2	5.5
7	18.7	2.0	2.06	28.9	20.4	8.5	.04	10.1	26.2
8	-	0.2	1.78	29.6	18.8	8.6	.00	8.7	28.3
9	17.1	0.4	1.38	23.6	16.2	7.4	.13	3.8	4.3
10	-	0.2	1.38	20.8	15.0	5.8	.02	4.0	4.3

Sample #7 ozone residual = 0.60 mg/l

Sample #9 ozone residual = 1.11 mg/l

table 2.1 (cont.)

Effect of Treatments on the SDI

Run #5 3 Nov 1981

Sample Number	SDI	Turbidity	Silica	TC	TIC	TOC	AA		
							Fe	Mg	Ca
1	19.5	2.0	4.28	77.5	67.0	10.5	.08	19.5	58.2
2	-	1.7	4.17	71.2	42.3	28.9	.01	20.0	59.6
3	19.0	1.3	3.83	83.8	66.2	17.6	-	-	-
4	-	1.1	3.69	54.3	39.7	14.6	.01	18.5	57.6
5	15.5	2.9	3.38	41.2	32.7	8.5	.00	.3	2.7
6	-	1.0	3.33	34.9	25.2	9.7	.00	.4	2.7
7	18.7	1.5	4.20	39.5	23.4	16.1	.06	19.8	58.0
8	-	1.4	3.93	37.4	22.7	14.7	.01	19.1	56.4
9	15.8	2.7	3.38	29.3	7.4	23.7	-	-	-
10	-	0.9	2.95	30.9	10.5	20.4	.00	.3	2.3

Sample #7 ozone residual = 1.92 mg/l

Sample #9 oxone residual = 0.73 mg/l

2. Results of the Preliminary Investigation of the SDI

An examination of the SDI data revealed that even the sum total of all the treatments did not reduce the SDI to a level which would be considered acceptable for feedwater for successful reverse osmosis operation.

a. Results of Before and After Membrane Filtration Analysis

Millipore membrane filters, with an effective pore size of 0.45 microns, did not retain the metals, as the pore size of the membrane is from two to three orders of magnitude larger than the metal species.

Since practical applications of membrane filtration usually involve the retention of particulates, microrganisms, and colloids, it was not surprising that particles large enough to be measured as turbidity were retained by the membrane.

There was a significant difference between the amount of silica in the water before and after filtration. Silica occurs in water as suspended particles, in a colloidal or polymeric state, and as silicic acids or silicate ions (69). The filter retained about 8% of the measured silica, indicating that most of the silica was the size that would pass through the filter.

b. Results of Effects of Various Treatments on Permeation

Table 2.2 represents the results of the various treatments on the permeation of the water through the membrane filters. The table contains data showing how the permeation flux was changed as specific possible parameters where affected by the various treatments.

The time of filtration, in seconds, for the first 500 mls, and after five minutes of continuous filtration, the second 500 mls, along with the total volume of water filtered, composes the left hand side of the table. The flux of the first 500 mls was calculated as J_1, the second 500 mls as J_2, and the total flux, (total volume filtered/membrane area - time) as J_t. The column, $J_{tx-\#1}$ represents the difference of the total flux for either treatments#3.5,7,9 and the untreated water, #1 for each run. The improvement factor is calculated as the ratio of this value to the flux of the raw water, #1

The addition of alum and the resultant reduction in turbidity improved the permeation through the membrane filter. The total permeation flux, J_t of the SDI test was almost doubled by the addition of alum.

table 2.2 The Effect of Various Treatments on SDI Permeate Flux

	sample number	time(sec) 1st 500 mls	time(sec) 2nd 500 mls	total vol filtered	J_1	J_2	J_t	$J_{t_{x-\#1}}$	Improvement Factor $\frac{J_{tx-\#1}}{J_{t\#1}}$
run#1	1	4560	12,300	1020	.063	.023	.034	---	---
	3	1736	9,000	1020	.166	.032	.053	.019	0.57
	5	1670	8,054	1020	.173	.036	.059	.025	0.73
	7	92	3,468	1270	3.14	.083	.190	.156	4.58
	9	1286	5,584	1040	.224	.052	.084	.050	1.46
run#2	1	115	3,576	1420	2.50	.081	.205	---	---
	3	223	2,415	1140	1.24	.119	.223	.018	.09
	5	375	3,965	1080	.77	.073	.134	.071	-.34
	7	75	871	1820	3.84	.331	.842	.637	3.11
	9	96	717	1820	3.00	.402	.942	.737	3.60

#1 = sand filtered water
#3 = alum treated, sand filtered water
#5 = NaOH, alum treated, sand filtered water
#7 = Ozonated, sand filtered water
#9 = Ozonated, alum, NaOH treated, sand filtered water

table 2.2 (cont.) The Effect of Various Treatments on SDI Permeate Flux

	sample number	time(sec) 1st 500 mls	time(sec) 2nd 500 mls	vol filtered	J_1	J_2	J_t	$J_{tx-\#1}$	Factor $\frac{J_{tx-\#1}}{J_{t\#1}}$
run#3	1	450	9,000	1030	.640	.032	.061	---	---
	3	305	3.065	1060	.945	.094	.166	.105	1.72
	5	210	990	1160	1.372	.291	.446	.385	6.31
	7	74	195	1990	3.90	1.48	2.02	1.96	32.11
	9	345	1,650	1160	.84	.18	.29	.23	3.77
run#4	1	8.340	10,800	500	.035	0	.01	---	---
	3	4,260	10,800	772	.068	0	.029	.014	.93
	5	1.490	8.940	1025	.193	.032	.055	.040	2.66
	7	671	10,500	1040	.430	.027	.052	.037	1.80
	9	610	4,250	1090	.472	.068	.122	.107	7.13
run#5	1	205	8,100	1030	1.40	.036	.069	---	---
	3	192	4,020	1190	1.50	.072	.152	.083	1.20
	5	192	850	1230	1.50	.339	.528	.459	6.65
	7	78	1,179	1630	3.69	.244	.603	.534	7.74
	9	241	1,160	1270	1.19	.248	.430	.361	5.23

Alum and sodium hydroxide addition, though not a consistently successful treatment, did improve the permeation flux three-fold.

Ozone represented the treatment which improved permeation the most. The ozonation of the raw water resulted in almost a ten-fold improvement in membrane flux (0.132 to 0.0136 ml/m^2-sec).

Although the combination of all treatments, (alum, NaOH. ozone) improved the permeation flux by six-fold, the mix of all treatments smoothed out the variations which developed for unknown reasons.

The statistics on which the results and conclusions are based for both the before and after filtration studies (table 2.1) and the permeation studies (table 2.2) are included as Appendix XI.

3. Determination of the SDI of the Humic Solutions

SDI tests were performed on the humic solutions used in the fouling experiments, described in section I, to determine whether the test would react linearly to differences in the concentration of humic acid.

Samples were withdrawn from the tank just prior to start-up for the fouling study. The results of the

SDI tests are given in table 2.3.

table 2.3 SDI of Tank Humic Acid Solutions

Humic conc. (mg/l)	pH	total vol. filtered (mls)	J_t mls/m^2-sec	SDI
0	7.0	5880	3246.3	1.03
30	7.0	3030	913.9	6.20
60	7.0	1045	21.3	6.16
100	7.0	1600	215.0	6.52
225	7.0	104	8.3	*

The time of continuous filtration, T was 15 minutes.

* The filter clogged and the SDI could not be determined.

J_t was the total flux through the membrane.

Experimentation with the SDI of humic acid in sodium chloride solutions was carried a step further in order to determine a range of concentrations which would result in an SDI value (2 - 5.3) that is considered safe for reverse osmosis operation.

The following concentrations of humic acid were prepared as described before, and the SDI values determined. The results are shown in table 2.8.

table 2.4 SDI of Humic Acid Solutions

humics conc. (mg/l)	total vol. filtered (mls)	J_t l/m^2-sec	SDI
0.0	5880	3.79	1.03
0.5	5160	2.38	3.68
0.5	5425	3.13	4.73
0.5	5120	2.23	4.97
1.0	5400	2.24	5.40
1.0	3660	1.50	5.16
1.0	4480	1.93	4.52
2.0	3650	1.00	6.03
2.0	3080	0.78	6.13
2.0	3650	0.95	6.08
5.0	2080	0.32	6.49
5.0	2170	0.27	6.52
5.0	2100	0.27	6.46

Results of these experiments showed that the SDI did respond to differences in concentration of humic acid, though not linearly. An acceptable concentration of humic acid in the feedwater, as determined by SDI values, is between 0.0 and 1.0 mg/l.

AD-A135 437 A REPLACEMENT FOR THE SILT DENSITY INDEX: PERMANGANATE 2/3
DEMAND TO PREDICT..(U) AIR FORCE INST OF TECH
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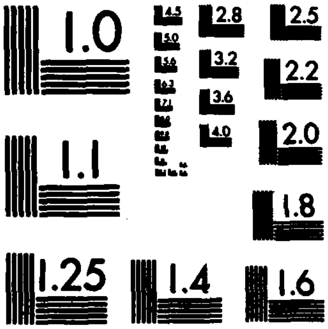


MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

III. Predicting RO Fouling with the Permanganate Demand Test

A. Literature Review

1. Permanganate to Predict Fouling

The SDI clearly has little value in any quantitative attempt to predict RO fouling, and may or may not be of value in the operation of an RO unit. A test measuring the permanganate demand of the feedwater could be used in either application.

Cruver and Nusbaum (37) examined several feed characterization methods to predict the fouling tendency of a feed stream. They considered that the aromatic hydroxyl content seemed to be more related to fouling, as indicated by membrane deposit analysis.

Stewart (77) claimed that potassium permanganate is probably the most powerful of the oxidizing agents of the organic chemist's armory. The great reactivity of permanganate as an oxidant is reflected by its ability to use different reaction paths, depending on the structure of the organic substrate, and the acidity or basicity of the solution.

Permanganate may lower its chemical potential in any of several ways. It may react by electron abstraction, (equation 3.2), hydride ion removal (the prefered path of organic anions, equation 3.3), and oxygen donation to an organic substrate (equation 3.4).

$$*MnO_4^- + MnO_4^{-2} \rightleftharpoons *MnO_4^{-2} + MnO_4^- \qquad \text{eq 3.1}$$

$$MnO_4^- + RH \rightleftharpoons HMnO_4^- + R^{\cdot} \qquad \text{eq.3.2}$$

$$MnO_4^- + ZH^- \rightleftharpoons HMnO_4^{-2} + Z \qquad \text{eq.3.3}$$

$$MnO_4^- + Z^- \rightleftharpoons MnO_3^- + ZO \qquad \text{eq.3.4}$$

Manganous ion is the end product of permanganate oxidation in acid solution and only when fairly good reducing agents such as iodide or ferrous ions are used. Most organic compounds reduce permanganate to manganese dioxide even in acidic solution.

To correlate with the findings of Cruver and Nusbaum, in weakly acidic and neutral solutions, the manganaous ion reacts with permanganate to form manganese dioxide.

$$2MnO_4^- + 3Mn^{+2} + 4OH^- \rightleftharpoons 5MnO_2 + 2H_2O \quad \text{eq. 3.5}$$

Mechanistic factors are of greater importance than the magnitude of oxidation potentials in determining the degree of oxidation of organic substrates.

Permanganate absorbs strongly in the visible spectrum, producing the characteristic purple color.

Both spectrophotometry and volumetric determinations have been used to detect permanganate in solution.

2. Detection and Analysis of Permanganate

a. Spectrophotometry

The characteristic colors of permanganate, due to the tetrahedral paramagnetic ion, MnO_4^-, of the strong acid, $HMnO_4$, and manganate, can be used to detect their presence in small concentrations. Suitable wavelengths of measurement of permanganate and manganate are 522 and 426 nm, respectively.

$$(MnO_4^-) = \frac{Abs_{522} - 0.282\ Abs_{426}}{2348}$$

for a pathlength of 1 cm (70).

Spicher and Skirnde (71,72) applied the peak-height method of Wright (73) to investigate the possible use of potassium permanganate as an innovative new water treatment for trace organics. The method involves the measurement of the heights of the peaks formed by the scanning spectrophotometer as it scans, from 550 to 500 nm, samples of varying concentrations of permanganate. The peak heights vary linearly with permanganate concentrations, as permanganate observes Beer's Law to concentrations of 100 mg/l.

Rawoof and Sutter (74) recorded the rapid reaction of the decomposition of ferrocyanide with permanganate using a special rapid mixing device and photographed the resulting decrease in transmittance of the permanganate with a Polaroid camera.

b. Volumetric Determination

Potassium iodide, sodium oxalate, oxalic acid, potassium ferrocyanide, ferrous ammonium sulfate, and other reducing agents have been used to determine permanganate concentrations.

The addition of an excess of potassium iodide in acidic solution, to a solution of permanganate, reduces the permanganate to manganese (II) instantly.

$$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{+2} + 5I_2 + 8H_2O \quad \text{eq. 3.7}$$

The liberated iodine can be titrated to the starch endpoint with standard thiosulfate.

$$I_2 + 2S_2O_3^{-2} \longrightarrow 2I^- + S_4O_6^{-2} \qquad \text{eq. 3.8}$$

An iodimetric determination of permanganate in a manganate-permanganate mixture is likely to be imprecise because of the relatively small change in the thiosulfate titer and interferences at the endpoint.

Oxidability of potassium permanganate is often used in Europe as a test for chemical oxygen demand (75). Chloride in brackish waters interferes less with this test than by the acid-dichromate method, in spite of difficulties with incomplete oxidation and reproducibility.

3. Permanganate Oxidation of Inorganic Substances

Kirk and Brown (76) classified permanganate as a complex delectronator, as it can function as a one or two equivalent oxidant, depending on the characteristics of the substrate it is attacking.

a. Derivitives of Ammonia

Ammonia is slowly oxidized by permanganate to a mixture of products, chiefly nitrogen, nitrates, and nitrites. Derivatives of ammonia are almost all oxidized more rapidly than the parent compound. Aromatic primary amines suffer immediate ring degradation when treated with permanganate (77).

b. Sulfur Ions - Sulfide, Sulfite

Excess permanganate oxidizes sulfide to sulfate in basic solution. (eq. 3.9)

$$8MnO_4^- + 3S^{-2} + 4H_2O \longrightarrow 8MnO_2 + 3SO_4^{-2} + 3SO_4^{-2} + 8OH^-$$

In neutral or acid solution, the reaction tends to be incomplete, with sulfur and tetrathionate as by-products.

Permanganate in excess or in basic solution forms sulfate;

$$2MnO_4^- + 3SO_3^{-2} + H_2O \longrightarrow 2MnO_2 + SO_4^{-2} + 2OH^- \quad \text{eq. 3.10}$$

or if reacted in acidic or neutral solution, in stoichiometric proportions, tends to produce dithionate.

$$2MnO_4^- + 6SO_3^{-2} + 4H_2O \longrightarrow 2MnO_2 + 3S_2O_6^{-2} + 8OH^- \quad \text{eq. 3.11}$$

c. Metals

Most metals with multiple oxidation states are oxidized by permanganate. Examples of these ions are ferrous, ferrocyanide, chromium, and plumbous.

d. Halides

Chloride in basic solution is, for all practical purposes, inert to oxidation by permanganate. The same can be said for neutral solutions, as well. In highly acidic solution, chloride, in the form of hydrochloric acid, can reduce permanganate in two reactions, depending on the concentration of HCl (91).

$$2KMnO_4^- + 8HCl \longrightarrow 3Cl_2 + 2MnO_2 + 4H_2O + 2KCl \quad \text{eq. 3.12}$$

Since concentrated hydrochloric acid will dissolve the manganese dioxide, the reaction equation becomes:

$$2KMnO_4^- + 16HCl \longrightarrow 5Cl^- + 2MnCl_2 + 8H_2O + KCl \quad \text{eq. 3.13}$$

In acid solutions, all halides are oxidized to a great degree. Iodide is the most reactive in both acid, neutral and basic solutions.

$$2MnO_4^- + I^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^- \quad \text{eq. 3.14}$$

4. Permanganate Oxidation of Organics

The great reactivity of permanganate as an oxidant is reflected in its ability to use different reaction paths, depending on the pH of the solution and the structure of the organic substrate (78). It attacks, to some degree, all organic solvents in which it is soluble. Permanganate exchanges its oxygen with the aqueous solvent rapidly in acidic solution, but more slowly in neutral and basic solutions. The increase in oxidation rate that invariably occurs when reaction conditions are strongly acidic is caused mainly by the conversion of the permanganate ion to the still more active oxidant, permanganic acid (77).

Manganese dioxide is the usual product of organic oxidation in all but strongly basic solutions (91).

a. Oxidation of Alkyl Side Chains

The usual products of permanganate oxidation of side chains of arenes are the corresponding carboxylic acids (78), Under neutral or basic conditions, little ring degradation takes place. In very acidic solutions, electrophilic attack of the aromatic nucleus occurs.

A particular example of the use of side chain oxidations has been in the degradation of humic matter.

Humic substances are complex mixtures of organic chemical compounds which can be extracted from soils, marine and freshwater sediments, and aqueous sources as well. Humic substances are subdivided into a number of categories according to increasing hydrophilic properties. Oden (79) used the terms which are applied currently, humic acids (soluble above pH 7), fulvic acids (soluble below 7), and hymatomelanic acids (soluble in both ranges).

Fulvic acids have been shown to account for 80-90% of the organic material in natural waters (80). Llao et.al. (81) studied the degradation products of the reaction of humic acid with potassium permanganate by GC/MS techniques. The dominant products produced from the oxidation are benzenecarboxylic acids, followed by aliphatic monoacids, and glyoxylic (carboxyphenyl) acids. Aliphatic tribasic acids were present in relatively low yields.

Humic substances, in the form of fulvic acids, can react with metal ions and hydroxides (82). The inability of exchangeable cations, such as Ba^{+2} and K^{+} to replace all Cu^{+2} and Zn^{+2} adsorbed by humic substances, has been taken as an indication that humics form complexes with certain metal species (89).

Humic and fulvic acids are among the most widely distributed products of plant decomposition on the earth's surface. They are amorphous, yellow-brown or black, hydrophilic, acidic, polydisperse substances of wide ranging molecular weight (less than 10,000 for fulvic acid, 10,000 - 300,000 for humic acid are the usual ranges) (84).

b. Aromatic Rings

Permanganate can break the rings of aromatic compounds with electron donating groups attached (77). Phenols and analines are very rapidly degraded to carbon dioxide. Xylene, toluene, and benzene are more resistant to oxidation, in order of their listing.

More aromatic primary amines are oxidized almost immediately in neutral or basic solutions of permanganate to give cleavage products and eventually carbon dioxide and ammonia. (The permanganate demand of analine was studied in section IV).

Further studies of permanganate reactions with organics are given in many standard textbooks on Organic Chemistry (77,78,91,94). (Sodium lauryl sulfate, phenol, trichlorethylene, and butyric acid were reacted with permanganate and discussed in section IV.)

Spicher and Skrinde (71) subjected 27 pure organic compounds to permanganate oxidation in aqueous solution. The reactions were carried out to simulate treatment of organic compounds with permanganate at water plants. The concentration of the organics was 50 mg/l; and 31.6 mg/l of permanganate was reacted. The reactions were carried out at pH 7 and 10, at a reaction temperature of 25°C, for four to six hours. Their results are presented in table 3.1.

table 3.1 Reaction of $KMnO_4$ with Pure Organic Compounds in Distilled water

Compound	Reaction*	
	pH 7	pH 10
Saturated 3-carbon		
proprionic acid	-	-
proprional	-	-
proprionaldehyde	+	+
propylamine	-	+
ethyl formate	-	+
acetone	-	-
glycerol	-	-
lactic acid	-	-
methyl acetate	-	-
alanine	-	+
pyruvic acid	+	+
Unsaturated 3-carbon		
acrolein	+	+
allylamine	+	+
acrylic acid	+	+
allyl alcohol	+	+
Aromatic		
benzene	-	-
benzaldehyde	+	+
phenol	+	+
analine	+	+
benzoic acid	-	-
benzyl alcohol	+	+
Mscellaneous		
octyl alcohol	-	-
caproic acid	-	-
ABS	-	-
2-butanone	-	+
starch	-	-
creatine	-	-

* Plus sign indicates reaction, minus sign indicates no reaction.

5. Development of the Permanganate Demand Test

The procedure developed to test the fouling potential of a feedwater, utilizes the difference between the permanganate demand of the feed and the permanganate demand of the permeate. Simplistically, that concentration of solute which passes through the membrane in the permeate is not involved in the fouling process and is subtracted out. Variations in the spectrophotometric determination of permanganate due to pH and interferences caused by buffering components are lessened or eliminated by using the permeate to prepare the spectrophotometric standards.

This difference in permanganate demand, and thus, in concentration, affects both the flow of the solvent (water) and the solute through the membrane.

For solute flow, from the diffusion model and Fick's Law, and recalling equation 1.2, the mass flux across the membrane is:

$$J_s = B (C_f - C_p) \qquad \text{eq. 1.2}$$

where the difference in concentration represents the chemical driving force.

Recalling equation 1.1, the permeate flux, J_w is:

$$J_w = A\,(\Delta P - \pi) \qquad \text{eq. 1.1}$$

and the osmotic pressure is;

$$\pi = \frac{\phi RTN\,(C_f - C_p)}{MW\,(10^3)} \qquad \text{eq. 3.15}$$

using an adapted Van Hoff equation (86).

Substituting equation 3.12 into equation 1.1, then:

$$J_w = A\,\left(\Delta P - \frac{\phi RTN(C_f - C_p)}{MW\,(10^3)}\right. \qquad \text{eq. 3.16}$$

where: ϕ = osmotic pressure coefficient
T = temperature, absolute, K
N = number of ions per salt molecules
MW = gram molecular weight of salt
R = universal gas constant, l-atm/°K-mole

For the fouling of a membrane by a gel layer, without the effects of other membrane phenomena, the difference $(C_f - C_p)$ characterized by the permanganate demand test represents the decrease of permeate flux due to the buildup of solute, increasing osmotic pressure.

Recent studies (92) have reported that equation 1.1 and 1.2 do not adequately describe transport through the membrane, since they neglect the account for water and salt flux coupling. Such a model was proposed by Kedem and Katchalsky. This model, based on irreversible thermodynamics, is represented by the following equations : (93)

$$J_w = A\,(\Delta P - \Delta\pi\sigma) \qquad \text{eq. 3.17}$$

$$J_s = \omega\Delta\pi + (1 - \sigma)J_w\,\bar{C}_s \qquad \text{eq. 3.18}$$

where: σ = reflection coefficient
ω = solute permeability coefficient
$\bar{C}_s$ = average concentration or log mean solute concentration

Here the $\bar{C}_s$ is approximated by the difference in permanganate demand of the feed and the permeate. (The permanganate demand is the difference in the log function, absorbance at 526 nm, of the feed and permeate.)

a. 0.1 N Potassium Permanganate Solution Preparation

3.3 g potassium permanganate was dissolved in 200 mls LPW and diluted to one liter. The solution is stoppered and allowed to stand on the countertop overnight. It is filtered through a glass filtering crucible and standardized against reagent grade sodium oxalate. The standardization procedure is contained in standard texts of Quantitative Analysis (85). The solution was stored in the refrigerator in brown glass bottles.

b. Preparation of the Calibration Curve

Permanganate obeys Beer's Law in concentrations to 100 mg/l. One ml of 0.1 N $KMnO_4$ in 100 mls results in a permanganate concentration of 31.605 mg/l.

(1) Application to a Scanning Spectrophotometer

The useful range of permanganate varies with the limitations of the spectrophotometer. For example, the B&L Spec 505 utilizes two ranges, with a range of 0-50 mg/l permanganate at the 100% setting, and 70-90 mg/l at the 10% setting. The Hitachi Perkin Elmer Coleman 124 provides essentially 0-100 mg/l in one setting, 0-2. This allows the entire Beer's

Law range to be measured with recorder adjustment only. This provides for better correlation between concentration and absorbance.

Peak heights were determined by constructing a line on the permanganate trace from the trough at 512 nm and the trough at 538 nm. A line is constructed from the peak at 526 nm to this other line, and this distance is measured as the peak height, as shown in figure 3.1.

At plot of the peak heights and the concentration of permanganate results in a straight line with excellent correlation (.99+). The plot is shown as figure 3.2.

(2) Application to a Standard Spectrophotometer

Although not all spectrophotometers may be sensitive enough to repond to wavelength change, meters like the B&L Spectronic 80, with a bandwidth of 2 nm, can accurately plot the shape of the permanganate spectra. The geometric shape of the plot allows the peak height to be determined by recording the absorbance of the trough at 538 nm, the peak at 526 nm, and the second trough at 512 nm. The peak height, A_p, in absorbance units, can then be calculated as follows:

$$A_p = A_{526} - A_{538} + 0.462(A_{538} - A_{512}) \quad \text{eq. 3.19}$$

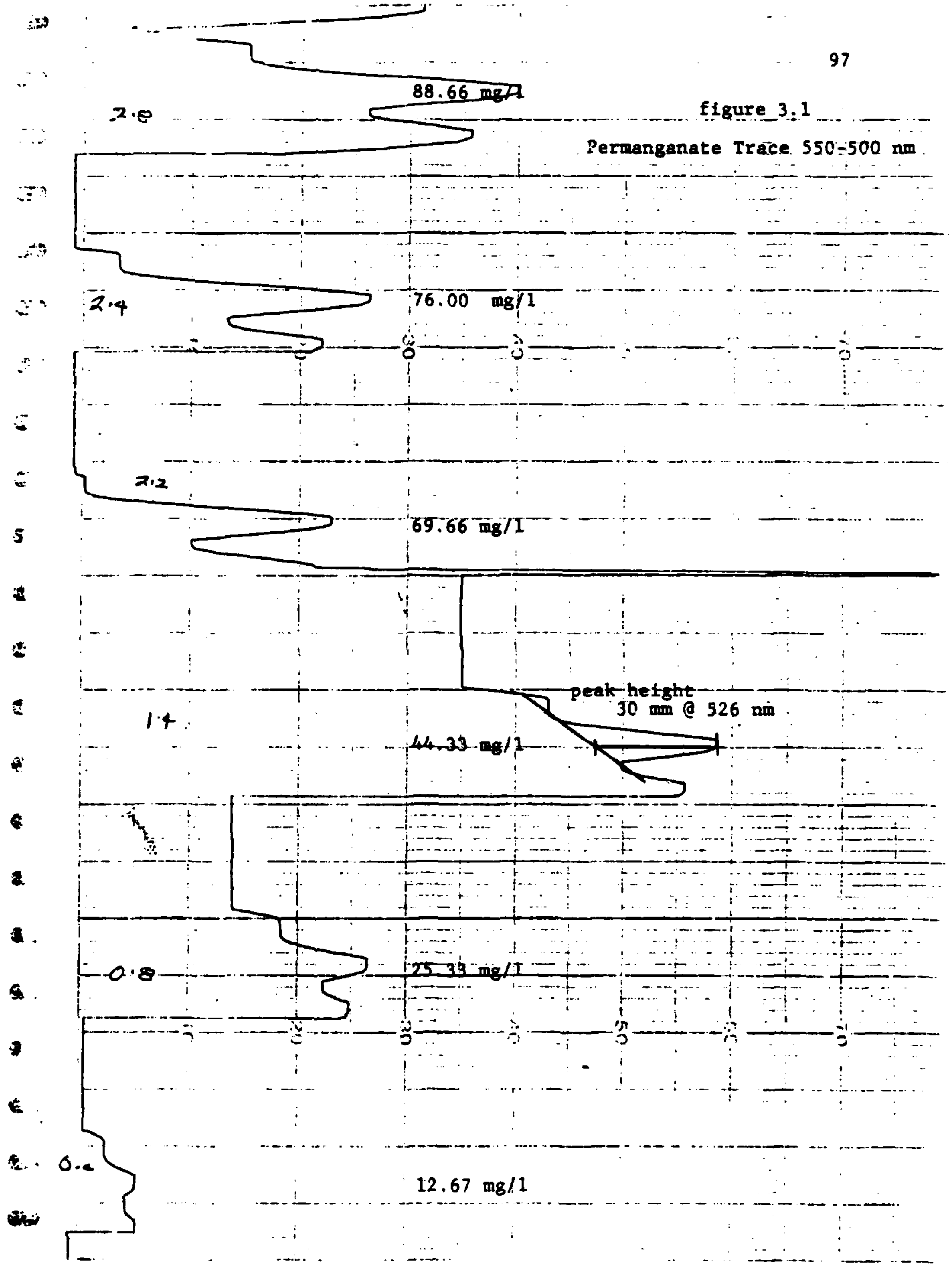
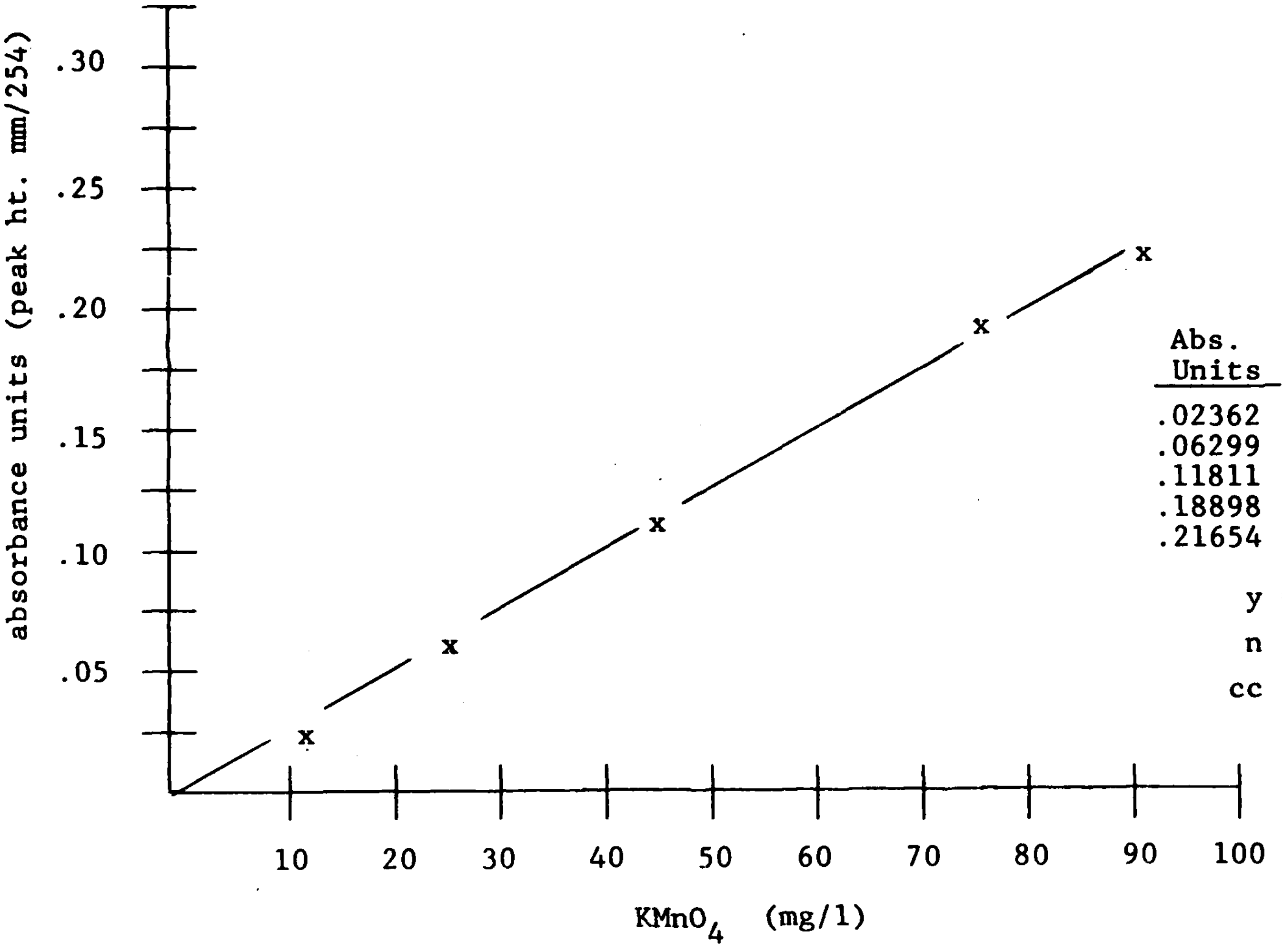


figure 3.1

Permanganate Trace 550-500 nm

figure 3.2 The Absorbance at 526 nm of $KMnO_4$

Calibration Curve, 22 April 83



Abs. Units	$KMnO_4$ mg/1
.02362	13.02
.06299	26.04
.11811	45.57
.18898	78.13
.21654	91.15

y = 1.20

n = 402.3

cc = .997

where A_{xxx} is the absorbance at that numbered wavelength.

The same plot of absorbance and concentration, can be developed by which any permanganate concentration, 1-100 mg/l can be determined from absorbance readings.

c. Procedure for the Permanganate Demand Test

A sufficiently descriptive representation of the relationship between the peak heights and the concentration was obtained from six concentrations of permanganate, prepared by adding, by 5 ml syringe, 0.4, 0.8, 1.2, 2.2, 2.4, and 2.8 mls of 0.1 N $KMnO_4$ to 100 ml volumetric flasks and diluting to 100 mls with RO permeate water. The solutions were transfered to 125 ml flasks, then placed in boiling water in a waterbath. The flasks were covered with 200 ml beakers, inverted over the flask's mouth. The standards remained in the waterbath for two hours, then withdrawn and placed in cool water for 10 minutes. Samples of the solutions, now at room temperature, were transfered to 1 cm quartz cuvettes. The samples were analyzed in a scanning spectrophotometer, for the visible spectra from 550-500 nm. A plot of the line formed by the linear regression of the peak heights at 526 nm and the permanganate concentrations was prepared using the linear regression routine of the TI-58C/59 programmable calculator.

The determination of the permanganate demand of an unknown sample involves the introduction of a known quantity of permanganate into the sample, or a dilution of the sample, allowing the sample to react with the permanganate in the waterbath, as described before. The permanganate concentration remaining is determined by comparing its peak height to the regression line of the standards. The permanganate demand can then be determined by subtracting the residual concentration from the concentration of permanganate applied.

The procedure for determining the permanganate demand of a sample was altered slightly from that described for permanganate standards preparation. A provision was made for the removal of the reduced manganous or manganese dioxide precipitate prior to spectrophotometric analysis. The manganate was removed by filtering the cooled solution through a glass fiber filter. Whatman 934-AH filters were used for this purpose. Paper filters were found to be unacceptable, as the permanganate reacted with the paper.

6. Permanganate Demand of Potential Foulants

a. Ferrous Ammonium Sulfate (ferrous ion)

Permanganate was reacted with varying concentrations of ferrous ammonium sulfate in aqueous and sodium chloride solutions. The reaction is pH dependent, as the ferrous ion formation is favored in acidic solution, and is the species which will react with permanganate. The reaction with permanganate in saline solution was expected to oxidize the ferrous chloride to ferric chloride.

The average of two trials results of the permanganate oxidation of the ferrous ions in 1000, 5000, and 10,000 mg/l NaCl is given in table 3.2. The raw data is included as Appendix VII.

table 3.2 Permanganate Demand of Ferrous Ammonium Sulfate in the Presence of Sodium Chloride

Fe mg/l	NaCl mg/l	pH	Demand mg/l	St. Dev.
1	1000	4.2 4.3	5.18	1.53
"	5000	4.3	2.53	3.05
"	10,000	3.1,3.9	11.28	1.56

Fe mg/l	NaCl mg/l	pH	Demand mg/l	St. Dev
5	1000	3.9,4.0	10.78	.24
"	5000	3.9	6.09	5.34
"	10,000	3.2,3.9	15.08	.93
10	1000	3.7	14.49	.87
"	5000	3.7	8.71	3.10
"	10,000	3.1,3.7	19.30	2.09
20	1000	3.5	22.73	4.86
"	5000	3.5	21.87	.88
"	10,000	3.0,3.5	36.61	.13

The results of the permanganate reaction in aqueous solution are presented in table 3.3.

table 3.3 Permanganate Demand of Ferrous Ammonium Sulfate in Aqueous Solution

Number Observed	Fe mg/l	pH range	Demand mg/l	St. Dev.
10	1	4.3-7.4	6.21	6.03
4	2	4.7-6.5	5.81	5.67
10	5	3.9-5.3	10.03	6.87
17	10	3.6-5.1	15.61	8.77
10	20	3.3-5.0	28.17	13.01
2	30	3.4,4.8	47.74	25.93
1	40	3.3	70.60	—

The raw data for this table appears in Appendix VII.

The large variation in the results of these reactions may be due to the pH differences, small concentrations of iron, and the variable distribution of the iron in the reactive ferrous or non reactive ferric oxidation state, and the oxidation of ammonia (section 3a.).

b. Humic Acid

The permanganate reaction with humic acid was discussed previously. The source of humic acid was the same used in the fouling study. A stock solution of 1000 mg/l was prepared in LPW and stirred vigorously. Concentrations of 1-40 mg/l were prepared in 100 ml volumetric flasks from the stock solution. The permanganate solution was injected into the flask, then the solution was diluted to 100 mls with LPW. The solution was transfered to 125 ml flasks and placed into the waterbath at 100°C for two hours, covered by 200 ml beakers. The flasks were withdrawn from the waterbath and cooled in a sink to room temperature. The solutions were filtered and the permanganate demand was determined by spectrophotometry. Reactions were carried out in both sodium chloride and aqueous solutions.

To correlate with the results of the fouling study, the results of the permanganate demand of humic acid in the range 6.7-7.2 are of particular interest. A summary of these results is presented in table 3.4, and shown graphically in figure 3.3. A compilation of values is included as Appendix VI.

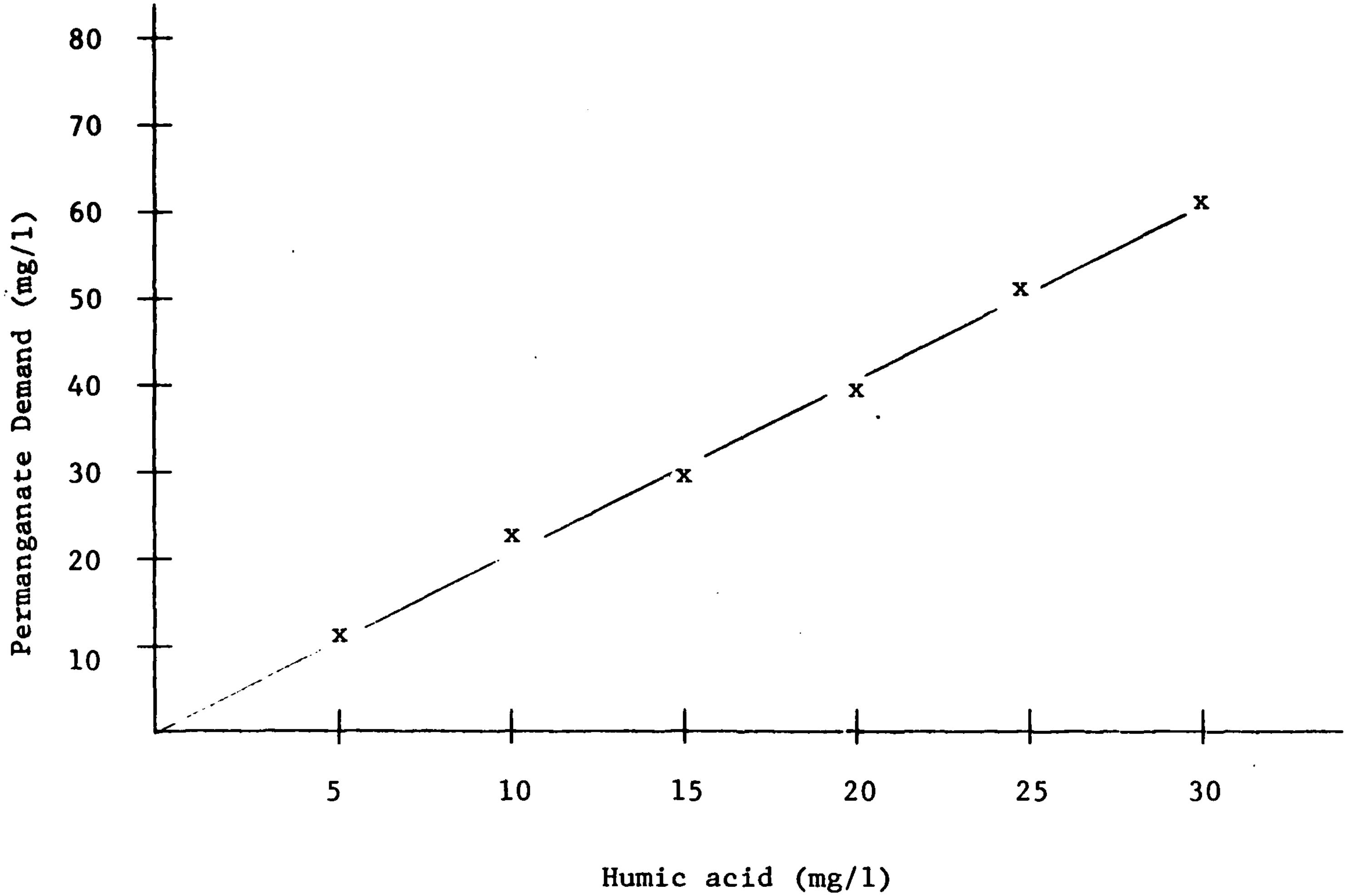
table 3.4 Summary of Permanganate Demand of Humics, pH 6.7-7.2.

Humic conc. mg/l	$KMnO_4$ demand mg/l	Number Observed	St. Dev.
0	0.00	—	——
5	11.62	5	1.49
10	20.91	13	3.30
15	28.07	4	1.00
20	37.34	8	3.34
25	48.80	4	3.36
30	60.42	4	10.88

An excellent correlation (correlation coefficient = .998) was obtained between the humic acid concentration and the permanganate demand in this pH range. The regression equation formed by the relationship is:

$$KMnO_4 \text{ (mg/l)} = 1.942 \text{ Humics(mg/l)} + .471 \quad \text{eq. 3.20}$$

figure 3.3 Summary of Permanganate Demand of Humic Acid



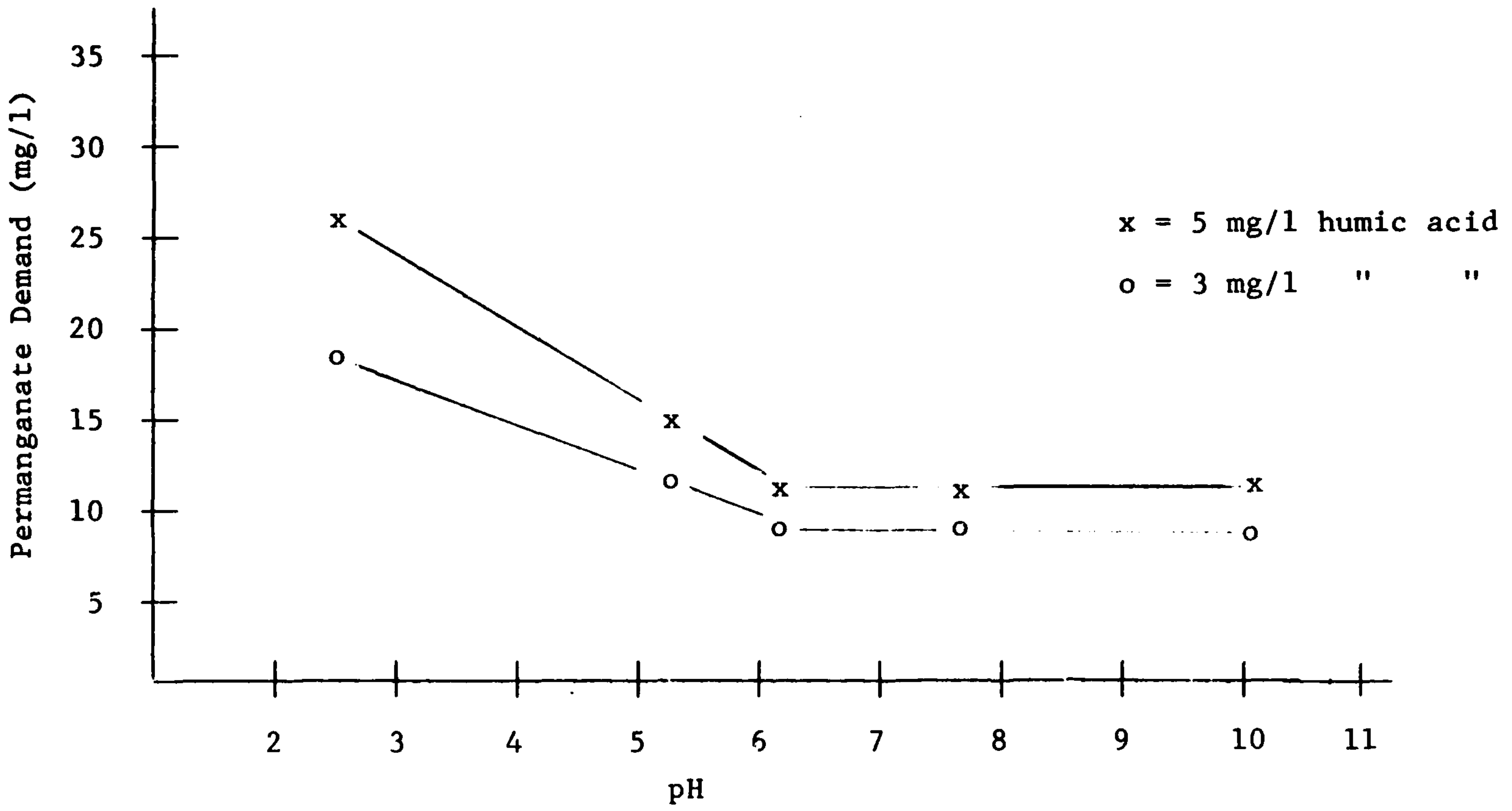
Since the reaction between permanganate and humic acid is pH dependent, the effect of pH on the permanganate demand was also studied. Reactions were carried out in the buffered solutions of Clark and Lubs (87). The pH values chosen were 2.5, using hydrochloric acid and potassium chloride, 5.1,6.1,7.7 with sodium hydroxide and monopotassium phosphate, and 10.1 with a sodium hydroxide and boric acid buffer system. The humic acid solution was prepared as before, however, the buffer replaced the LPW as the diluter. The permanganate was injected, the reaction carried out in a waterbath, and the demand determined.

A summary of results is presented as table 3.5, for the humic concentrations of 3 and 5 mg/l and represented graphically as figure 3.4.

table 3.5 Summary of pH Effects on the Permanganate Demand of Humic Acid

humic acid		permanganate demand(mg/l)				
mg/l	pH	2.5	5.4	6.1	7.7	10.1
3		18.04	11.67	8.62	7.92	7.65
5		25.88	15.25	11.30	11.33	12.33

figure 3.4 Effect of pH on the Permanganate Demand of Humic Acid



The results showed that the permanganate demand stayed constant in the recommended range of pH (5.8-8.0) for the operation of a reverse osmosis unit with cellulose acetate membranes. Therefore the effects of pH on the permanganate demand test performed on feedwaters in this range would not be significant.

c. Combined Effect of Iron and Humic Acid

The combined effect of iron, as ferrous ammonium sulfate and humic acid on the permanganate demand was studied, as these substances frequently occur together in cases of membrane fouling (23). The iron may occur as either ferrous or ferric in aqueous, or the ferric state in saline solution.

The procedure for the experiment was similar to the preceding experiments in this section. Stock solutions of both ferrous ammonium sulfate and humic acids were prepared as described before. Amounts of both were withdrawn and pipetted into 100 ml volumetric flasks, and the permanganate injected. The mixture was transfered to 125 ml flasks, covered, and placed in a waterbath at 100°C for two hours. The flasks were cooled to room temperature, filtered, transfered to a cuvette and analyzed spectrophotometrically.

The results of this experiment are difficult to interpret quantitatively because of the differences in the resultant pH values of the solutions. The permanganate values of the combined effects of iron and humic acid seem to be additive when the pH values stay within the same order of magnitude. For example, the permanganate demand of 1 mg/l Fe at pH 6.9 was 0.97, the permanganate demand of 10 mg/l of humic acid was 17.03 at pH 6.7, and the permanganate demand of the combined solution at pH 6.8 was 18.64.

This relationship seemed to be valid as long as the pH values remained close and excess permanganate remained in solution after the reaction was completed. The complete results are given in Appendix VIII for reactions carried out in aqueous and sodium chloride solutions.

d. Algal Effect on Permanganate Demand

The growth of microrganisms on the membrane has been reported to cause reverse osmosis fouling (88). The major fouling problems encountered in a long-term operation of a RO system for the treatment of wastewater was identified as biological in nature (89). Experiments were carried out to determine the permanganate demand of concentrations of the algae, *Selenastrum Capricornutum.*

Seven day cultures of the algae were obtained from the USEPA Newtown Fish Toxicology Laboratory. The cells concentration was determined there, with a Coulter Counter. The cells were transported, along with additional culture media in glass containers, to the University of Cincinnati where the permanganate demand was determined. The culture medium served both as the dilution liquid used to prepare the spectrophotometric standards and as make-up water for volumetric dilutions.

The preparation of the culture medium, along with other details about the algae, used in the Printz Algal Assay Test, is presented elsewhere. (90). Since the medium may influence the permanganate reaction with the algae, its composition will be included here.

To appoximately 900 mls of LPW, one ml of the following stock solutions is added:

Sodium nitrate	25.5 mg/l

Magnesium chloride	12.164 mg/l
Calcium chloride	4.41 "
Magnesium sulfate	14.7 "
Potassium phosphate	1.044 "
Sodium bicarbonate	15.0 "

Micronutriuent Stock Solution to include:

Boric acid	185.520 μg/l
Manganese chloride	416.610 "
Zinc chloride	3.271 "
Cobalt chloride	1.428 "
Copper chloride	0.012 "
Sodium molybdate	7.260 "
Ferric chloride	160.000 "
Sodium EDTA	300.000 "

The test algae *Selenastrum Capricornutum* Printz is a green alga (chlorophyceae) of the order chlorococcales.

Two range of permanganate were used in the experiment, 31 and 78 mg/l, to react with the algae. A series of concentrations of algae were allowed to react with the permanganate. A summary of the results is presented in table 3.6.

table 3.6 *Selenastrum Capricornutum* Effect on Permanganate Demand

mg/l $KMnO_4$ (mean)	cells(mean)/ mg/l $KMnO_4$
31.38	6.04×10^6
78.64	2.97×10^6

A complete set of results is included as Appendix IX.

The permanganate demand of algal cells was found to be in the order of magnitude of one million cells per one mg/l permanganate.

IV. Predicting Membrane Fouling from Permanganate Demand

A. Correlation of Permeate Flux Decline with Feedwater Properties

1. Literature Review

A scant few articles have been published which correlate permeate flux decline with feedwater properties. A few authors (20,38) have speculated on the factors which determine the magnitude of the permeate flux decline. The factors include the nature and composition of the feedwater, the hydraulic conditions prevailing near the membrane surface, the solute concentration, and other operating parameters.

Two articles have been published (31,37) which compare the slope of the log-log permeation coefficient decline (equation 1.8) with various stages in the treatment of sewage. Table 4.1 summarizes their results.

---

table 4.1 Flux Decline Coefficients for Various Types of Feedwaters

Flux decline	Feedwater type	%COD rejection
0.243	Trickling filter effluent with dual media filtration	NR
0.202	Trickling filter effluent with alum coagulation, clarification, mixed media filtration	NR

0.202	Trickling filter effluent with alum coagulation, clarification, mixed media filtration	NR
0.204	Trickling filter effluent with organic polymer coagulation, direct mixed media filtration	NR
0.146	Trickling filter effluent with ferric chloride coagulation, clarification, mixed media filtration	NR
0.0136	Tap water (TDS = 100)	NR
0.9	Raw wastewater	88.2
0.56	Primary effluent	92.7
0.35	Secondary effluent	93.2
0.14	Carbon treated secondary effluent	83.6

NR = not reported

An equation relating turbidity of the feedwater and the product water flux was developed from this data (31). The equation is:

$$A = 0.709\ A_o\ T_f^{-0.379} \qquad \text{eq. 4.1}$$

where A is the expected product water coefficient and A_o is the intrinsic membrane water permeation coefficient, expressed in gal/ft^2-day. T_f is the feed water turbidity in Jackson Turbidity Units (JTU). The correlation coefficient was reported as 0.869.

Cruver and Nusbaum (37) and this research found that a general correlation of turbidity and membrane fouling may be tenuous or nonexistent. Cruver found that the aromatic hydroxyl concentration may be the most valuable correlating parameter.

2. Correlating Flux Decline with Permanganate Demand

What is presented in this section may be the first study which concludes that the rate at which fouling develops is dependent on the concentration of humic acid in the feedwater, as represented by the permanganate demand. The fouling was primarily due to the formation of an organic gel layer.

When a similar concentration (20 mg/1) of iron, as ferrous ammonium sulfate, was tested to determine the rate of fouling with the same procedure as was used in the humics study, no fouling ocurred. The ferrous ammonium sulfate tank solution did not react with permanganate, resulting in a permanganate demand of zero.

a. Permanganate Demand of Tank Solutions

Samples of the tank concentrations of humic solutions of section 1.3 were withdrawn, and the

the Permanganate Demand Tests of section 3E performed. The results are presented as table 4.2.

table 4.2 Permanganate Demand of Tank Solutions

concentration (mg/l)	demand (mg/l)
0 humic acid	0.0
30 " "	68.8
60 " "	144.0
100 " "	287.0
225 " "	648.2
20 Fe	0.0

Recalling that the best fit of the flux decline versus time relationship was best approximated by linear regression, the slopes of these are given in table 1.5 and contrasted to the corresponding permanganate demand. The results are presented in table 4.3.

table 4.3 Correlation of Slopes and Permanganate Demand

conc. (mg/l)	demand (mg/l)	slope
0 humic acid	0.0	- 0.0154
30 " "	68.8	- 0.0378
60 " "	144.0	- 0.0603
100 " "	287.0	- 0.0522
225 " "	648.0	- 0.1924

The predictive equation which was developed was:

$$a = -.01191 + (-2.600 \times 10^{-4} \mathrm{MnO}_4^-) \quad \text{eq. 4.2}$$

Where(a) is the slope of permeate flux decline (gal/ft^2-day^2), and(MnO_4^-) is the permanganate demand (mg/l).

The correlation coefficient for this regression was .960.

b. Flux Decline Reported in the Literature and Permanganate Demand

Anderson et.al. (94) studied the irreversible fouling caused by plasticization of the reverse osmosis cellulose acetate membrane. Measurements of permeation changes were reported on aqueous solutions of phenol, p-nitrophenol, analine, coumarin, sodium lauryl sulfate, and sodium naphthalene sulfonate. Their flux decline data could be correlated with the Permanganate Demand Test developed herein.

The permanganate demand of analine, phenol, p-nitrophenol, and sodium lauryl sulfate was determined by the method described in section III. The results of the correlation are given in table 4.4. Anderson ran solutions sequentially through the membrane.

This is shown under the columns, Flux, 1, 2, and 3. This represents the flux that was obtained from (1) the passage of 0.1 M NaCl through the membrane, (2) the passage of salt and the concentration listed of the organic additive, and (3) the passage of salt once again through the membrane. The change in flux is the difference between the values of (1) and (3). The column "Conc. mg/l reacted" indicates the concentration of organic in aqueous solution when reacted with 2.5 mls of 0.1 N potassium permanganate. The column "mg/l $KMnO_4^-$ / mg Reactant" is the ratio of permanganate demand and the milligrams of the organic.

The results of table 4.4 showed that the permanganate demand correlated well with the permeate flux decline, in three of the four organic compounds.

Sodium lauryl sulfate caused little flux decline and also caused little if any permanganate demand. Phenol and p-nitrophenol both caused flux decline, phenol causing the larger decline, with the higher permanganate demand.

Analine, the compound that didn't correlate well, had the largest permanganate demand. Instead of causing flux decline, it hydrolyzed the membrane, causing increased permeate flux.

table 4.4 Correlation of Permanganate Demand with Anderson's (94) Data

Organic additive	Conc.	Flux $(g\text{-}cm^{-1}\text{-}g^{-1})$			Change in flux	Conc mg/1 reacted	mg/1 $KMnO_4^-$ / mg reactant
		1*	2*	3*			
analine	0.022	4.15	1.66	4.98	+ 0.83	1.0	15.72
phenol	0.020	2.67	0.92	0.0	- 2.67	1.0	12.42
p-nitro phenol	0.014	7.10	1.66	5.25	- 1.85	2.0	10.59
sodium lauryl sulfate	0.014	2.67	0.64	2.58	- 0.09	97.5	0.14

*Feed solutions run sequentially (Anderson's experimental procedure)

1 0.1 M NaCl

2 0.1 M NaCl and organic additive

3 0.1 M NaCl

V. Conclusions

A. The Permanganate Demand Test accurately predicted the rate by which a spiral wound reverse osmosis membrane fouled.

B. The test responded linearly to varying concentrations of humic acid. The values of the tests were directly related to the rate at which the permeate flux declined. The ferrous ammonium sulfate did not exert a measurable permanganate demand, and did not cause fouling.

C. The Permanganate Demand Test can be performed with simple apparatus to predict the useful membrane life or the need for feedwater pretreatment.

D. The predictive equation developed, allows the operator to calculate when the membrane will fail to process the desired amount of water.

E. The time (x), in days, when the permeate flux (y) (gal/ft^2-day) will fall to an unacceptable level, can be predicted by solving for (a) in the following equation;

$$a = -.01191 + (-2.600 \times 10^{-4} \; MnO_4^-) \qquad \text{eq. 4.1}$$

Where: (MnO_4^-) is the permanganate demand (mg/l) of the feedwater

and substituting (a) and (b) into the linear equation form, $y = ax + b$.

The value (a) is the slope of the relationship of permeate flux decline and time (gal/ft^2-day^2).

The value of (b) is the membrane flux at time equal to zero (gal/ft^2-day). This is the pure water permeation flux; the manufacturer's specified flux determined at the factory.

F. The pH problems associated with the quantitative analysis of organics using permanganate are minimized in this application. The permanganate demand of humic acid remained constant through the recommended pH range for cellulose acetate membranes.

G. Interferences which might influence the results of the permanganate demand determination by other methods are minimized by preparing the standards with RO permeate, and by filtering with glass fiber filters.

H. The ability of permanganate demand to predict feedwater fouling of humic acid solutions is contingent on the rate of fouling being concentration dependent. This finding might seem obvious, however when the effects of concentrate turbulence, membrane phenomena, and other parameters are not held constant, this relationship may remain hidden. It has been alluded to in the literature but not reported before now.

I. A phenomenological model was used to determine the permeate decline slope. The zero order relationship showed slightly better correlation with the experimental data than the more popular first order or other straight line functions.

J. A clearcut difference between the two models was not apparent. Many researchers may be observing this in their research but follow the convention of using geometric regression. An example of this is given (101). Had regression analysis been performed on the data used to construct the following graph, a straight line might have been drawn instead of a curved one.

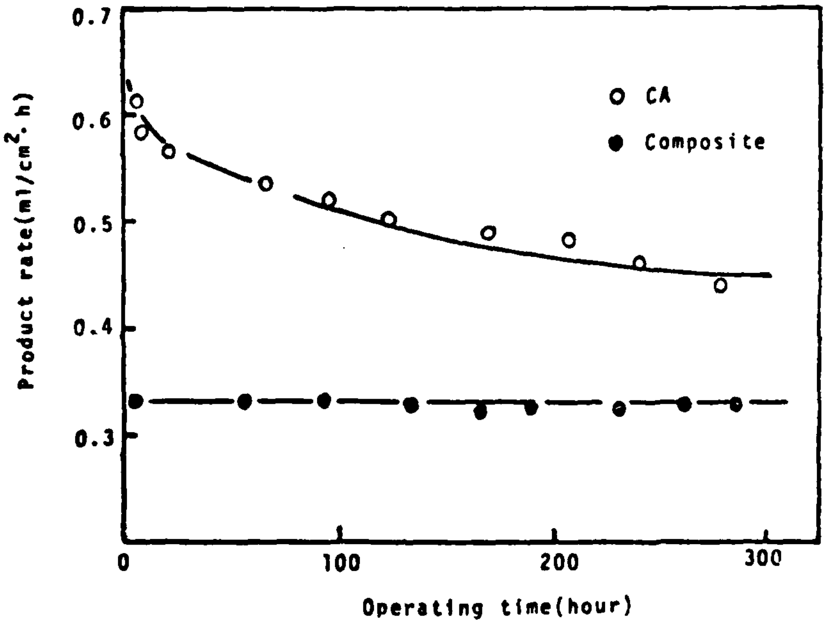


Fig. 2. Product rate with operating time (hours) at 25°C. Feed: 0.5N NaCl.

K. The Silt Density Index does not respond linearly to feedwater concentrations of humic acid. The SDI range of values considered acceptable for successful RO operation is very conservative in its characterization of a feedwater's potential to foul. Humic concentrations as low as 1 mg/l are considered unacceptable, possibly warranting pretreatment.

L. The permanganate demand of other organic compounds and their correlation with permeate flux decline is a subject for future research. Anderson's data (94) provided a good step-off point in that direction.

M. Fouling is a complex phenomena, that could result from the formation of a gel layer, clogging the membrane by precipitates, or changes in membrane structure. This will make attempts to develop a theoretical model extremely difficult.

VI. Research Needs

The study of reverse osmosis fouling is still a wide open area for additional research. The following are research needs:

(1) A theoretical model that can successfully predict fouling is needed.

(2) The applicability of the Permanganate Demand Test should be determined in field studies.

(3) Further investigation into the action of iron on the membrane is needed. Iron was not a foulant in this study.

(4) The degree of fouling by biological action needs to be quantified. A Coulter Counter could provide monitoring of the algal concentrations of the feed, concentrate, and permeate.

Other areas of the literature of reverse osmosis technology which have not been adequately explored are:

(1) The influence of organics on rejection and the ability to predict organic rejection by the membrane.

(2) The mode in which substances are transported across the membrane.

(3) The development of membranes which are less

resistant to hydrolysis by extremes in pH, or destruction by microbial action.

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Appendix I - 0 mg/l Humics

date	pH			conductivity			% salt
April 83	P	F	C	P	F	C	rejection
17	6.6	7.0	6.7	208	2533	3420	93.0
19	7.0	6.9	6.9	140	1750	2200	94.1
21	7.2	6.9	6.9	195	2550	3100	93.1
22	6.7	6.9	6.9	125	1650	2100	93.3
23	7.4	7.1	7.0	120	1700	2050	93.6
25	6.9	7.0	6.9	120	1700	2050	93.6
26	6.7	6.9	6.9	115	1650	1950	93.6
27	6.5	6.7	6.9	110	1700	2050	94.1
28	6.5	7.0	7.0	108	1550	1900	93.7

P = permeate

F = feed

C = concentrate

Appendix I (cont.) - 30 mg/l Humics

date	pH			conductivity			turbidity			% salt
	P	F	C	P	F	C	P	F	C	rejection
16 Feb	5.9	7.0	7.0	200	2050	2400	0.3	3.2	3.6	91.0
18	6.2	7.3	7.6	180	2400	3100	0.2	2.6	2.6	93.4
19	6.3	7.5	7.4	170	2400	3300	0.3	2.4	2.6	94.0
21	6.9	7.0	7.0	150	2500	3000	1.2	2.3	2.3	94.5
22	6.7	7.0	7.1	145	2400	2900	0.3	2.2	2.3	94.5
23	6.1	6.9	7.2	145	2200	3100	0.2	1.8	2.1	94.5
24	6.6	6.9	6.9	120	2200	2700	-	-	-	95.1
25	6.7	6.9	7.0	100	1600	2300	0.3	1.9	2.0	94.9
26	7.2	7.0	7.1	135	2200	2700	0.4	2.7	2.2	94.5
28	6.9	6.9	7.0	125	2200	2700	0.2	1.9	2.2	94.9
1 Mar	6.6	7.0	7.3	130	2150	3000	-	-	-	94.9
2	7.0	7.1	7.1	130	2100	2700	0.3	2.2	2.2	94.6
3	6.7	7.1	7.1	125	2100	2700	0.2	2.0	2.1	94.8
4	6.2	7.0	7.1	120	2100	2600	0.1	1.9	1.9	94.9
5	6.3	7.1	7.1	115	2100	2700	0.2	1.9	1.8	95.2
7	6.3	7.0	7.1	130	2000	2600	0.1	1.2	1.1	94.3
8	6.3	7.1	7.1	125	2100	2700	0.2	1.2	1.0	94.8
9	6.3	6.9	6.9	120	2100	2600	0.2	0.9	0.9	94.5
11	6.4	7.0	7.0	120	2100	2600	0.2	0.8	0.8	94.9
12	6.2	7.0	7.0	100	2150	2750	0.3	1.0	1.1	94.9
14	6.5	7.0	7.0	100	1750	2100	0.3	0.9	0.9	94.8
15	6.6	7.1	7.1	-	-	-	0.3	0.9	0.9	-
17	6.6	7.0	7.0	110	1750	2100	0.2	0.8	0.8	94.3
18	6.6	7.0	7.0	110	1800	2100	0.0	0.7	0.7	94.4
21	6.4	7.0	7.1	110	1800	2100	0.3	0.8	0.7	94.4
23	6.7	7.0	7.1	95	1850	2300	-	-	-	95.4

Appendix I - 30 mg/1 Humics (cont.)

date	pH			conductivity			turbidity			% salt rejection
	P	F	C	P	F	C	P	F	C	
24 Mar	6.7	7.1	7.1	125	2100	2500	0.1	1.1	1.1	94.6
25	6.8	7.0	7.0	125	1890	2520	0.3	1.0	1.1	94.8
26	7.0	7.0	7.2	95	1850	2350	0.2	0.7	0.7	95.4
29	7.0	7.1	7.1	110	1700	2400	0.2	0.7	0.7	94.6
30	7.0	7.0	7.0	115	2100	2600	0.1	0.7	0.7	95.1
31	6.6	7.0	7.0	120	2160	2700	0.2	0.8	0.7	95.1
1 Apr	7.0	6.9	6.9	135	2160	2700	0.1	0.9	0.9	94.5
2	7.0	6.9	6.9	120	2100	2450	0.3	0.8	0.8	94.8
4	6.7	6.9	6.9	110	2100	2550	0.2	0.7	0.7	95.3
5	7.2	7.2	7.2	120	2100	2800	0.2	0.7	0.8	95.1
6	7.2	7.0	7.0	120	2100	2800	0.3	0.7	0.8	95.1
7	7.3	7.0	7.0	135	2100	2700	0.3	0.7	0.7	94.3

Appendix I (cont.) - 60 mg/1 Humics

date	pH			conductivity			turbidity			% salt
	P	F	C	P	F	C	P	F	C	rejection
13 Jan	6.0	6.9	6.9	510	2200	2600	0.1	1.1	1.3	78.8
14	6.1	6.9	6.9	640	2100	2600	0.1	1.1	1.3	71.8
15	6.5	7.0	7.0	510	2100	2700	0.7	1.2	0.9	78.8
16	6.5	7.0	7.0	510	2100	2700	0.7	1.2	0.9	78.8
17	6.2	7.0	7.0	800	2200	2550	0.2	0.7	0.7	66.3
18	6.4	7.0	7.0	880	2100	2400	0.2	0.7	0.7	60.9
19	6.5	6.9	6.9	810	2100	2500	0.2	0.8	0.8	64.8
20	6.3	6.9	6.9	860	2100	2400	0.4	0.6	0.7	61.8
21	6.3	7.0	7.0	800	2100	2400	0.3	0.6	0.5	64.4
22	6.4	7.1	7.1	780	2100	2600	0.4	0.5	0.5	66.1
24	6.3	7.1	7.1	760	2100	2600	0.3	0.5	0.5	67.6
25	6.6	7.0	7.1	800	2100	2500	0.3	0.6	0.5	65.2
26	6.6	7.0	7.2	815	2100	2300	0.1	0.7	0.5	62.9
27	6.3	7.0	7.0	860	2100	2300	0.2	0.6	0.5	60.9
29	6.4	7.0	7.0	860	2100	2400	0.3	0.5	0.4	61.8
31	6.7	7.0	7.0	900	1800	2200	0.4	0.4	0.4	55.0
1 Feb	7.0	7.0	7.0	1000	2100	2500	0.3	0.5	0.5	56.5
2	6.4	7.0	7.0	1040	2100	2300	0.3	0.4	0.5	52.7
5	7.0	7.1	7.0	680	2100	2100	0.4	1.0	1.1	67.6
8	7.0	7.2	6.9	-	-	-	0.4	1.6	1.8	-
9	7.0	6.9	7.1	1650	2100	2100	0.4	1.0	1.1	26.6
10	6.9	7.1	7.1	1800	2100	2300	0.5	1.6	0.9	18.2
11	-	-	-	1850	2200	2700	-	-	-	17.8
12	-	-	-	1500	2100	2200	0.3	3.2	2.9	30.2

Appendix I (cont.) - 100 mg/l Humics

Date	pH			conductivity			turbidity			% salt
	P	F	C	P	F	C	P	F	C	rejection
Nov 3	6.9	6.9	7.2	260	2100	2800	5.1	4.0	0.1	89.3
5	6.5	7.4	7.5	210	2100	2700	0.2	1.3	1.1	91.2
7	6.8	7.3	7.3	200	2150	3000	0.3	1.1	1.1	92.2
8	6.6	6.6	6.6	180	2100	2900	0.3	0.8	0.5	92.8
9	6.6	7.0	6.9	260	2250	3000	0.4	0.7	0.7	90.1
10	6.4	7.0	6.8	180	2100	2900	0.2	0.5	0.6	92.7
11	7.0	7.0	7.1	215	2200	2800	0.2	0.6	0.6	91.4
12	7.0	7.0	7.0	225	2100	2400	0.3	0.5	0.3	90.0
14	6.8	7.0	7.1	215	2200	2800	0.2	0.6	0.4	91.5
15	6.6	7.0	7.1	200	2050	2450	0.3	0.6	0.3	91.1
16	6.6	6.9	7.1	200	2150	2600	0.2	0.5	0.3	91.6
17	6.5	7.0	7.0	230	2300	2700	0.1	0.3	0.3	90.8
18	6.4	7.0	7.1	230	2300	2700	0.3	0.5	0.4	90.8
19	6.7	7.0	7.1	225	2250	2900	0.3	0.3	0.3	91.3
20	7.1	7.0	7.2	210	2200	2700	0.3	0.4	0.3	91.4
22	7.4	7.0	7.2	200	2100	2600	0.1	0.3	0.3	91.5
23	7.4	7.0	7.4	210	2200	3100	0.3	0.5	0.4	92.1
24	6.5	7.1	6.8	190	2150	2600	0.2	0.4	0.4	92.0
25	6.9	7.0	7.1	205	2100	2600	0.1	0.4	0.3	91.3
26	6.8	7.0	7.3	220	2200	2800	0.2	0.4	0.3	91.2
27	7.0	7.0	7.0	250	2200	2400	0.1	0.3	0.3	91.5
29	7.0	7.0	7.0	250	2200	2400	0.1	0.3	0.3	91.5
30	6.6	6.9	6.9	220	2300	2750	0.3	0.3	0.3	91.3
Dec 1	7.4	7.0	7.0	220	2100	2500	0.3	0.3	0.3	90.4
2	7.6	7.0	7.3	210	2300	2800	0.3	0.4	0.4	91.8

Appendix I. - 100 mg/1 Humics (cont.)

Date	pH			conductivity			turbidity			% salt rejection
	P	F	C	P	F	C	P	F	C	
Dec 3	6.8	6.9	7.0	210	2000	2800	0.2	0.4	0.4	91.3
4	7.2	7.0	7.0	245	2200	2700	0.2	0.3	0.3	90.0
6	7.4	7.1	7.2	210	2000	2700	0.2	0.3	0.3	91.1
7	7.6	7.1	7.3	240	1900	2400	0.2	0.3	0.3	88.9
8	-	7.2	7.2	240	2100	2400	0.2	0.3	0.3	89.0
9	7.5	6.8	6.8	240	2100	2600	0.2	0.3	0.3	88.3
10	7.5	6.8	6.9	320	2100	2700	0.2	0.3	0.3	86.7
11	7.0	6.8	6.9	300	2000	2600	0.2	0.3	0.2	86.9
13	6.8	7.0	7.2	275	2100	2500	0.2	0.2	0.2	88.0
14	6.9	7.2	7.3	330	2100	2700	0.3	0.3	0.3	86.3
15	7.2	7.0	7.3	340	2100	2700	0.2	0.3	0.3	85.8
16	7.3	7.1	7.2	350	2100	2700	0.1	0.2	0.2	85.4
17	7.3	7.0	7.2	340	2100	2600	0.3	0.4	0.3	85.5
18	7.3	7.0	7.1	310	2100	2400	0.2	0.3	0.3	86.2
20	7.2	7.0	7.2	340	2000	2200	0.3	0.3	0.3	83.8
21	7.1	7.4	7.4	350	2000	2500	0.4	0.5	0.4	84.4
22	6.8	7.2	7.3	360	2000	2400	0.4	0.5	0.4	83.6
23	7.4	7.0	7.0	390	2050	2600	0.2	0.3	0.3	83.2
24	7.4	7.0	7.0	380	2200	2700	0.2	0.2	0.2	84.5
25	7.1	6.8	6.9	365	2100	2600	0.3	0.3	0.3	84.4
27	6.9	6.9	6.9	380	2100	2400	0.1	0.3	0.2	83.1
28	7.2	6.9	6.9	400	2100	2600	0.3	0.3	0.3	83.0
29	6.0	6.4	6.5	380	2100	2600	0.4	0.4	0.3	83.8
30	6.7	6.2	6.4	380	2100	2500	0.1	0.2	0.2	83.5

Appendix I (cont.) - 225 mg/l Humics

date	pH			conductivity			turbidity			% salt
Oct 82	P	F	C	P	F	C	P	F	C	rejection
25	7.2	7.5	7.5	270	2600	3250	0.2	1.9	1.3	90.8
26	7.2	6.9	7.0	290	2400	3200	0.4	0.8	0.8	89.6
27	7.4	6.9	7.1	310	2500	3300	0.3	0.5	0.3	89.3
28	7.5	6.9	7.1	265	2300	3000	0.3	0.4	0.3	90.0
29	7.0	7.1	7.1	260	2250	2900	0.4	0.3	0.3	89.9
31	6.8	7.0	7.0	-	-	-	-	-	-	-

Appendix II

Chromatographic Measurement of Humic Acid Rejection

18 Jan 83	% permeate flux reduction	% salt rejection	$CHCl_3$ conc. ppb	$CHCl_3$ conc. mg/l	% humic rejection
unchlor. permeate	1.0	61.0	8.38		
chlor. permeate	1.0	61.0	24.89		99.6
unchlor. feed			5.08		
chlor. feed				4.69	
29 Jan 83					
unchlor. permeate	10.0	60.5	---		
chlor. permeate	10.0	60.5	26.00		99.5
unchlor. feed			7.37		
chlor. feed				5.22	
9 Feb 83					
unchlor. permeate	19.0	27.0	---		
chlor. permeate	19.0	27.0	88.80		97.7
unchlor. feed			---		
chlor. feed				3.89	

feed tank concentration = 30 mg/l

Appendix II (cont.)

Chromatographic Measurement of Humic Acid Rejection

	% permeate	% salt	$CHCl_3$ conc.		% humic
18 Feb 83	flux reduction	rejection	ppb	mg/1	rejection
unchlor. permeate	0.0	93	14.09		
chlor. permeate	0.0	93	72.38		89.4
unchlor. feed			16.76		
chlor. feed				.683	
24 Feb 83					
unchlor. permeate	21.5	95	1.64		
chlor. permeate	21.5	95	4.51		99.5
unchlor. feed			7.63		
chlor. feed				.641	
3 Mar 83					
unchlor. permeate	25.4	95	.61		
chlor. permeate	25.4	95	25.52		98.0
unchlor. feed			0.0		
chlor. feed				1.47	

feed tank concentration = 30 mg/1 humic acid

Appendix II (cont.)

Chromatographic Measurement of Humic Acid Rejection

17 Mar 83	% permeate flux reduction	% salt rejection	$CHCl_3$ conc.		% humic rejection
			ppb	mg/l	
unchlor. permeate	25.3	94.3	0.0		
chlor. permeate	25.3	94.3	26.4		99.1
unchlor. feed			0.0	3.18	
31 Mar 83					
unchlor. permeate	28.5	95.1	0.0		
chlor. permeate	28.5	95.1	122.0		97.1
unchlor. feed			0.0		
chloro. feed				4.84	
7 April 83					
unchlor. permeate	30.3	94.3	0.0		
chlor. permeate	30.3	94.3	23.3		93.8
unchlor. feed			0.0		
chloro. feed				.376	

Appendix III

Flux Decline Data - 0 mg/l Humics

date	permeate flux liter/m^2-hr	gal/ft^2-day*
13 April 83	10.84	6.21
14	11.72	6.70
15	11.72	6.70
17	11.13	6.19
18	11.13	6.19
19	11.28	6.10
20	11.38	6.17
21	11.38	6.32
22	11.01	6.30
23	11.28	6.27
25	11.03	6.63
26	10.96	6.26
27	10.96	6.27
28	10.89	6.23

Appendix III (cont.)

Flux Decline Data - 30 mg/l Humic Acid

Date	Permeate Flux liter/m^2-hr	Permeate Flux gal/ft^2-day	Date	Permeate Flux liter/m^2-hr	Permeate Flux gal/ft^2-day
16 Feb	8.94	5.27	11 Mar	10.66	6.28
16	14.48	8.53	12	10.73	6.32
18	14.48	8.53	14	10.62	6.26
19	14.00	8.25	15	10.66	6.28
21	12.74	7.51	17	10.84	6.34
22	12.74	7.51	18	11.08	6.53
23	13.07	7.70	19	10.73	6.32
24	11.38	6.71	21	10.96	6.46
25	11.33	6.68	23	11.32	6.67
26	10.96	6.46	24	10.62	6.26
28	11.03	8.50	25	10.57	6.23
1 Mar	11.45	6.75	26	10.62	6.26
2	11.20	6.60	28	11.08	6.53
3	10.80	6.36	29	10.62	6.26
4	10.66	6.28	30	10.36	6.10
5	10.66	6.28	1 Apr	10.09	5.95
7	10.73	6.32	2	10.09	6.10
8	10.62	6.26	4	9.99	5.89
9	10.84	6.39	5	11.09	6.53

Appendix III (cont.)

Flux Decline Data - 60 mg/l Humics

date	permeate flux		date	permeate flux	
	liter/m^2-hr	gal/ft^2-day		liter/m^2-hr	gal/ft^2-day
12 Jan	9.27	5.46	28	8.64	5.09
13	10.82	6.10	29	8.42	4.97
14	10.35	6.10	31	8.49	5.00
15	10.35	6.10	1 Feb	8.22	4.84
17	9.47	5.58	2	8.47	4.99
18	9.20	5.42	4	8.22	4.84
19	8.91	5.25	5	8.71	5.14
20	8.97	5.29	8	7.55	4.45
21	9.13	5.38	9	7.55	4.45
22	9.06	5.35	10	7.28	4.29
24	9.06	5.35	11	6.93	4.08
25	9.27	5.46	12	7.18	4.23
26	9.27	5.46			

Appendix III (cont.)

Flux Decline Data - 100 mg/l Humic Acid

Date	Permeate Flux		Date	Permeate Flux	
	liter/m^2-hr	gal/ft^2-day		liter/m^2-hr	gal/ft^2-day
3 Nov	10.62	6.26	2 Dec	9.62	5.67
4	12.44	7.34	3	9.44	5.57
5	11.72	6.91	4	9.44	5.57
7	11.33	6.68	5	9.44	5.57
8	11.58	6.68	6	9.44	5.57
9	11.46	6.76	7	9.27	5.47
10	10.96	6.47	8	9.27	5.47
11	10.85	6.40	9	9.14	5.39
12	11.08	6.54	10	8.64	5.10
14	10.73	6.33	11	8.53	5.03
15	10.40	6.14	13	8.36	4.93
16	10.28	6.06	14	8.16	4.81
17	10.24	6.04	15	8.33	4.91
18	10.24	6.04	16	8.16	4.81
19	10.36	6.11	17	8.16	4.81
20	10.20	6.02	18	7.58	4.47
22	10.12	5.97	20	7.82	4.61
23	10.32	6.09	21	7.34	4.33
24	10.00	5.90	22	7.30	4.22
25	10.00	5.90	23	7.27	4.29
26	10.00	5.90	24	7.24	4.27
27	9.96	5.87	25	7.13	4.21
29	9.48	5.59	27	7.08	4.18
30	9.44	5.57	28	6.88	4.06
1 Dec	9.48	5.59	29	6.62	3.90
			30	6.58	3.88

Appendix III (cont.)

Flux Decline Data - 225 mg/l Humics

date	permeate flux	
	liters/m^2-hr	gal/ft^2-day
22 Oct 82	11.59	6.84
24	11.08	6.54
25	10.96	6.47
26	10.62	6.27
27	10.51	6.20
28	9.10	5.37
29	9.99	5.90
31	9.27	5.47
1 Nov	0.0	0.0

Appendix IV

Runs # 1-5

Statistics - Permeation Data - Paired t-Test

Stage of treatment	No. of cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	t value	2-tail p
sand filtered	5	.0768	.0748	.0478	.0192	2.489	$.05 > p > .025$
alum treated + sand filtered	5	.1247	.0812				
sand filtered	5	.0768	.0748	.1676	.1052	1.594	$.1 > p > .05$
alum+NaOH treated+ sand filtered	5	.2444	.2256				
sand filtered	5	.0768	.0748	.6646	.2678	2.481	$.05 > p > .025$
ozonated+ sand filtered	5	.6936	.0748				
sand filtered	5	.0768	.0748	.2968	.1224	2.425	$.05 > p > .025$
alum+NaOH+ozone+ sand filtered	5	.3737	.3466				

Appendix IV (cont.)

Runs #1-5

Statistics - Before and After Membrane Filtration

Parameters	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Turbidity									
(before)	25	1.71	0.895	0.97	0.90	0.301	5.40	24	0.00
(after)		0.73	0.562						
Silica									
(before)	25	2.18	1.290	0.19	0.24	0.983	3.86	24	0.001
(after)		2.00	1.236						
TC									
(before)	25	34.51	15.999	4.12	6.462	0.934	3.19	24	0.004
(after)		30.39	11.949						
TIC									
(before)	25	22.82	14.982	4.21	7.390	0.928	2.85	24	0.009
(after)		18.61	9.065						
TOC									
(before)	25	11.74	4.773	-0.0480	5.418	0.495	-0.04	24	0.965
(after)		11.78	5.848						
Fe									
(before)	25	0.06	0.052	0.00	0.05	0.624	-0.22	24	0.826
(after)		0.06	0.068						

Appendix IV (cont.)

Runs #1-5

Statistics - Before and After Membrane Filtration (continued)

Parameters	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Mg									
(before)	25	8.35	7.283	0.555	6.336	0.581	0.44	24	0.665
(after)		7.79	6.474						
Ca									
(before)	25	20.70	17.021	-2.308	12.204	0.753	-0.95	24	0.354
(after)		23.00	17.648						

Appendix IV (cont.)

Runs #1-5

Statistics - Before and After Membrane Filtration - Total Carbon

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Value	DF	P
Sand filtered								
(before)	5	39.6	22.16	6.45	21.8	2.18	4	.05-.10
(after)	5	33.15	21.53					
Alum treated								
(before)	5	43.92	22.92	11.28	17.84	3.16	4	.02-.05
(after)	5	32.64	12.77					
NaOH+alum treated								
(before)	5	27.10	9.86	1.90	9.16	.99	4	> .20
(after)	5	25.20	8.46					
Ozone treated								
(before)	5	31.36	6.93	1.32	7.19	.78	4	> .20
(after)	5	30.04	7.45					
Alum+NaOH+ozone								
(before)	5	25.5	6.63	1.28	6.66	.78	4	> .20
(after)	5	24.22	6.69					

Appendix IV (cont.)

Runs #1-5

Statistics - Before and After Membrane Filtration - Total Inorganic Carbon

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	t Value	DF	P
Sand filtered (before)	5	31.7	20.7	5.6	16.00	2.21	4	.05-.10
(after)	5	26.1	11.31					
Alum treated (before)	5	31.72	20.8	9.0	15.73	3.59	4	.02-.05
(after)	5	22.72	10.67					
Alum+NaOH treated (before)	5	18.66	8.40	4.86	7.79	2.75	4	.05-.10
(after)	5	13.8	7.18					
Ozone treated (before)	5	19.2	5.27	- .4	5.14	- .279	4	> .20
(after)	5	19.6	5.02					
Alum+NaOH+ozone (before)	5	12.24	4.33	.3	3.28	.262	4	> .20
(after)	5	11.94	2.24					

Appendix IV (cont.)

Runs #1-5

Statistics - Turbidity - Paired t-Test

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Sand filtered	5	2.2800	1.108	0.5740	0.601	0.877	2.14	4	0.099
Alum treated+ sand filtered	5	1.7060	0.694						
Sand filtered	5	2.2800	1.108	0.5080	1.554	-0.073	0.73	4	0.508
Alum+NaOH treated+ sand filtered	5	1.7720	1.027						
Sand filtered	5	2.2800	1.108	0.9200	0.798	0.842	2.58	4	0.061
Ozonated+ sand filtered	5	1.3600	0.404						
Sand filtered	5	2.2800	1.108	0.8220	1.585	-0.097	1.15	4	0.313
Alum+NaOH+ozone+ sand filtered	5	1.4580	1.046						

Appendix IV (cont.)

Runs #1-5

Statistics - Silica - Paired t-Test

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Sand filtered	5	2.5440	1.539	0.1220	0.299	0.982	0.91	4	0.413
Alum treated+ sand filtered	5	2.4220	1.436						
Sand filtered	5	2.5440	1.539	0.5840	0.378	0.997	3.46	4	0.026
Alum+NaOH treated+ sand filtered	5	1.9600	1.175						
Sand filtered	5	2.5440	1.539	0.3480	0.308	0.980	2.52	4	0.065
Ozonated+ sand filtered	5	2.1960	1.462						
Sand filtered	5	2.5440	1.539	0.8480	0.515	0.954	3.67	4	0.021
Alum+NaOH+ozone+ sand filtered	5	1.6960	1.241						

AppendixIV (cont.)

Runs #1-5

Statistics - Total Carbon - Paired t-Test

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Sand filtered	5	42.3400	21.610	-2.7200	4.319	0.982	-1.41	4	0.232
Alum treated+ sand filtered	5	45.0600	22.469						
Sand filtered	5	42.3400	21.610	15.2400	14.640	0.821	2.33	4	0.080
Alum+NaOH treated+ sand filtered	5	27.1000	9.867						
Sand filtered	5	42.3400	21.610	10.9800	15.720	0.895	1.56	4	0.193
Ozonated+ sand filtered	5	31.3600	6.928						
Sand filtered	5	42.3400	21.610	16.8400	19.667	0.433	1.91	4	0.128
Alum+NaOH+oxone+ sand filtered	5	25.5000	6.634						

Appendix IV (cont.)

Runs #1-5

Statistics - Total Inorganic Carbon - Paired t-Test

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Sand filtered	5	31.7000	20.718	-0.0200	2.202	0.994	-0.02	4	0.985
Alum treated+ sand filtered	5	31.7200	20.817						
Sand filtered	5	31.7000	20.718	13.0400	13.598	0.904	2.14	4	0.099
Alum+NaOH treated+ sand filtered	5	18.6600	8.404						
Sand filtered	5	31.7000	20.718	12.5000	17.486	0.692	1.60	4	0.185
Ozonated+ sand filtered	5	19.2000	5.274						
Sand filtered	5	31.7000	20.718	19.4600	23.326	-0.535	1.87	4	0.136
Alum+NaOH+ozone+ sand filtered	5	12.400	4.332						

Appendix IV (cont.)

Runs #1-5

Statistics - Total Organic Carbon - Paired t-Test

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Sand filtered	5	10.6200	3.994	-2.7200	6.072	0.267	-1.00	4	0.373
Alum+treated+ sand filtered	5	13.3400	5.760						
Sand filtered	5	10.6200	3.994	2.0800	2.373	0.807	1.96	4	0.122
Alum+NaOH treated+ sand filtered	5	8.5400	2.985						
Sand filtered	5	10.6200	3.994	-1.5400	3.948	0.374	-0.87	4	0.432
Ozonated+ sand filtered	5	12.1600	2.858						
Sand filtered	5	10.6200	3.994	-3.0000	6.410	0.400	-1.05	4	0.354
Alum+NaOH+ozone+ sand filtered	5	13.6200	6.861						

Appendix IV (cont.)

Runs #1-5

Statistics - Calcium - Paired t-Test

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Sand filtered	5	33.4400	15.297	6.8600	29.032	-0.811	0.53	4	0.625
Alum treated+ sand filtered	5	26.5800	15.215						
Sand filtered	5	33.4400	15.297	26.6000	16.403	0.070	3.63	4	0.022
Alum+NaOH treated+ sand filtered	5	6.8400	7.088						
Sand filtered	5	33.4400	15.297	1.1400	9.511	0.801	0.27	4	0.802
Ozonated+ sand filtered	5	32.3000	14.836						
Sand filtered	5	33.4400	15.297	29.1200	16.911	-0.360	3.85	4	0.018
Alum+NaOH+ozone+ sand filtered	5	4.3200	3.566						

AppendixIV (cont.)

Runs #1-5

Statistics - Iron - Paired t-Test

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Sand filtered	5	0.0780	0.058	0.0300	0.046	0.615	1.46	4	0.217
Alum treated+ sand filtered	5	0.0480	0.041						
Sand filtered	5	0.0780	0.058	0.0320	0.060	0.309	1.20	4	0.297
Alum+NaOH treated sand filtered	5	0.0460	0.042						
Sand filtered	5	0.0780	0.058	-0.0060	0.022	0.964	-0.61	4	0.573
Ozonated+ sand filtered	5	0.0840	0.071						
Sand filtered	5	0.0780	0.058	0.0200	0.075	0.162	0.59	4	0.584
Alum+NaOH+ozone+ sand filtered	5	0.0580	0.058						

Appendix IV (cont.)

Runs #1-5

Statistics - Magnesium - Paired t-Test

Stage of Treatment	No. of Cases	Mean	Std. Dev.	Diff. Mean	Std. Dev.	Corr. Coef.	t Value	DF	2-Tailed P
Sand filtered	5	13.3000	5.052	1.3400	10.930	0.084	0.27	4	0.798
				1.3400	10.930	0.084	0.27	4	0.798
Alum treated+ sand filtered	5	11.9500	10.124						
Sand filtered	5	13.3000	5.052	10.4800	5.216	0.281	4.49	4	0.011
Alum+NaOH treated+ sand filtered	5	2.8200	3.322						
Sand filtered	5	13.3000	5.052	1.9200	4.458	0.634	0.96	4	0.390
Ozonated+ sand filtered	5	11.3800	5.339						
Sand filtered	5	13.3000	5.052	11.0200	5.343	0.176	4.61	4	0.010
Alum+NaOH+ozone+ sand filtered	5	2.2800	2.815						

Appendix V

Humic Acid's Effect on Permanganate Demand in Aqueous Solution

Humic conc.(mg/1)	pH	mg/1KMnO$_4$	MnO$_4^-$ demand (mg/1)
1.0	4.6	78.85	14.51
"	4.9	80.12	1.62
"	4.9	50.57	7.51
"	6.1	81.02	1.25
"	6.1	79.24	1.44
"	6.6	76.58	1.20
"	6.8	51.39	0.80
"	6.8	76.48	6.92
"	7.1	50.41	2.27
"	7.1	83.72	7.52
"	7.2	80.50	4.36
"	7.2	78.35	9.41
"	7.2	80.64	6.93
"	7.6	49.73	15.28
"	7.6	79.57	6.76

Appendix V (cont.)

Humic Acid's Effect on Permanganate Demand in Aqueous Solution

Humic conc. mg/l	pH	$KMnO_4$ mg/l	(MnO_4^-) demand mg/l
2.0	6.2	50.57	7.51
"	6.3	79.24	4.77
"	6.7	76.91	4.90
"	7.0	51.39	4.49
"	7.1	76.25	2.72
"	7.1	85.65	1.24
"	7.2	80.64	22.62
"	7.3	50.41	6.26
"	7.4	71.46	6.89
3.0	5.0	78.18	15.78
"	5.1	80.12	4.38
"	6.2	77.91	5.26
"	6.6	76.91	6.10
"	6.7	79.24	6.99

Appendix V. (cont.)

Humic Acid's Effect on Permanganate Demand in Aqueous Solution

Humic conc. mg/l	pH	$KMnO_4$ mg/l	MnO_4^- Demand mg/l
5	6.0	75.85	0.87
"	6.2	79.24	11.44
"	6.4	50.57	11.05
"	6.7	76.56	8.21
"	6.7	84.83	14.02
"	6.8	76.58	12.42
"	6.8	76.48	13.16
"	6.9	49.73	11.99
"	7.1	49.73	9.54
"	7.1	83.72	12.17
"	7.1	84.64	10.59
"	7.2	76.37	14.48
"	7.2	84.64	10.67
"	7.4	78.35	11.94
"	7.4	76.25	6.15
5	7.4	50.41	14.13
"	7.4	51.39	10.09
"	7.4	85.65	12.72
"	7.6	80.64	30.53

Appendix V (cont.)

Humic Acid's Effect on Permanganate Demand in Aqueous Solution

Humic conc. mg/1	pH	$KMnO_4$ mg/1	MnO_4^- Demand mg/1	Humic conc. mg/1	pH	$KMnO_4$ mg/1	MnO_4^- Demand mg/1
10.0	4.7	50.57	19.92	10	7.5	51.39	12.44
"	5.3	80.12	5.68	"	7.6	76.25	8.74
"	5.5	79.80	20.57	"	7.6	84.83	20.18
"	5.9	75.85	8.05	"	7.7	50.41	31.90
"	6.1	78.18	24.61	"	7.8	49.13	18.14
"	6.1	79.24	19.21	"	7.8	79.57	13.82
"	6.7	76.56	23.25	"	7.8	76.48	18.88
"	6.7	89.61	18.39				
"	6.8	76.91	13.27				
"	6.8	77.91	8.03				
"	7.0	76.58	22.17				
"	7.0	84.83	21.73				
"	7.1	76.37	30.30				
"	7.1	83.72	18.39				
"	7.2	78.35	20.76				
"	7.2	49.73	17.84				
"	7.3	85.65	21.90				

Appendix V (cont.)

Humic Acid's Effect on Permanganate Demand in Aqueous Solution

Humic conc. mg/l	pH	$KMnO_4$ mg/l	MnO_4^- Demand mg/l
20	6.1	79.24	28.10
"	6.3	78.35	12.68
"	6.6	80.12	10.22
"	6.7	76.56	34.68
"	6.7	78.28	40.39
"	6.8	77.91	13.55
"	7.0	76.58	35.57
"	7.0	84.83	43.29
"	7.0	84.64	36.14
"	7.0	84.83	43.29
"	7.1	83.72	33.88
"	7.1	84.64	40.68
"	7.2	80.05	35.98
"	7.3	84.53	36.50
"	7.8	76.48	40.63
25	7.2	84.64	47.38

Appendix VI

Humic Acid's Effect on Permanganate Demand in Buffered Solution

Humic conc. mg/l	pH	buffer	mg/l $KMnO_4$	MnO_4^- Demand mg/l
1	2.5	HCl+KCl	79.88	8.89
2	"	"	"	12.81
3	"	"	"	18.04
5	"	"	"	25.88
10	"	"	"	54.63
20	"	"	"	—
30	"	"	"	—

Appendix VI (cont.)

Humic Acid's Effect on Permanganate Demand in Buffered Solution

Humic conc. mg/1	pH	buffer	mg/1 $KMnO_4$	MnO_4^- Demand mg/1
1	5.4	$NaOH+KH_2PO_3$	77.08	——
2	"	"	"	2.13
3	"	"	"	11.67
5	"	"	"	15.25
10	5.5	"	"	35.51
20	"	"	"	51.01
30	"	"	"	71.28
40	5.6	"	"	——

Appendix VI (cont.)

Humic Acid's Effect on Permanganate Demand in Buffered Solution

Humic conc. mg/l	pH	buffer	mg/l $KMnO_4$	MnO_4^- Demand mg/l
1	6.1	$NaOH+KH_2PO_3$	76.90	3.25
2	"	"	"	5.94
3	"	"	"	8.62
5	"	"	"	11.30
10	"	"	"	38.14
20	"	"	"	54.21
30	"	"	"	67.66
40	"	"	"	—

Appendix VI (cont.)

Humic Acid's Effect on Permanganate Demand in Buffered Solution

Humic conc. mg/l	pH	buffer	mg/l $KMnO_4$	MnO_4^- Demand mg/l
1	7.7	$NaOH+KH_3PO_4$	75.22	2.24
2	"	"	"	3.37
3	"	"	"	7.92
5	"	"	"	11.33
10	"	"	"	29.50
20	"	"	"	44.26
30	"	"	"	59.03
40	"	"	"	65.85

Appendix VI (cont.)

Humic Acid's Effect on Permanganate Demand in Buffered Solution

Humic conc. mg/l	pH	buffer	mg/l $KMnO_4$	MnO_4^- Demand mg/l
1	10.1	KH_2PO_4+NaOH	79.58	——
2	"	"	"	5.31
3	"	"	"	7.65
5	"	"	"	12.33
10	"	"	"	29.91
20	"	"	"	42.79
30	"	"	"	61.54

Appendix VII

Permanganate Demand of Ferrous Ammonium Sulfate Solution in the Presence of Sodium Chloride

trial #	pH	NaCl(mg/l)	Fe(mg/l)	$KMnO_4$ Demand
1	4.3	1000	1	6.26
2	4.2	"	"	4.09
1	4.0	"	5	10.61
2	3.9	"	"	10.95
1	3.7	"	10	13.87
2	3.7	"	"	15.10
1	3.5	"	20	19.30
2	"	"	"	26.17
1	4.3	5000	1	4.69
2	"	"	"	0.38
1	3.9	"	5	9.86
2	"	"	5	2.31
1	3.7	"	10	10.90
2	"	"	"	6.51
1	3.5	"	20	21.24
2	"	"	"	22.49

Appendix VII (cont.)

Permanganate Demand of Ferrous Ammonium Sulfate Solution in the Presence of Sodium Chloride

trial#	pH	NaCl(mg/l)	Fe(mg/l)	$KMnO_4$ Demand
1	3.1	10,000	1	10.17
2	3.9	"	"	12.38
1	3.2	"	5	14.42
2	3.9	"	"	15.74
1	3.1	"	10	17.82
2	3.7	"	"	20.77
1	3.0	"	20	36.51
2	3.5	"	"	36.70

AD-A135 437 A REPLACEMENT FOR THE SILT DENSITY INDEX: PERMANGANATE 3/3
DEMAND TO PREDICT..(U) AIR FORCE INST OF TECH
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UNCLASSIFIED AFIT/CI/NR-83-72D F/G 7/4 NL

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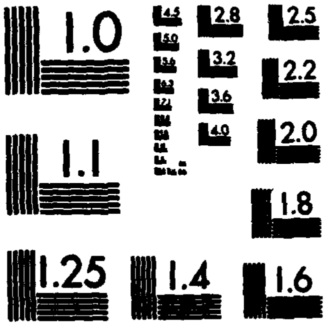

MICROCOPY RESOLUTION TEST CHART
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Appendix VII (cont.)

Permanganate Demand of Ferrous Ammonium Sulfate Solution in Aqueous Solution

Iron(mg/1)	pH	$KMnO_4$(mg/1)	$KMnO_4$ Demand(mg/1)
1	4.3	76.64	——
"	4.4	76.59	8.82
"	4.4	75.85	3.61
"	4.6	80.12	6.16
"	4.7	81.35	0.56
"	5.2	50.01	4.22
"	5.8	80.82	16.64
"	6.0	84.09	6.26
"	6.6	83.14	15.82
"	7.4	51.96	——
2	4.7	50.01	12.42
"	4.8	80.02	——
"	5.9	51.96	8.46
"	6.5	83.14	2.34

Appendix VII (cont.)

Permanganate Demand of Ferrous Ammonium Sulfate Solution in Aqueous Solution

Iron(mg/l)	pH	$KMnO_4$(mg/l)	$KMnO_4$ Demand(mg/l)
5	3.9	75.85	3.88
"	4.0	81.35	27.67
"	4.0	76.59	7.61
"	4.4	51.96	6.86
"	4.4	83.14	13.13
"	5.0	84.83	3.24
"	"	84.64	9.00
"	5.2	84.64	9.00
"	5.3	84.09	10.89
"	5.3	83.22	9.00
10	3.6	76.64	22.72
"	3.7	75.85	7.35
"	"	80.12	9.57
"	"	81.35	31.07
"	3.8	50.01	19.27
"	"	80.02	28.99
"	"	51.96	5.26
"	"	77.91	24.05
"	"	76.59	15.43

Appendix VII (cont.)

Permanganate Demand of Ferrous Ammonium Sulfate Solution in Aqueous Solution

Iron(mg/l)	pH	$KMnO_4$(mg/l)	$KMnO_4$ Demand (mg/l)
10	3.9	83.14	25.94
"	5.0	84.83	3.24
"	"	"	"
"	"	84.64	10.59
"	"	"	"
"	5.1	84.09	17.07
"	5.1	83.22	15.43
"	"	84.09	15.52
20	3.3	76.64	48.60
"	3.5	50.01	28.84
"	"	80.02	33.71
"	"	81.35	45.18
"	"	77.91	35.04
"	"	76.59	29.26
"	"	75.85	12.20
"	3.6	80.12	16.22
"	4.9	84.64	21.70
"	5.0	84.83	10.94

Appendix VII (cont.)

Permanganate Demand of Ferrous Ammonium Sulfate Solution in Aqueous Solution

Iron(mg/l)	pH	$KMnO_4$(mg/l)	$KMnO_4$ Demand(mg/l)
30	3.4	81.35	66.08
"	4.8	84.09	29.41
40	3.3	81.35	70.60

Appendix VIII

The Combined Effect of Ferrous Ammonium Sulfate and Humic Acid on Permanganate Demand in the Presence of Sodium Chloride

1000 mg/1 NaCl

trial#	NaCl mg/1	Fe mg/1	Demand mg/1	Humics mg/1	Demand mg/1	Fe mg/1	+	Humics mg/1	Demand mg/1
1	1000	1.0	6.26	1.0	4.09				
"	"	5.0	10.61	5.0	10.61	1.0		5.0	13.87
"	"	10.0	13.87	10.0	16.04				
"	"	20.0	19.30	20.0	36.68				
2	"	1.0	4.09	1.0	4.03				
"	"	5.0	10.95	5.0	16.48	1.0		5.0	13.72
"	"	10.0	15.10	10.0	45.56	1.0		10.0	24.79
"	"	20.0	26.17	20.0	40.01				

Appendix VIII (cont.)

The Combined Effect of Ferrous Ammonium Sulfate and Humic Acid on Permanganate Demand in the Presence of Sodium Chloride

5,000 mg/1 NaCl

trial#	NaCl mg/1	Fe mg/1	Demand mg/1	Humics mg/1	Demand mg/1	Fe mg/1	Humics mg/1	Demand mg/1
1	5000	1.0	4.69	1.0	2.62			
"	"	5.0	9.86	5.0	15.03	1.0	5.0	22.27
"	"	10.0	10.90	10.0	27.45	1.0	10.0	30.55
"	"	20.0	21.24	20.0	44.50			
2	"	1.0	0.39	1.0	4.84			
"	"	5.0	2.31	5.0	14.55	1.0	5.0	17.46
"	"	10.0	6.51	10.0	23.29	1.0	10.0	25.23
"	"	20.0	22.49	20.0	39.79			

Appendix VIII (cont.)

The Combined Effect of Ferrous Ammonium Sulfate and Humic Acid on Permanganate Demand in the Presence of Sodium Chloride

10,000 mg/1 NaCl

trial#	NaCl mg/1	Fe mg/1	Demand mg/1	Humics mg/1	Demand mg/1	Fe + mg/1	Humics mg/1	Demand mg/1
1	10,000	1.0	10.17	1.0	5.07			
"	"	5.0	14.42	5.0	36.51	1.0	5.0	36.51
"	"	10.0	17.82	10.0	45.86	1.0	10.0	46.71
"	"	20.0	36.51	20.0	77.04+			
2	10,000	1.0	12.38	1.0	7.35			
"	"	5.0	15.74	5.0	13.22	1.0	5.0	26.64
"	"	10.0	20.77	10.0	29.16	1.0	10.0	34.19
"	"	20.0	36.70	20.0	45.09			

Appendix VIII (cont.)

Combined Effect of Ferrous Ammonium Sulfate and Humic Acid on Permanganate Demand in Aqueous Solution

	Fe			Humic Acid			Fe	+	Humic Acid		
$KMnO_4$ mg/l	conc. mg/l	demand mg/l	pH	conc. mg/l	demand mg/l	pH	conc. mg/l		conc. mg/l	demand mg/l	pH
79.91	10.0	24.05	3.5	10.0	8.03	6.8	10.0	+	10.0	22.08	5.1
80.12	1.0	6.16	4.6	10.0	5.68	5.3	1.0	+	10.0	11.19	5.9
80.12	1.0	6.16	4.6	20.0	10.22	6.6	1.0	+	20.0	16.38	6.6
76.59	1.0	8.82	4.4	10.0	23.25	6.7	1.0	+	10.0	26.26	6.7
75.85	1.0	3.61	4.4	5.0	0.87	6.0	1.0	+	5.0	4.11	6.0
75.85	1.0	3.61	4.4	10.0	8.05	5.9	1.0	+	10.0	10.60	4.0
83.22	1.0	0.97	6.9	10.0	17.03	6.7	1.0	+	10.0	18.64	6.8
83.22	5.0	9.00	5.3	10.0	17.03	6.7	5.0	+	10.0	33.10	6.8
83.22	10.0	15.43	5.1	10.0	17.03	6.7	10.0	+	10.0	49.16	6.6
84.83	5.0	3.24	5.0	5.0	14.02	6.7	5.0	+	5.0	23.26	6.5
"	"	"	"	10.0	20.18	7.0	5.0	+	10.0	34.05	6.9
"	"	"	"	20.0	43.29	7.0	5.0	+	20.0	60.23	6.9
84.64	"	9.00	4.9	5.0	10.59	7.1	5.0	+	5.0	16.93	6.1
"	"	"	"	10.0	20.09	7.0	5.0	+	10.0	31.18	6.5
"	"	"	"	"	18.51	"	"	+	"	"	6.9
84.83	5.0	3.24	5.0	10.0	21.73	7.0	5.0	+	10.0	34.05	"
84.64	"	9.00	4.9	20.0	40.68	7.1	5.0	+	20.0	56.52	"

Appendix IX

Permanganate Effect on the Alga, *Selenastrum Capricornutum*

trial#	$KMnO_4$ mg/l	algal conc. cells/ml	mls. algae	algae,total cells	$KMnO_4$ demand, mg/l	cells/ mg/l $KMnO_4$
1	31.14	1.200×10^6	99.0	118.8×10^6	20.27	5.9×10^6
2	"	"	"	"	21.47	5.5×10^6
3	31.23	1.012×10^6	"	100.2×10^6	18.92	5.3×10^6
4	"	"	"	"	"	"
5	31.29	$.644 \times 10^6$	"	63.8×10^6	8.52	7.5×10^6
6	"	"	"	"	10.71	5.9×10^6
7	"	"	"	"	11.81	5.3×10^6
8	31.34	1.152×10^6	50.0	57.6×10^6	5.87	9.8×10^6
9	31.34	"	75.0	86.4×10^6	"	14.7×10^6
10	31.34	"	100.0	115.2×10^6	14.68	7.9×10^6
11	31.61	$.652 \times 10^6$	5.0	3.3×10^6	2.64	1.3×10^6
12	"	"	25.0	16.3×10^6	5.07	3.2×10^6

Appendix IX (cont.)

Permanganate Effect on the Alga, *Selenastrun Capricornutum*

trial#	$KMnO_4$ mg/l	algal conc. cells/ml x 10^6	mls. algae	algae, total cells x 10^6	$KMnO_4$ demand, mg/l	cells x 10^6/mg/l $KMnO_4$
13	31.61	.652	50.0	32.6	7.51	4.3
14	"	"	75.0	48.9	9.94	4.9
15	"	"	99.0	64.5	17.24	3.8
16	77.85	1.200	97.5	117.0	27.46	4.3
17	"	"	"	"	29.86	3.9
18	"	"	"	"	28.66	4.1
19	78.22	.644	"	62.8	21.37	2.9
20	"	"	"	"	"	"
21	"	"	"	"	"	"
22	78.35	1.152	5.0	5.8	7.89	0.8
23	"	"	25.0	28.8	"	3.7
24	"	"	50.0	57.6	16.69	3.5

Appendix IX (cont.)

Permanganate Effect on the Alga, *Selenastrum Capricornutum*

trial#	$KMnO_4$ mg/l	algal conc. cells/ml x 10^6	mls.algae	algae,total cells x 10^6	$KMnO_4$ demand,mg/l	cells x 10^6 mg/l $KMnO_4$
25	78.35	1.152	75.0	86.4	17.67	4.9
26	"	"	97.5	112.3	29.41	3.8
27	79.01	1.192	20.0	23.8	14.62	1.6
28	"	"	20.0	23.8	14.62	1.6
29	"	"	40.0	47.6	13.57	3.5
30	"	"	"	"	"	"
31	"	"	60.0	71.5	11.47	6.3
32	"	"	60.0	"	24.06	3.0
33	"	"	80.0	95.4	23.02	4.1
34	"	"	"	"	"	"
35	"	"	1.0	1.2	2.03	0.6
36	"	"	"	"	13.62	0.1

Appendix IX (cont.)

Permanganate's Effect on the Alga, *Selenastrum Capricornutum*

trial#	$KMnO_4$ mg/l	algal conc. cell/ml	mls algae	algae, total cells	$KMnO_4$ demand, mg/l	cells/ mg/l $KMnO_4$
37	79.01	652,000	5.0	3.3×10^6	1.39	2.4×10^6
38	"	"	25.0	16.3×10^6	7.47	2.2×10^6
39	"	"	50.0	32.6×10^6	13.55	2.4×10^6
40	"	"	97.5	63.6×10^6	58.16	1.1×10^6

Statistics: Permanganate's effect on S. Capricornutum

Means: #1-15 $KMnO_4$ = 31.38 mg/l, cells/mg/l $KMnO_4$ = 6.04×10^6
Standard deviation " = 0.18 " , " " = 3.12×10^6
Variance = 0.03 " , " " = 9.11×10^6

Means: #16-40 $KMnO_4$ = 78.64 mg/l, cells/mg/l $Kmn0_4$ = 2.97×10^6
Standard deviation " = 0.44 " , " " = 1.45×10^6
Variance = 0.19 , " " = 2.01×10^6

Appendix X

Flux Decline Data - 20 mg/l Fe

Date	Permeate Flux		Date	Permeate Flux	
	liter/m^2-hr	gal/ft^2-day*		liter/m^2-hr	gal/ft^2-day*
15 June	11.85	5.92	1 July	12.59	6.06
16	12.31	6.00	2	12.74	6.06
17	12.31	6.15	4	12.90	5.85
20	11.99	5.92	5	12.05	6.02
21	11.91	5.95	6	12.90	6.14
22	11.91	5.95	7	13.01	6.14
23	11.91	5.95	8	13.07	6.22
24	12.25	5.97	9	13.59	6.46
25	11.85	5.92	11	13.41	6.40
27	12.19	5.87	12	13.41	6.54
28	13.24	5.94	13	13.59	6.46
29	12.19	5.80	14	13.24	6.45
30	12.62	6.00	15	14.56	6.52

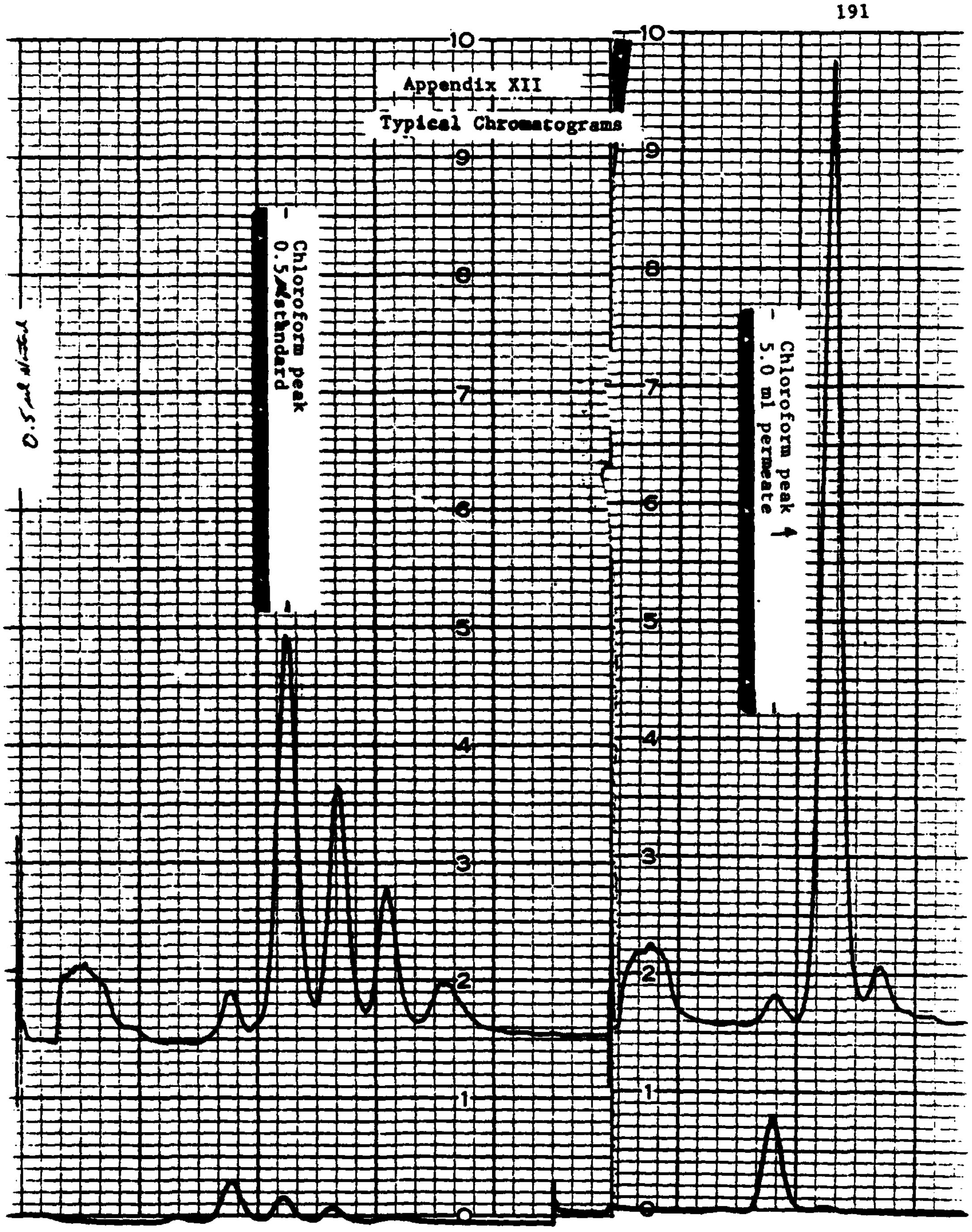
* = temperature corrected

Appendix XI - Data 20 mg/l Fe

date		pH			conductivity			turbidity		% salt
June	P	F	C	P	F	C	P	F	C	rejection
15	---	7.0	---	150	1400	1800	---	---	---	90.6
16	7.1	7.0	7.0	150	1400	1750	0.5	6.2	1.1	92.1
17	4.7	5.2	5.2	150	1400	1900	0.0	1.2	0.2	87.9
20	7.8	7.1	7.1	206	1900	2400	---	---	---	90.4
21	---	---	---	---	----	----	---	---	---	---
22	---	6.6	---	---	----	----	---	---	---	---
23	7.2	6.8	6.8	200	1700	2400	0.3	16.9	6.2	90.2
24	7.2	6.7	6.7	220	1900	2700	0.3	13.9	4.9	90.4
25	7.2	6.7	6.7	180	1700	2400	0.3	19.9	6.2	91.2
27	7.6	7.2	7.2	190	1800	2350	0.0	13.5	5.1	90.8
28	7.7	7.0	7.0	190	1700	2100	0.0	13.6	4.1	90.0
29	---	7.0	---	---	----	----	---	---	---	---
30	6.9	6.7	6.3	160	1600	2100	0.0	12.5	4.2	91.4
July										
1	7.0	6.5	6.5	170	1600	2200	0.0	13.8	7.1	90.1
4	6.5	6.3	6.4	170	1500	1800	0.0	34.8	19.7	89.7
5	6.7	6.7	6.6	180	1500	2000	0.3	38.6	8.2	89.7
6	6.7	7.0	6.7	210	1300	2100	0.3	21.3	11.2	87.6
7	6.7	6.4	6.4	240	1500	2500	0.3	18.0	7.5	88.0
8	7.1	6.6	6.6	215	1600	2100	0.2	16.5	21.9	88.4
9	6.3	6.3	6.4	210	1600	1900	0.3	19.9	9.7	88.0
11	6.7	6.6	6.5	215	1450	1750	0.3	19.9	9.7	86.6
12	6.6	6.5	6.5	240	1600	2000	0.4	31.4	25.4	86.7
13	7.2	6.8	6.7	215	1500	1800	1.1	27.1	11.9	87.0
14	6.7	6.7	6.9	250	1500	2000	0.3	22.6	12.2	85.7

Appendix XII

Typical Chromatograms



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