

The Removal of Organic Matter from Water Supplies by Ion Exchange

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The work upon which this publication is based was supported in part by funds provided by the United States Department of the Interior as authorized under the Water Resources Research Act of 1964, Public Law 88-379

February, 1977
Minneapolis, Minnesota

WATER RESOURCES RESEARCH CENTER
UNIVERSITY OF MINNESOTA
GRADUATE SCHOOL

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FOREWORD

This bulletin is published in furtherance of the purposes of the Water Resources Research Act of 1964. The purpose of the Act is to stimulate, sponsor, provide for, and supplement present programs for the conduct of research, investigations, experiments, and the training of scientists in the field of water and resources which affect water. The Act is promoting a more adequate national program of water resources research by furnishing financial assistance to non-Federal research.

The Act provides for establishment of Water Resources Research Centers at Universities throughout the Nation. On September 1, 1964, a Water Resources Research Center was established in the Graduate School as an interdisciplinary component of the University of Minnesota. The Center has the responsibility for unifying and stimulating University water resources research through the administration of funds covered in the Act and made available by other sources; coordinating University research with water resources programs of local, State and Federal agencies and private organizations throughout the State; and assisting in training additional scientists for work in the field of water resources through research.

This Bulletin is number 91 in a series of publications designed to present information bearing on water resources research in Minnesota and the results of some of the research sponsored by the Center. This Bulletin presents a short review of what is known in regards to the organic compounds found in our surface waters, discusses their removal in general, and their removal using anion exchange resins in more detail.

This Bulletin serves as the Research Project Technical Completion Report for the following Center project:

OWRE Project No.: A-030-Minn

Project Title: Analysis of Organic Carbon as a Pollution Index

Principal Investigator: Walter J. Maier, Department of Civil and Mineral Engineering, University of Minnesota

Project Began: July 1, 1973

Project Completed: June 30, 1976

FCST Research Category: 05-C

Publication Abstract:

This study was initiated to provide quantitative information on the use of anion exchange resins for organic removal. It was shown that the organics that are present in surface waters which currently pass through conventional treatment could be removed by anion exchange with the use

of strongly basic anion exchange columns. It was observed that the organics were removed to the lower limits of detection of the total organic carbon analysis with the use of the high porosity strongly basic resins. These resins were also found to be easily regenerated with the use of sodium chloride.

The selectivity and kinetics of the chloride versus organic exchange process was briefly investigated. The reason being that this is a new approach to this problem and no data was available in the literature to provide information which could be used for preliminary design of a full scale treatment plant.

A preliminary plant design was done, the result showed that the process would be economically feasible and certainly competitive with alternate methods of organic removal, assuming that they would also prove to be as effective at organic removal as ion exchange. So, ion exchange could prove to be an effective, reliable and economical method to provide for the removal of organics for drinking water.

Publication Descriptors: *Organic Matter/*Pollutants/*Water Pollution/*Carbon Anion exchange/

ORGANICS IN SURFACE WATERS

Introduction

It is now well established that a large variety of organic chemical compounds are present in surface waters. Their presence is very much a current topic of discussion in the press along with the scientific journals. The reason for concern is due to the ubiquity of low amounts of known carcinogenic and toxic compounds, and the fact that as of today we do not know at what concentrations detrimental health effects begin. Only within the past few years has the presence of these compounds been made evident through the applications of new and sophisticated advances in analytical instrumentation and techniques which can measure very small quantities of contaminants. This has helped provide an impetus for research in this area.

Another important reason is the critical shortage of water now being forecasted in some areas of the country. Reuse of water is an important possible future source of this vital resource. However, progress in this area is lagging due to the largely unknown nature of the organics present in treated wastewaters. Research has thereby become urgent to allow progress to ensue.

In addition to these concerns, there is the possible harmful effects that these organic compounds may have on the aquatic ecology of our natural waters. Direct effects caused by the organic compounds may be exhibited on a single species or a group of organisms. Examples would include certain organic poisons which may be toxic at very low concentrations, or organic compounds which tend to accumulate in tissues and reach toxic or harmful levels as they are concentrated in the higher levels of the food chain. Indirect effects may also have a profound ecological impact. For instance, if the reaeration capability of a stream or lake is not sufficient to meet the oxygen required due to the biological degradation of the organics present, dissolved oxygen levels will fall causing populations which require high oxygen levels to move or die off. If the environment should become anoxic, there will be a complete change in the predominate species of micro and macroorganisms from those which must utilize oxygen to those microorganisms which can use inorganic or organic compounds as their electron acceptor to carry out cellular functions.

The largely unknown nature of the organics in our surface and ground waters is of course a reason for concern. However, the recently established fact that these organics are not being removed in conventional water supply treatment makes knowledge of these compounds and the concentrations at which they are present critically important.

This paper presents a short review of what is known in regards to the organic compounds found in our surface waters, discusses their removal in general, and their removal using anion exchange resins in more detail.

Generally in the past, organics have been measured by conventional methods which tend to measure groups of compounds rather than specific chemical compounds. These methods include:

1. BOD - Biological Oxygen Demand. This test is a measurement of the biodegradation of oxidizable materials.
2. COD - Chemical Oxygen Demand. A measure of the concentration of materials that can be oxidized during chemical digestion.
3. CCE - Carbon Chloroform Extract. A measurement of the organics that are adsorbed on activated carbon and desorbed with chloroform.
4. CAE - Carbon Alcohol Extract. A measurement of the organics that are adsorbed on activated carbon that can be extracted with methanol.
5. Color - A measurement of the absorbance of light in the visible region of the spectrum.

With the development of an instrument that measures Total Organic Carbon (TOC) it became evident that the above mentioned measurement methods were deficient in providing an accurate picture of the full extent of the presence of organics in natural waters. The conventional methods do provide important specific information about the properties of certain compounds or classes of compounds, but they are inadequate as a measure of the overall problem of organics in natural waters and public water supplies.

The concentrations of organic carbon in natural waters as measured by TOC has been used in a number of investigations (7,22,23,35). The results of these studies show that organic carbon concentrations fluctuate both seasonally and from year to year. There is also a geographical variation in the concentrations of organic carbon observed. For surface waters concentrations of organic carbon vary anywhere from 1.0mg/l to 50mg/l with average concentrations tending to be in the 10-15 mg/l range. The concentration of organics which would include hydrogen and oxygen is approximately 2.5 times higher.

In a recent study (7), it was determined that a significant amount of the organic carbon was not being removed during conventional alum-lime water treatment. The amount of organics passing through treatment was often as high as 40-60% of the incoming flow. The magnitude of these numbers was confirmed by a recent study by the EPA (35) in which non volatile total organic carbon was measured.

Nature and Characteristics of Organic Carbon

To date several hundred specific organic chemical compounds have been identified in various water supplies throughout the United States. Unfortunately for any one given sample the identified compounds can only begin to account for a fraction of the bulk of the organics present due to the low concentrations at which the identified compounds occur. It has been noted that a major amount of the organic material which is present in

surface waters is a material of low biodegradability made up of a residue remaining after biodegradation of the bulk of the natural common polymeric molecules which originate predominately from vegetative growth.

The chemical and physical properties of some of the organics that are found in natural waters have been investigated to obtain insight on their effects on water quality. Molecular size is an important characteristic which has been investigated. Several experimental techniques have been used which include ultracentrifugation and molecular weight determinations. However, ultrafiltration with the use of precalibrated membrane filters or by separation through gel filtration has been the most successful methods for obtaining size distribution data.

The size distribution for the organics contained in a sample of Mississippi River water was obtained by the use of commercially available precalibrated membrane filters. To determine the size distribution a portion of the sample was filtered through one of five different membrane filters. The filtrate was collected and the concentration of organics in the filtrate was measured using a Total Carbon Analyzer. The distribution of the organic carbon that was obtained is shown in Figure 1. An interpolation of this data reveals that the average molecular weight is about 1500 Molecular Weight Units (MWU). It shows that the organics have a very diverse size distribution with the largest amount of material being contained in the low molecular weight fraction (less than 1000 MWU). The remaining material is distributed in the higher molecular weight fractions with only about 2% of the organics being greater than one million MWU. Other investigators have reported finding similar trends (14,17). These organics are therefore in the soluble and colloidal particle size range with very little being of a particulate nature.

Degradation studies by Christman and Ghahremani (10) have shown that the colored material found in natural waters is negatively charged and of an aromatic nature. Their proposed structure for this macromolecule is given as figure 2.

The ultraviolet adsorption spectrum for the river water organics is typically a curve in which adsorption increases as the wavelength decreases. There are no discernable peaks in a typical sample in the 200nm - 400nm range.

These general properties of organics are similar to properties of the humic acids which have been described in the Soil Science literature. The book by Schnitzer and Khan (30) is an excellent summary of this information. The humic acids are considered to be a broad group of compounds which are formed in the soil and originate from the degradation of vegetative materials.

The molecular weight of the humic acids varies from several hundred into the millions. They tend to be negatively charged and consist of an aromatic backbone which is substituted with oxygen containing functional groups such as alcohols, aldehydes and acids.

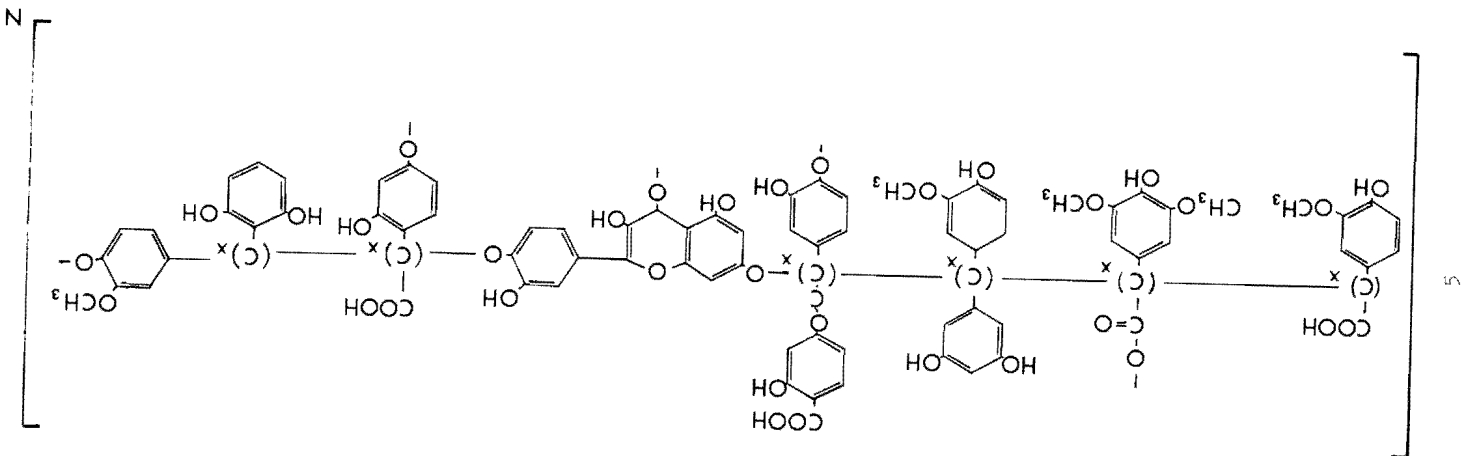
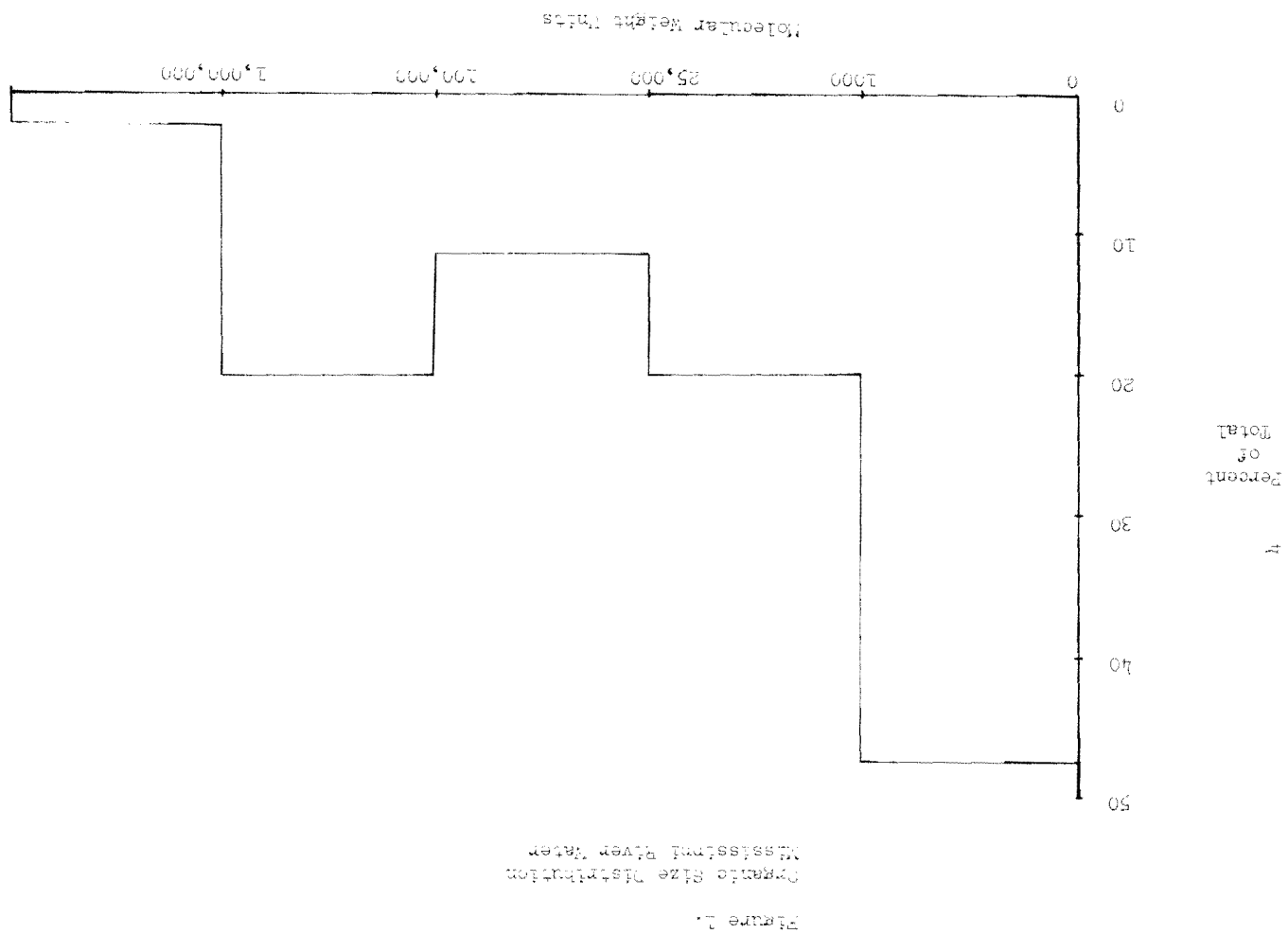


Figure 2.
 Structure of Color Macromolecule of Natural Waters
 as Proposed by Christman and Masseni (10)



Although there is a similarity between the properties of humic acid soil extracts and the organics present in surface waters. This in itself is not sufficient to show that they are identical, and it is therefore not possible to make precise quantitative comparisons between these two groups. However, when trying to get a better understanding of the processes occurring in natural waters it is often helpful to use some of the data and methodologies collected by the soil scientists in their investigations. Although their data is more meaningful than other model compounds would be, it is of course necessary to apply this knowledge with caution.

One possible use for the humic acid information that is available is for the estimation of the equivalent weight of the organics in Mississippi River Water. The equivalent weight is an important parameter in later sections of this paper, and it is possible to estimate it using molecular weight and carboxyl concentration data on the fulvic acid fraction of a soil extract. The chemical composition of fulvic acid, which is the humic acid fraction that is soluble in both acidic and basic solutions, is reported by Schulzinger (30). The average molecular weight of fulvic acid is 1400 and 77.2% of the oxygen groups are carboxyl functional groups. The elemental composition of fulvic acid is listed below. The equivalent weight was calculated by dividing the molecular weight (1400) by the number of carboxyl groups.

Element	Percentage	Atoms/Mole
Carbon	46.2	53.9
Hydrogen	5.9	82.6
Nitrogen	2.6	2.6
Oxygen	45.3	39.6

Number of charged groups = 5.38

Equivalent weight = 260

Table 1. Elemental Composition of Humic Acid.

Reasons for Removal of Organics

Historically the concern for organic removal has dealt with the problem of color and odor causing organics. This is of course still a concern today and is currently the only reason that organics are now being removed at all. From recent research it is clear that potential health hazards are present due to the toxic nature of some of these organics as well as the interactions with other elements or compounds with a harmful result. The extent of these hazards probably depends on the composition and concentrations of the organics.

One of these such reactions that has been noted to occur and is currently receiving attention is the formation of organohalides in our water supplies. These compounds, of which chloroform is the predominate species,

are known to be carcinogenic at high levels, although their levels in water supplies are generally very low. From recent work by Root (33,39) it seems that organohalides are formed during chlorination through the reaction of chlorine with the organic compounds that are present in the raw water supplies. The U.S. Environmental Protection Agency has recently issued guidelines detailing methods to help control this problem (34) and is currently considering what if any limits should be placed on chloroform concentrations in our water supplies (36).

Another detrimental effect is derived from the chelation of organic molecules with trace metals, thereby increasing their solubility (32). Unfortunately the possible repercussions of these types of interactions are not yet known and await further study.

The magnitude of the problem that is due to the toxicity of the organics that are found in water supplies has not been established. However, if the presence of these organics is allowed, the potential for toxic or carcinogenic effects will always be present. Although no acute effects due to the presence of organics have been conclusively documented, we can not yet rule out possible long range or accumulative effects.

The question of whether additional treatment for the specific removal of organics from public water supplies is justified has not been resolved, although it is currently the subject of much debate (36). Questions of (a) potential long range health hazards, as opposed to demonstratable acute effects, (b) aesthetic considerations, and (c) the cost of treatment are not yet resolved and in fact have received little attention. Research now underway may help to resolve some of the questions, but additional information is needed on all aspects. One of the areas where added information is critically needed is in regards to the application of current technology for the removal of organics, which would include the effectiveness and the costs of such treatment processes.

Treatment Alternatives

An inspection of the literature (37,29,34) reveals that the possible types of treatment available for the removal of organics include (a) separation by ultrafiltration techniques through filter beds or membranes, (b) coagulation - flocculation to allow removal by sedimentation, (c) adsorption on surfaces such as activated carbon, ion exchange media or flocc particles, and (d) oxidation to convert the organics to carbon dioxide and water.

The use of ultrafiltration is necessary due to the small size of the organics present (see previous section). In order to use this process a high pressure gradient is required to force the water through the small openings which must hold back the organics. This generally makes it an uneconomical process for municipal water supplies due to the large head losses which require enormous energy inputs at the flow rates involved. Electrodialysis, where a charge gradient is used to remove ions, has been economically used on some instances for the removal of inorganic salts.

The effectiveness or cost of this process for the removal of organics is not known. Generally however electrodialysis becomes economical only at high (greater than 1000 mg/l) salt concentrations. It therefore would likely be an expensive process for organic removal for the concentrations we find in natural waters.

Conventional water treatment of surface waters typically includes lime softening, alum flocculation, sedimentation, chlorine disinfection and filtration. These processes represent a number of possible removal mechanisms for organics which include (a) coagulation-flocculation by aluminum ions, (b) adsorption on calcium carbonate or aluminum hydroxide precipitates, (c) removal by sedimentation, (d) oxidation by chlorine and (e) removal by filtration. In a treatment plant process it is very difficult to separate the effects due to the items (a) and (b), although recent research suggests (b) may be the predominate mechanism of removal (37,38).

In a recent study (7) it was observed that removals of organics from a surface water were typically from 40% - 60% of the incoming flow. In the softening process during which lime and alum were added an average of 30% removals were obtained. If alum was again added following sedimentation and recarbonation another 30% of the incoming organic material could be removed. This data suggests that the high pH's during the softening process limit the effectiveness of alum addition when it is added at this time. This suggests that facilities that now have a separate alum coagulation basin may be able to provide better treatment and at the same time have lower chemical costs than other plants due to the increased flexibility provided by the additional tanks. The chlorination and filtration processes remove a relatively small amount (<10%) of the incoming organics in a conventional water treatment plant.

Although chlorine does not account for a significant amount of organic removal, it has been shown that there is at least a partial oxidation of the organic matter by chlorine (28,29). Other chemicals that are also strong oxidizing agents and can be purchased at a cost where their use may be suitable for water treatment include: ozone, permanganate, ferrate, and chlorine dioxide. Because the demand for a chemical oxidant increases with the percentage removal required, the oxidation processes are most feasible where partial oxidation would be satisfactory. However, at this time there is not enough information available to determine the extent that oxidation would proceed with the various oxidizing agents and what the corresponding dosages and costs would be for whatever treatment is deemed necessary. Another important but unanswered question is what end products or intermediates would be present and what problems would result from their presence.

In addition to the adsorption that occurs on the surfaces of the calcium carbonate and aluminum hydroxide particles in water treatment, another adsorbing surface that is often used in water treatment is activated carbon. Activated carbon is typically applied in a powdered form as a slurry to provide additional removal of color and/or odor causing organics. Activated carbon beds are now being used where color and/or odor problems have been persistent in the finished waters.

To evaluate the effectiveness of activated carbon a 20 cm. deep column was set up using granular activated carbon. It was observed that a 60% removal was obtained of the 13 mg/l incoming TOC at a flow rate of 20 ml/min. (2.7 gpm/ft²). In a study by the EPA using Ohio River water, they found that the NPPOC (Non-Purgeable Total Organic Carbon) was reduced from an initial value of 1.0-1.5 mg/l in the incoming flow to less than 0.1 mg/l in the effluent (34). The observed life of the 2-3 foot bed was about a month with velocities of 2-3 gpm/ft².

The observed differences between the test results are probably due to the difference in the lengths of the columns. The type of organics in the raw water and the method of analysis may also be a factor. The reason is that to measure NPPOC the sample is acidified and stripped with nitrogen gas, while the TOC analysis would include volatile compounds.

The use of other adsorbants such as synthetic organic polymers is also a possible removal process. These would include the cationic, anionic and nonionic resins and are generally used in a column form. Although there is some initial adsorption of organics on a cation exchange column, they are not as such exchangeable and these resins are not a viable removal process. The nonionic resins may eventually have some usefulness in water treatment. Research is currently underway to evaluate their usefulness in the removal of the halogenated methanes. These resins are limited mainly to the removal of nonionic compounds and tend to have a lower capacity than activated carbon. They can however be regenerated using organic solvents, while heat regeneration is required for activated carbon. Anion exchange columns show the most potential for general organic removal and the remainder of this paper is devoted to their possible application as an organic removal process.

ION EXCHANGE

Nature of Ion Exchange

Ion exchange is a reversible process where an insoluble solid material carries exchangeable cations or anions and can exchange these in stoichiometrically equivalent amounts with other ions of the same sign in an electrolytic solution. Carriers of exchangeable cations are called cation exchangers, while carriers of exchangeable anions are called anion exchangers.

Anion exchangers, which are used in this study, are essentially a polymeric backbone to which positively charged ionic groups are attached. The polymeric backbone is usually a linear or branching polymer to which a crosslinking agent is added to give the resin its tertiary structure. In the manufacturing of a resin all of these parameters can be varied to some extent, and the result is a very wide array of types and properties of the resulting resins.

Most of the commercially used anion exchange resins have a nitrogen derivative as the charged functional group; the actual composition depending on the resin. The polymeric backbone usually consists of a styrene polymer and the crosslinking agent is usually divinylbenzene (Figure 3 for structures). Resins of different properties can be obtained by varying the nature of the substituted groups on the nitrogen molecule and the amount of divinylbenzene added, without radically changing the resin backbone.

If the resin nitrogen groups consist of an amine structure the resin is classified as a weakly basic anion exchange resin. Weakly basic resins do not have the ability to exchange the anions of weak acids such as bicarbonate, but only those of strong acids such as chloride, sulfate, and nitrate. This resin functional group (see Figure 3) is very pH dependent due to the pH dependence of the amine group. At pH's greater than pH 7 they are not ionized and therefore do not function as ion exchangers.

The other main group of anion exchangers are the strongly basic anion exchange resins. The nitrogen group on a strongly basic resin is substituted to form a quaternary amine. If the methyl groups were substituted on the nitrogen group the exchanger produced would have the structure given in Figure 3. These resins have the ability to operate effectively over the entire pH range of 0 to 14. They also have the ability to remove virtually all anions from a solution when used in a column form.

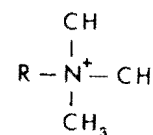
The amount of crosslinking agent (divinylbenzene) that is used has been varied from 0.25 to 25% but is most commonly in the 4 to 6% range. The amount used has an effect on the pore size of the resin along with an appreciable effect on the resins selectivity, which is the resins preference for one ion over another. Both of these effects are discussed in more detail below.

Selectivity

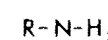
In the exchange reaction between ions in solution and the resin, the resin will have a preference for one ion over another. This will cause

Figure 3.

Common Chemical Components of Anion Exchange Resins

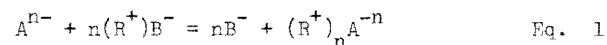


Methyl quaternary amine



Amine

the ratio of counter ions in the solution phase to differ from the corresponding concentration ratios in the resin phase. A quantitative description of this process can be developed by considering a stoichiometric reaction of an ion exchanger with two counterions (those ions whose charge is of an opposite sign to those of the fixed ionic groups on the exchanger). The reaction can be written as:



Where (A^{-n}) is the ion in solution, (B^-) is the ion originally on the resin and (R^+) represents the fixed groups attached to the ion exchange resin.

The equilibrium relationship for the reaction can be represented by the law of mass action and written as:

$$K_B^A = \frac{(B^-)^n (X_A)}{(A^{-n}) (X_B)^n} \quad \text{Eq. 2}$$

where K_B^A is the selectivity coefficient although it is not necessarily a constant, because it is concentration dependent. X_A and X_B are the equivalent fractions of these ions on the resin and (B^-) and (A^{-n}) are the activities of the ions in solution. For dilute solutions the activity of the solution is near unity and concentration can be used instead.

The selectivity of ion exchange resins has been discussed in the literature (11,19). The resin properties that have been listed as being important in influencing the selectivity coefficient include: (a) the degree of crosslinking of the resin, (b) available capacity, (c) physical and chemical nature of the polymer matrix and (d) type of fixed charged groups on the resin. The selectivity of a given resin for the various ions is influenced by the size, total charge, charge distribution and the degree of hydration of the ion. Through a consideration of these parameters the selectivity sequences for inorganic cations and anions can be predicted on a qualitative basis (11).

Organic ion selectivities are also influenced by these same effects, however the selectivity sequences cannot as yet be predicted even though a number of investigators have looked at the relationship between organic ion characteristics and resin selectivities.

Hale (16) has shown that the capacity of a resin is influenced by the size of an ion and the degree of crosslinking of the resin. The reason for this is that if the pores are small compared to the ion, the capacity of the resin is reduced for the larger ion. Depending on the resin and organic ion being considered, increasing the degree of crosslinking may cause the selectivity to increase, decrease or remain constant. The explanations for the varying types of behavior observed include: (a) swelling pressure effects, (b) ion accessibility to the exchange sites, (c) solubility in the resin phase and (d) interactions between the resin matrix and organic ion.

Selectivity coefficients for a number of organic ions have been tabulated by Semmens (31). From this list it is apparent that the selectivity can vary over a wide range depending upon the organic compound, the resin being evaluated and the experimental conditions.

In practice, a high selectivity is preferred if the objective is to remove a particular organic constituent from a mixed ion solution. High selectivity means that this ion would be preferred over other counter ions on the resin and in solution, thereby giving a high overall capacity along with a sharp breakthrough curve. Very high selectivities are undesirable because problems may arise in the regeneration cycle, namely the need for large quantities of regenerating solution.

Hinrichs and Snoeyink (15) investigated the adsorption of benzenesulfonates on weakly basic ion exchange resins and reported that adsorption was very pH dependent. The weakly basic resins had considerably lower capacities as pH increased from pH 2 to pH 4. However they obtained complete removal of these types of compounds using weakly basic resins in a column form.

The influence of the pH of a solution on the selectivity of a resin is through two main effects. The pH of a solution would affect the amount of an ion in its ionic form through its ionic distribution as defined by the ions pK. As the pH decreases and approaches the pK, less of the organic ion would be in an ionized form which is the form that is available for ion exchange. The solution pH also has an effect on the weakly basic resin. The amine group of the weakly basic resin tends to lose its positive charge as the pH increases, with pH 7 being the highest pH at which these types of resins can be operated effectively.

Kim et. al. (20) also investigated the weakly basic anion exchange resins for the removal of p-nitrophenol and compared these removals to those obtained with the nonionic resin XAD-7 and activated carbon. They showed that adsorption for p-nitrophenol was also pH dependent with best removals obtained on activated carbon, followed by the weakly basic resin and then the nonionic resin.

Gustafson and Lirio (19) studied the adsorption of aromatic sulfonates on anion exchange resins. They observed that the selectivity increased markedly as the degree of aromaticity increased. Charge densities alone cannot explain the differences in selectivities of the organic ions versus chloride ion since the charge density of the organic ions would be considerably less than those of the displaced chloride ion. They attributed the increase to a combination of electrostatic and hydrophobic bonding. They maintain that the presence of the charged groups of the resin will neutralize the charged portion of the organic molecule and permit a high degree of interaction between the remainder of the molecule and the styrene-divinylbenzene copolymers of the resin. They also observed that the rate of adsorption was strongly influenced by the size of the organic molecule. For instance, after an equal amount of time, about six times more benzenesulfonate (MW = 173) than anthraquinonesulfonate (MW = 288) was adsorbed by the resin.

The literature has shown that the reasons selectivity coefficients change with changing experimental conditions is not yet entirely understood. However, the parameters that have been shown to be important are (a) type of organic ion, (b) physical and chemical properties of the resin, (c) concentration of the organic ion, and (d) the pH of the solution.

The idea of using anion exchange resins for removing aquatic organics received impetus from two directions. There is a recognized need for methods to obtain quantitative recovery of aquatic organics to facilitate the study of these materials and more importantly there is a need for developing technology for treating public water supplies for reasons previously discussed. An experimental program was set up using Mississippi River water and a series of anion exchange resins. The objective was to obtain sufficient process data to allow formulating preliminary process design and cost estimates.

A series of screening tests were carried out using strongly basic and weakly basic anion exchange resins in short columns. The results showed that the strongly basic resins provided nearly complete removal (95 to 100 %) while the weakly basic resins removed approximately 50% of the incoming TOC. A detailed discussion of similar column runs using these materials is contained in a following section. However, the information that these preliminary tests provided suggested that further tests should be conducted to gain added information on the strongly basic anion exchange resins.

Experimental and Analytical Procedure

The first phase of the experimental work was to evaluate the selectivity of the strongly basic anion exchange resins. This would give information on the final equilibrium distribution of the ions in solution on the resin. A series of batch tests were set up in which a predetermined quantity of ion exchange resin was added to a fixed volume of river water. The mixture was stirred and sampled periodically. The resin was separated from the water by filtration, with the filtration step taking about thirty seconds.

Commercially available resins were used; all the resins were made from polystyrene but with varying amounts of the crosslinking agent (divinylbenzene) added. All the resins had the same charged groups, a trimethyl quaternary amine. Table 2 provides a listing of the resins used along with the amount and capacities used for this experiment.

Inspection of past data showed that the major anions in surface waters which were under consideration are chloride, sulfate, nitrate and bicarbonate alkalinity (inorganic carbon). Small concentrations of other ions such as nitrite and phosphate were also present, but can be neglected in this work because of their low concentrations. Methods for measuring the major ions were as follows.

Table 2. Anion Exchange Resins Used

Resin	Type	Porosity	Capacity (meq./gm.)	Size (US screen)
IRA-400	Strongly basic	medium	4.3	16-50
IRA-401E	"	high	3.4	16-50
IRA-938	"	very high	3.7	20-50
A-1P	"	very high	4.3	16-50
IR-45	weakly basic	medium	5.0	"
AGA-316	"	"	5.4	"

Sulfate: Turbidimetric method using barium chloride to precipitate the sulfate as barium sulfate. The resulting turbidity is measured in a spectrophotometer in a 1.5 cm. cell at 420 nm.. The spectrophotometer is calibrated using standard solutions with the lower limit of detection for this method being about 2 mg/l. This method is outlined in Standard Methods (5).

Nitrate: Nitrate was measured using an Orion specific ion electrode. During the course of this study the nitrate concentration was consistently below the lower limit of detection for this technique which is about 1 mg/l. In this case, there is no data available for nitrate, since it was a minor constituent in these samples.

Chloride: Chloride was measured by an Orion specific ion electrode. The lower limit of detection is about 3 mg/l, which was significantly below the levels encountered in these samples.

Bicarbonate Alkalinity: Bicarbonate alkalinity was measured indirectly through the use of a Beckman carbon analyzer. A 20 µl sample is injected into a 150°C furnace using nitrogen as a carrier gas. In this environment all carbonates and bicarbonates are converted to CO₂ which are subsequently measured by a carbon dioxide sensitive infrared detector. The lower limit of detection is approximately 0.5 mg/l.

Organic Carbon: Organic carbon is taken as the difference between the total carbon and the inorganic carbon. Total carbon is measured using the same instrument as described above, however the furnace for this measurement is set at 940°C, oxygen is used as a carrier gas and the combustion tube is packed with cobalt oxide impregnated asbestos. Under these conditions all carbon compounds are converted to carbon dioxide which can then be measured. The lower limit of detection of Total Organic Carbon (TOC) is also about 0.5 mg/l.

The analytical results of these tests are shown in Figures 4 to 7. Concentrations of sulfate, chloride, inorganic carbon (TIC), and total organic carbon (TOC) in the supernatant are shown as a function of time. The selectivity coefficients were calculated by using the equations previously discussed. The equilibrium concentrations used were obtained from Figures 4 to 7 and the values are expressed as meq/l in Table 3. The equivalent weight of the organics present was taken as 260 MWU which would correspond to a charge of 5.38 electrons per molecule. The equilibrium concentration of ions on the resin is the difference between the initial amount present and the amount present after equilibrium has been established. The results are expressed as a fraction of the total capacity of the resin. The total capacity of the resin was obtained by measuring the total weight of the resin used, then determining its moisture content by heating the resin to a constant weight at 103°C. The dry weight of the resin was then calculated and ultimately its total capacity. The resins were all initially in the chloride form so the value for the chloride after equilibrium was established is the difference between the total capacity and the amount of other ions adsorbed on the resin.

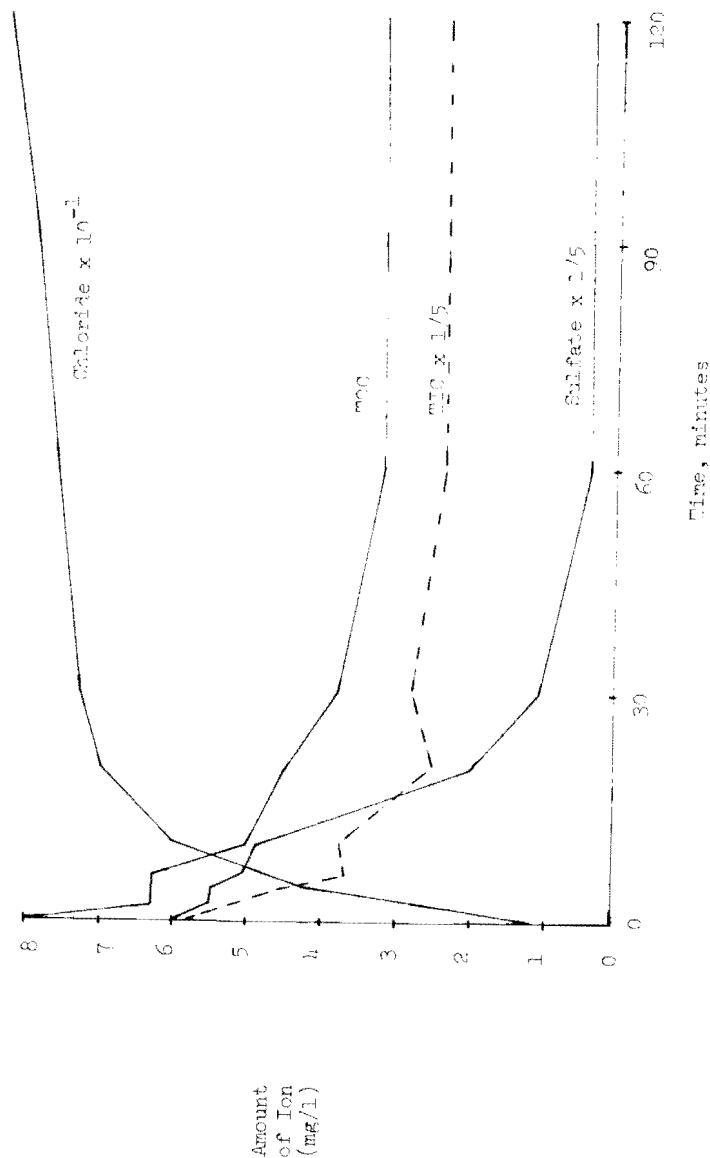
The calculated selectivity coefficients are listed in Table 4. The resins exhibit increasing selectivity for the ions in the order of TIC, chloride, sulfate and TOC. Although the resins tend to have increased selectivity with increased crosslinking (decreased porosity) it is apparent that there are other effects that cause exceptions to occur (IRA-400 in this case).

The fact that the selectivity coefficient for organics is high suggests that chloride on the resin will be easily displaced by the organics present when the resin is used in a column situation. The selectivity coefficient for TIC versus chloride is relatively low, which means that the bicarbonate which would originally displace some chloride ions in a column would in turn probably be displaced by organics thereby increasing the capacity of the column for organics. Although the selectivity coefficient for sulfate is fairly high for these resins, they are still below the values obtained for the organics and therefore should be displaced by the organics.

Because the equivalent weight is an estimated and not a measured quantity it was necessary to see how sensitive this calculated selectivity coefficient was to the equivalent weight. A change in the equivalent weight would affect the selectivity coefficient both through the organic carbon concentrations which are expressed in equivalents and in the charge balance of the reaction which determines the exponents to which the chloride concentrations are raised. Table 5 shows how the calculated selectivity coefficient changes as the number of charged groups per molecule increases from 1 to 7. This would correspond to equivalent weights from 1400 to 200.

The results show that the selectivity coefficients will change very dramatically depending upon the equivalent weight used. So although the relative selectivity between resins would not depend upon which equivalent weight is used, the absolute magnitude of the coefficients is very much dependent on the chosen equivalent weight. However, in order for the selectivity coefficients to be higher for the sulfates than they are for the organics, the charges on the organics would have to be less than three per molecule.

Figure 4.
Ion Uptake of Resin IRA-400 with Time



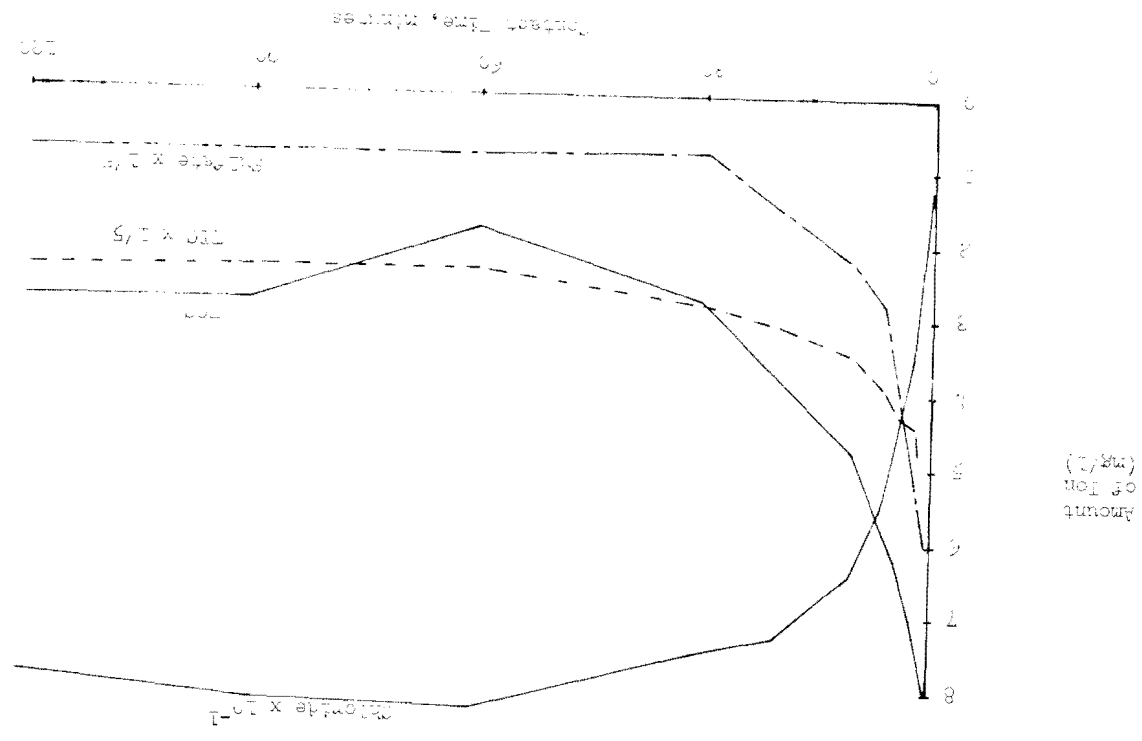


Figure 6. Ion Uptake of Resin A-1P with Time

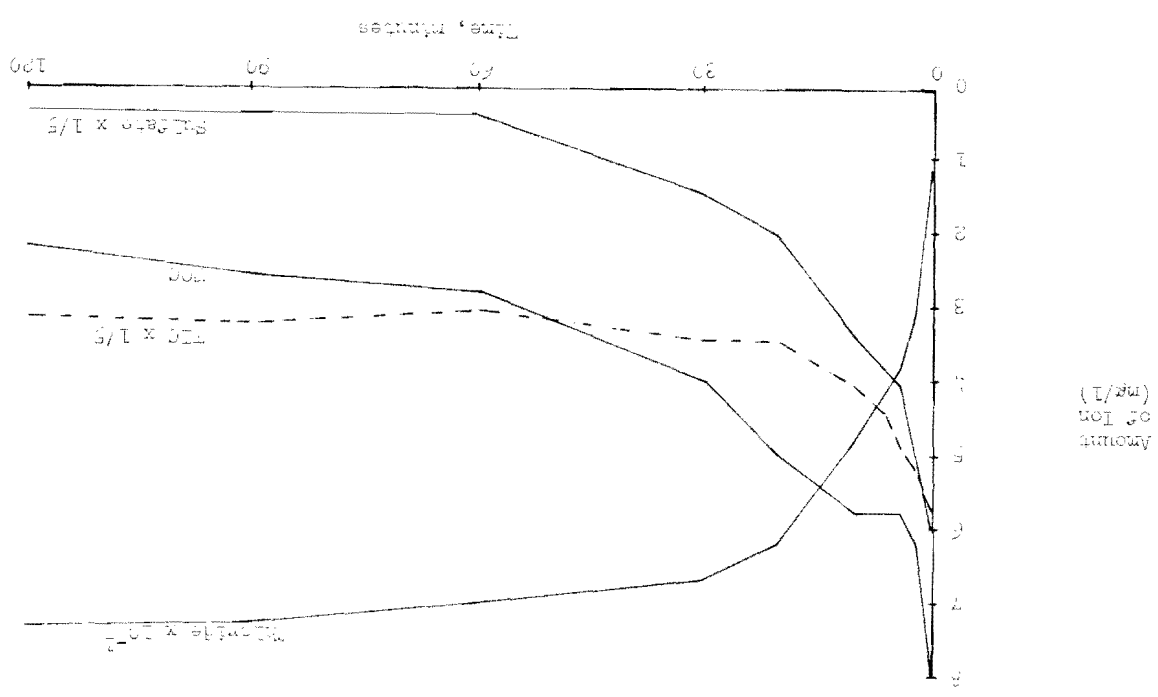


Figure 7. Ion Uptake of Resin A-1P with Time

Figure 7.
Ion Uptake of Resin IRA-938 with Time

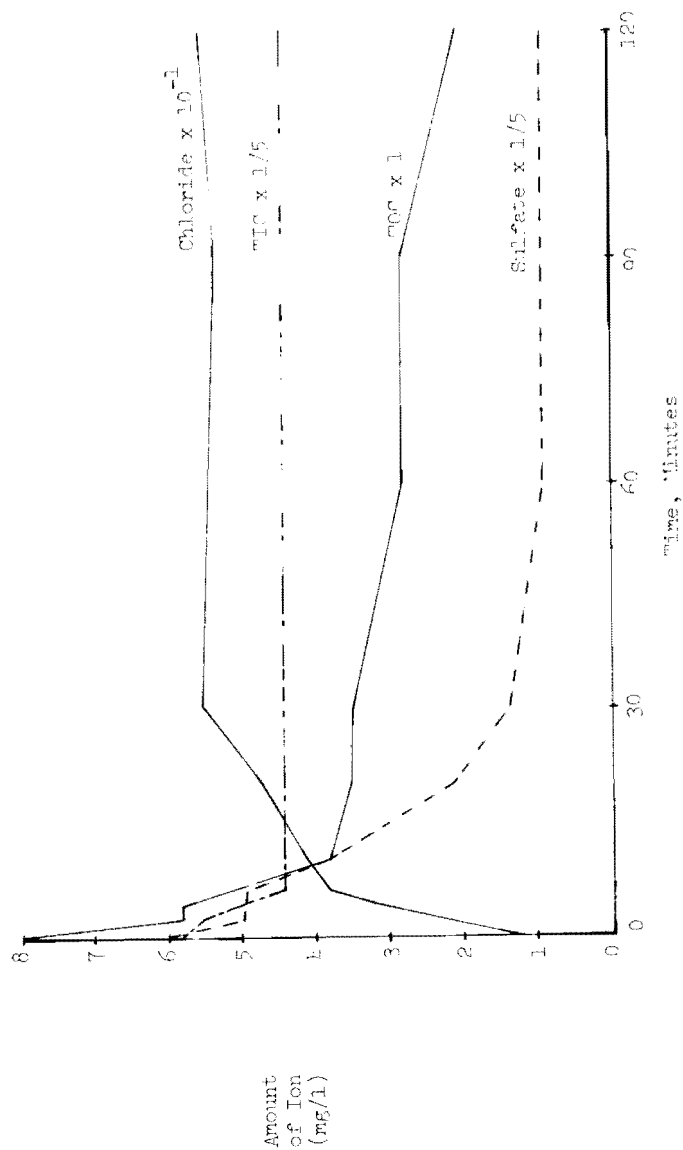


Table 3. Batch Test Results at Equilibrium

Resin	Ion	Total Wt. Grams	Dry Wt. Grams	Capacity meq.	Equilibrium Concentration	
					Solution (meq/l)	Resin (Fraction)
IRA-400	TIC	10.	5.25	22.6	1.00	0.25
	TOC				0.027	0.007
	SO ₄				0.042	0.10
	Cl				2.34	0.64
IRA-401S	TIC	10.	3.52	12.0	1.31	0.37
	TOC				0.018	0.017
	SO ₄				0.042	0.19
	Cl				2.06	0.42
A-1P	TIC	10.	5.09	21.9	1.0	0.26
	TOC				0.023	0.008
	SO ₄				0.083	0.099
	Cl				2.25	0.635
IRA-938	TIC	10.	2.38	12.6	1.83	0.19
	TOC				0.017	0.016
	SO ₄				0.104	0.16
	Cl				1.49	0.64

Table 4. Selectivity Coefficients

	IRA-400	IRA-401S	A-1P	IRA-938
K_{Cl}^{TIC}	0.91	1.39	0.92	0.24
K_{Cl}^{TOC}	277	4830	277	88.9
$K_{Cl}^{SO_4}$	31.8	110	15.0	8.34

Table 5. Variation in the Organic Selectivity Coefficient

Charge per molecule	IRA-400	IRA-401S	Al-P	IRA-938
1	1.0	4.6	1.2	2.2
2	3.5	22.7	4.4	5.1
3	12.7	111	15.5	11.9
4	46.3	547	54.8	27.7
5	169	2680	194	64.4
6	619	13150	688	150
7	2265	64590	2440	349

Modeling the Kinetics of Ion Exchange

Ion exchange kinetics, or the rate at which an ion is removed from the bulk solution is controlled by the slowest transport step by which ions migrate from the bulk solution to the ion exchange sites. Simultaneously a counter ion on the ion exchange resin must leave its site and migrate out of the particle into the water phase in order to maintain electro-neutrality. The literature indicates that the actual chemical exchange reaction is fast and therefore not rate limiting. Ion transport includes film diffusion which is the transport of ions within the boundary layer between the particle surface and the bulk solution and particle diffusion which is the transport of the ions within the ion exchange matrix. It is generally believed that it is an ion transport process that limits the rate of ion exchange (18).

In an ion exchange process both equilibrium and kinetic effects can control the response of the operation to the operating variables. It therefore becomes difficult to formulate an all encompassing mathematical description for the exchange process. For this reason simplifications or idealizations must often be used before a problem can be analyzed.

Equilibrium type models as first developed for ion exchange by Martin and Synge (24) are discontinuous models. Their model assumes that the incoming solution attains a local equilibrium in each section of the bed before it moves to the next section. The height of this section is called the height equivalent plate (HETP). The HETP depends on the operating conditions and because the HETP cannot be predetermined but must be found experimentally this model cannot be used for predictive purposes.

Complex rate theories which quantitatively describe the removal of an ion from a solution have been developed. These equations are based on the physical processes known to occur. Since ion exchange is diffusion controlled, investigators have developed appropriate flux equations for the diffusing species. These are based on the Nernst-Planck equations and have been summarized for both film and particle diffusion control by

Helfferich (18). The difficulty which arises with these equations is during their integration in instances where the restrictions and boundary conditions do not provide equations which are amenable to integration.

Due to this difficulty semiempirical rate equations involving rate or mass-transfer coefficients have been developed. These coefficients are determined by fitting the equations to the experimental results. Because of the complexity of fixed bed systems, this is the only other main approach (in addition to the previously mentioned equilibrium approach) that has been utilized for the analysis of ion exchange columns. The form of these equations has been varied, but they are usually based on first or second order reaction kinetics. The rate coefficient in these equations is assumed to be an overall mass transfer coefficient and is assumed to be related to the additive diffusion resistances in the film and particle phases of the resin.

The batch test data was analyzed in order to give insight on the relative rates of removal of the different ions by each of the resins used. The tests (Fig. 4 to Fig. 7) showed that inorganic carbon tended to reach equilibrium after 20 to 30 minutes with sulfates and the organics generally taking about one hour. Chloride would be expected to appear as the stoichiometric replacement due to the combined removals of the other ions.

When the batch test was plotted on semilog paper (Fig. 8 to 11), the plots revealed that the initial portions of the graphs tended to be linear for both sulfate and chloride. This indicates that the rate of removal is directly proportional to the concentration of the ion in solution and therefore a first order kinetic model would be appropriate. The removal of organic carbon on a semilog plot is not a linear function, except in the initial portions of the removal curve. This may be due to the fact that the organics consist of a diversity of compounds which have different molecular weights and charges.

To evaluate the relative rates of removal, the first order rate coefficients (expressed in base e) were calculated based on the initial linear portions of the removal curves for the various ions. (Table 6).

Table 6. Removal Rate Coefficients

	IRA-400 (k,min ⁻¹)	IRA-401S (k,min ⁻¹)	Al-P (k,min ⁻¹)	IRA-938 (k,min ⁻¹)
TIC	0.038	0.026	0.047	0.045
Sulfate	0.048	0.045	0.067	0.049
TOC	0.011	0.015	0.033	0.105

Figure 8.

Semilog Plot of Kinetic Data
Resin IRA-400

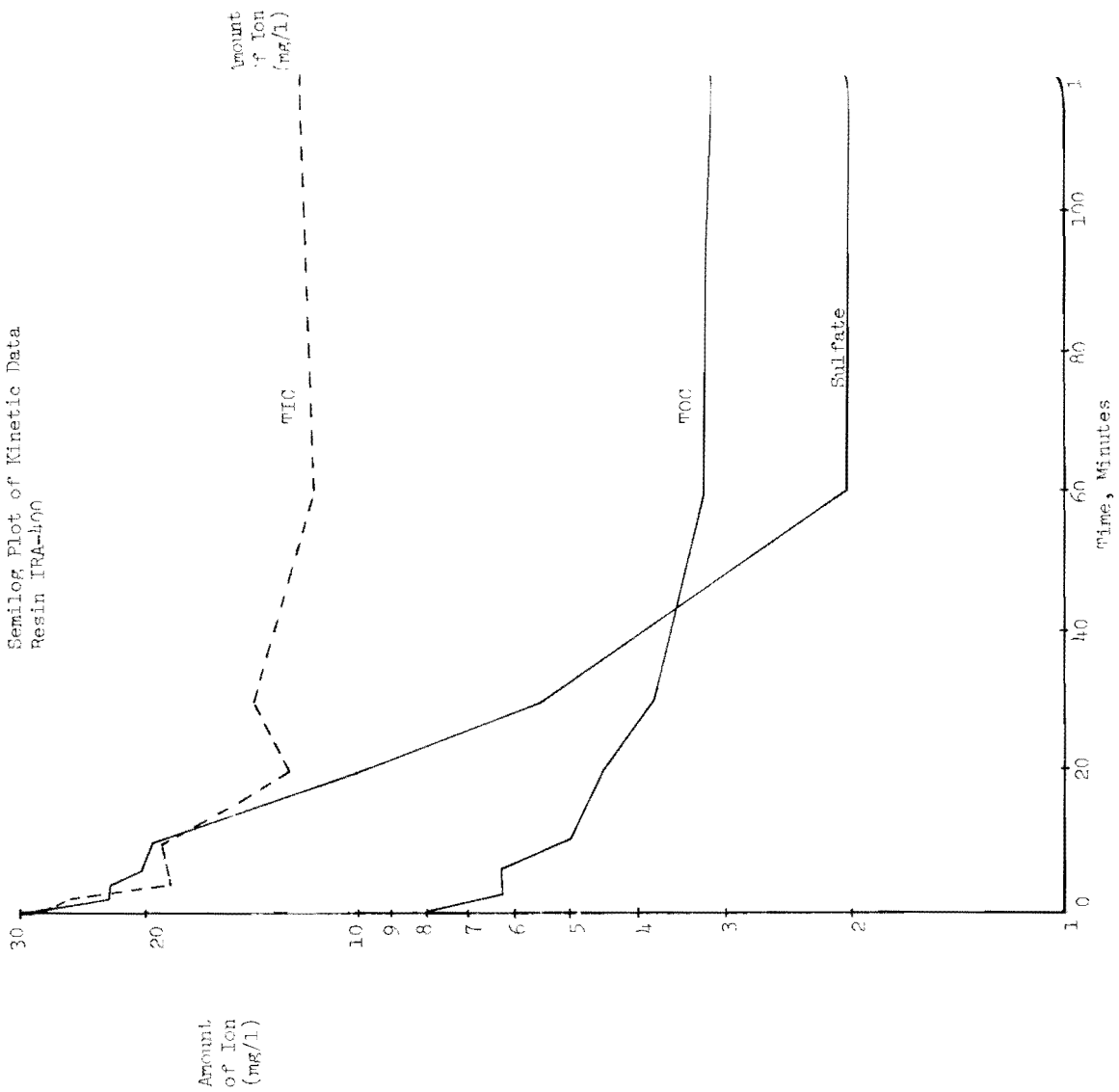


Figure 9.

Semilog Plot of Kinetic Data
Resin IRA-401S

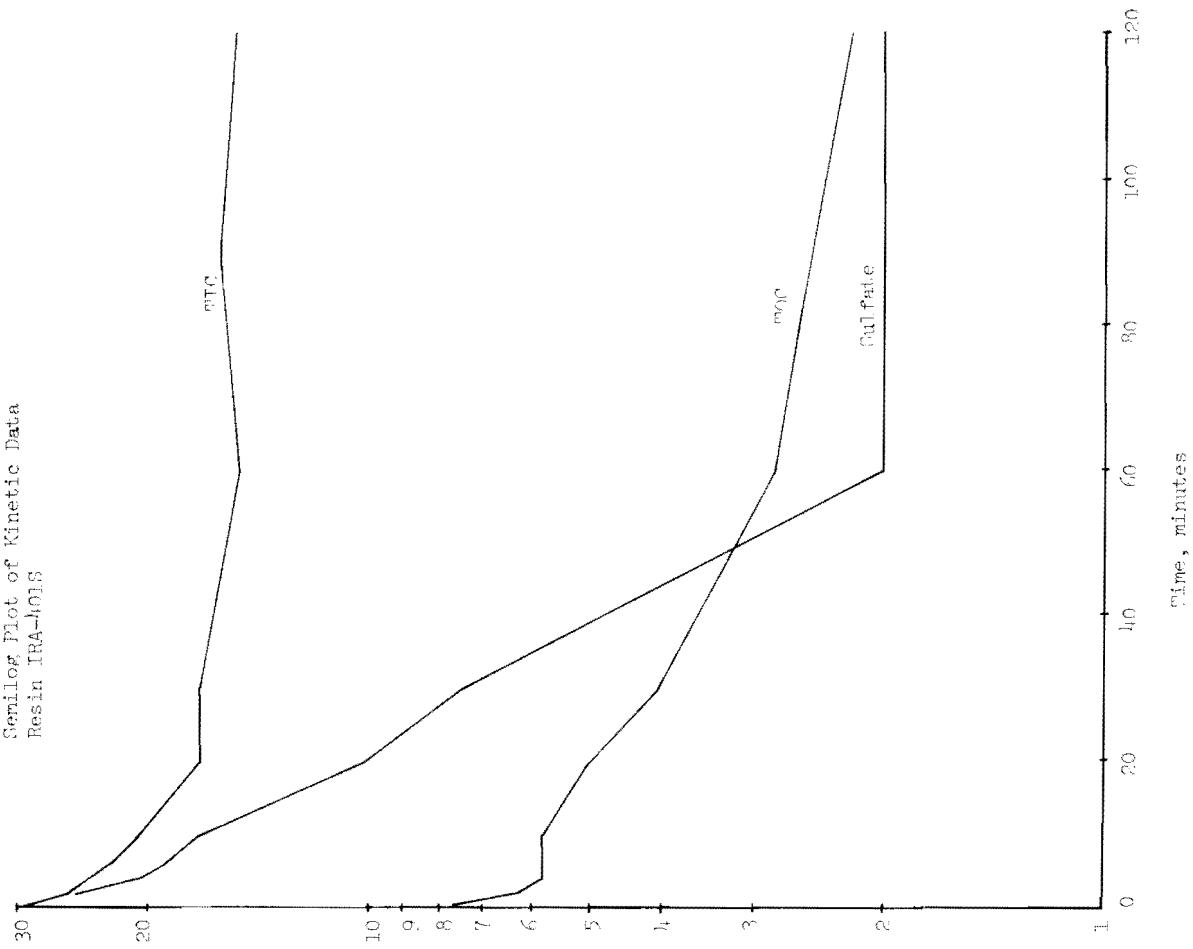


Figure 10.

Semilog Plot of Kinetic Data
Resin A-1P

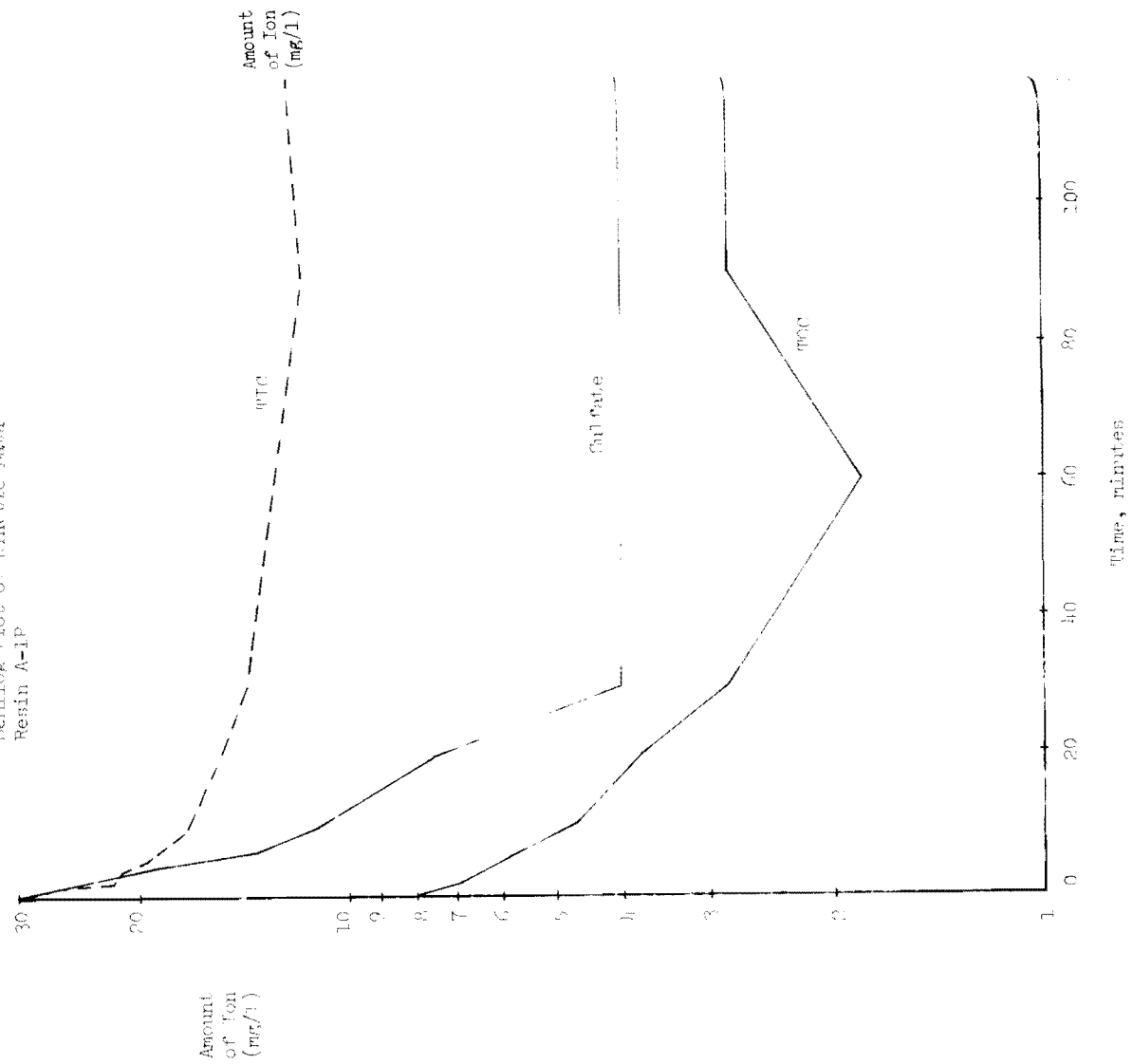
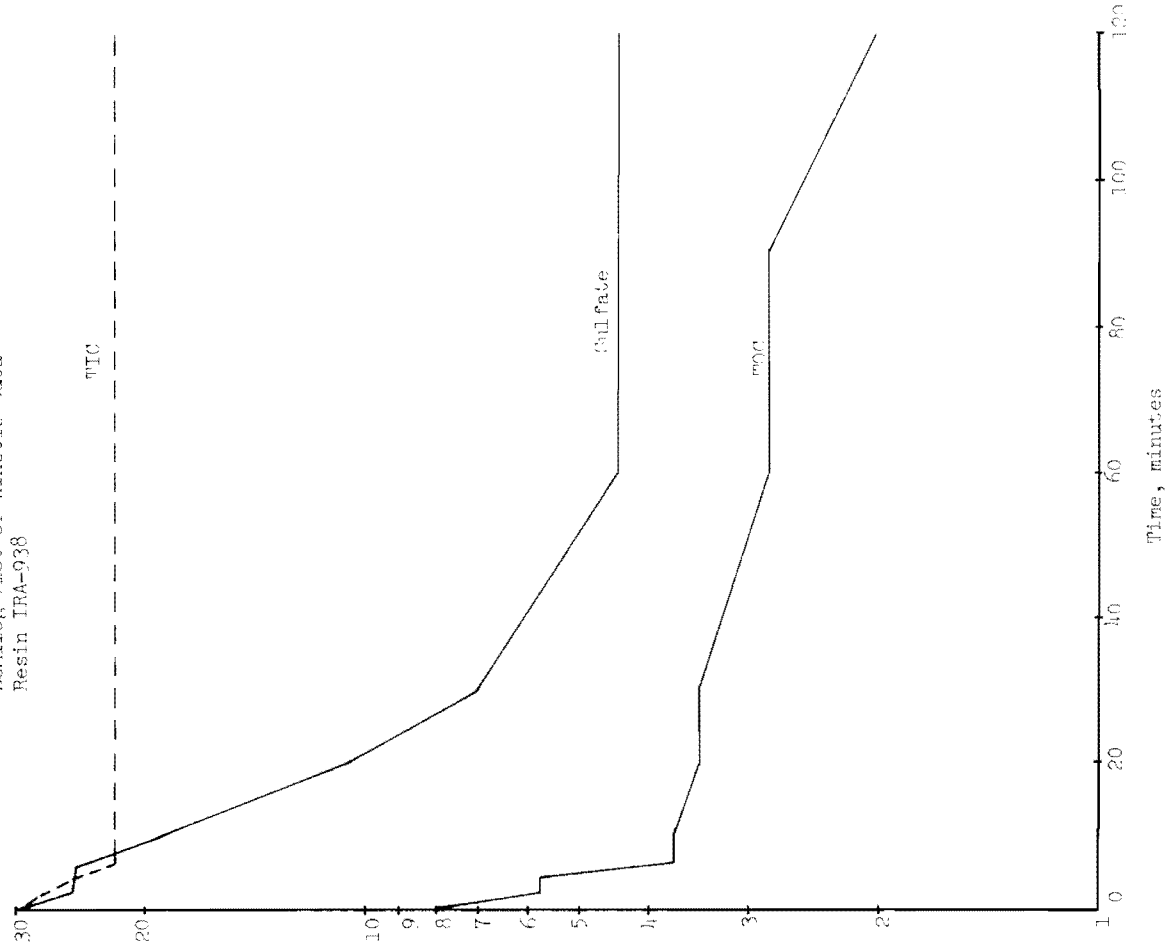


Figure 11.

Semilog Plot of Kinetic Data
Resin IRA-938



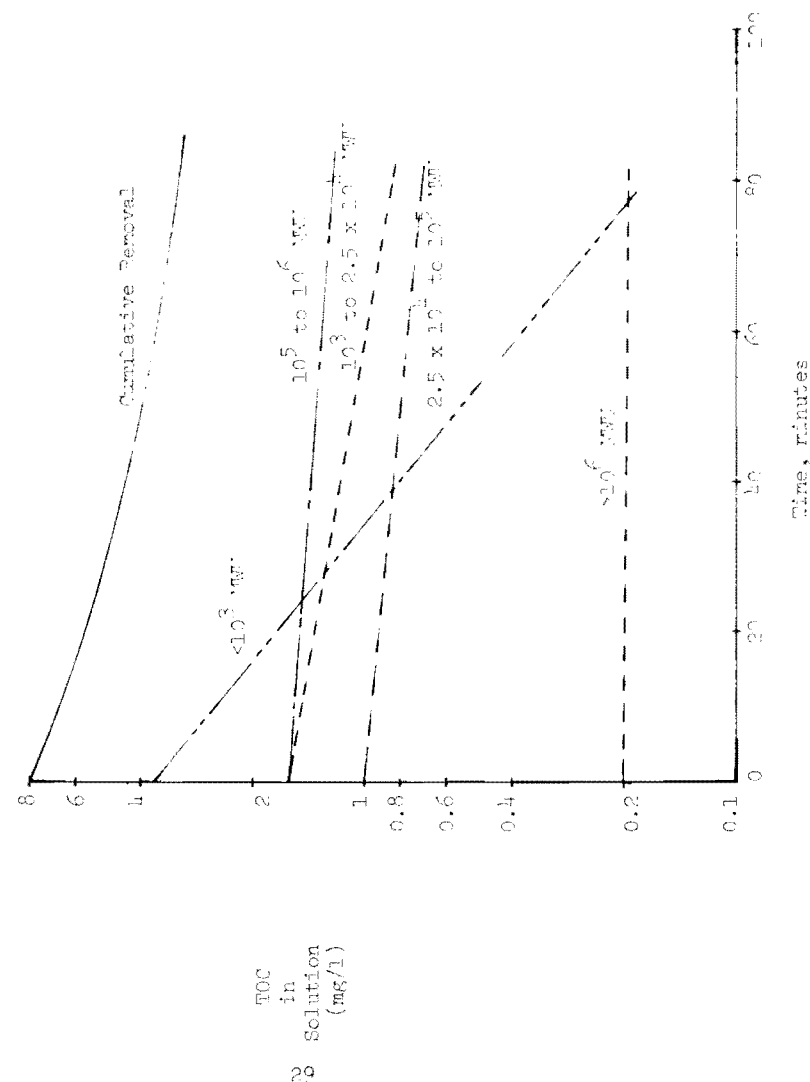
For bicarbonate and sulfate removal there is no definite trend which would relate removal to the extent of crosslinking, so the variation between resins is probably due to other factors, which may be influenced by crosslinking. Organics, on the other hand, do show a trend toward higher rates of removal with higher resin porosities. This implies that the rate of removal of organics in the highly crosslinked resins is limited due to the small pore size in relation to the relatively large organic molecules. It is interesting to note that the relative rates of removal for sulfate is higher than for inorganic carbon which is higher than the rate of removal of organic carbon, except in the case of the macro porous resin IRA-938 which has equal rates of removal for sulfate and inorganic carbon with a very high rate for organic carbon. However, it should be remembered that for the organic carbon rate coefficient, we are only using the first portion of the curve, and that following this there is a certain amount of organics that are being removed at a slower rate.

To test the hypothesis that the differences in molecular weights of the organics may be responsible for the curvature of the organic carbon removal versus time curve, the carbon data was analyzed by subdividing it into several average molecular weight fractions. The diffusion coefficients were calculated from published correlations (26) between the molecular size of a molecule and its diffusion coefficient in water. It was assumed that the first order rate coefficient for each molecular weight fraction is proportional to the diffusion coefficient. These coefficients are listed in Table 7. The rate coefficients for the organic fractions were obtained by assuming that the diffusion coefficient and removal rate coefficient of the organic fraction M.W. = 100 and the sulfate ion were equal. The rate coefficients for the other organic fractions were then backcalculated. These coefficients are also listed in Table 7. Figure 12 shows the removals of the various organic fractions using a first order kinetic relationship and the given coefficients. The resulting cumulative removal curve for total organic carbon is the summation of the individual fractions. The result is that the plot is indeed curved when plotted on similog paper. The fact that the curvature is not as pronounced as the actual data implies that the difference in diffusion coefficients in the resin were different than those used, which were in water.

Table 7. Variation of Organic Rate Coefficients Adjusted for Molecular Weight Differences.

Molecular Weight	TOC (%) (see Fig 1)	TOC (mg/l)	Diffusion-(Ref. 26) Coefficient (cm ² /sec)	Rate Coef ₁ (min ⁻¹)
100			0.7×10^{-5}	0.045
less than 10^3	48	3.6	0.5×10^{-5}	0.032
10^3 to 2.5×10^4	20	1.6	0.1×10^{-5}	0.0064
2.5×10^4 to 10^5	12	1.0	$.07 \times 10^{-5}$	0.0045
10^5 to 10^6	20	1.6	$.03 \times 10^{-5}$	0.0019
greater than 10^6	3	0.2	$.02 \times 10^{-5}$	0.0013

Figure 12.
Theoretical Cumulative Removal of Organics



Ion Exchange Columns

Ion exchange processes are generally carried out in fixed bed contactors with the solution passing through the bed. The fixed bed contacting method allows the solution to contact a number of layers of fresh resin in succession. It is therefore essentially a series of batch operations in which the solution does not necessarily come to equilibrium at each point. As the solution passes through the column, it exchanges its ions for the corresponding counterions on the resin until all the ions are exchanged. A continuing flow of fresh feed solution eventually saturates the column and the feed solution will pass through the column unchanged.

The ion exchange zone is the portion of the column in which the actual exchange process is taking place. As the run continues it will move down the column and eventually breakthrough will occur, that is some of the incoming ions will be found in the effluent. At breakthrough the bottom layers of the bed are not completely exhausted, thus the capacity at breakthrough is less than the resin's ultimate capacity. The breakthrough capacity is dependent on the nature of the process along with the operating conditions. The ultimate or total capacity is dependent on the resin capacity and the total amount of resin. Although the ultimate capacity does influence the breakthrough capacity, it is the breakthrough capacity which is utilized in an ion exchange process.

For any given resin and feed solution, the breakthrough capacity is determined by the depth of the adsorption zone (or zone of ion exchange). Each volume element of the resin is in contact with the solution for only a limited amount of time (usually 3 to 10 minutes for the entire column). This is usually an insufficient amount of time for the attainment of a local equilibrium, which means that kinetics are usually very important in determining the size of the ion exchange zone. Hence, any measure that increases the ion exchange rate, decreases the length of the ion exchange zone and thereby increases the effectiveness of utilization of the resin. There are a number of variables that can be controlled to some extent in water treatment which would help to promote a high utilization of the resin. These are; 1) small and uniform particle size, 2) a high volume capacity of the resin, 3) a low degree of crosslinking, 4) a low flow rate, 5) low concentrations of competing ions in the feed solution and 6) a long column. The optimum combination of these variables depends on the design requirements and economics. For design purposes, when a new application for a process is being considered, it is desirable to obtain data on the specific water to be treated.

In order to obtain data which could be used for preliminary design purposes, as well as to evaluate anion exchange columns as to their effectiveness for organic removal, a series of columns were set up using weakly basic anion exchange resins and strongly basic anion exchange resins with varying degrees of crosslinking (porosities) to evaluate their removal of organics from a natural surface water.

Experimental Procedure

Six columns of different anionic resins were used. Four of the resins were strongly basic anion exchange resins with differing porosities and two were weakly basic resins, their general characteristics listed in Table 2. The columns were prepared in 50ml burets in which a fiberglass plug approximately 5 cm in length was inserted to provide support for the resin. The resin was placed in water, allowed to swell and then approximately 25 ml (28 cm) was added to the columns. A Nalgene funnel was fitted on the top of the column to provide a fluid reservoir and the resulting joint was sealed using teflon tape. The flow rate of the column was adjusted using the valve at the base of the buret. The funnel reservoir was refilled as necessary and fractions were collected at the base of the columns.

The strongly basic resins were pretreated by alternate washings with normal solutions of sodium hydroxide and sodium chloride until no organic carbon, as measured by TOC analysis, was discernible in the effluent using the concentrated salt solution. The weakly basic resins were rinsed with hydrochloric acid rather than with sodium hydroxide since these resins are not ionized at high pH's. Methanol was also required since an organic free effluent could not be obtained without its use, due to a continual low level leaching of the column prior to its use.

The characteristics of each of the columns are listed in Table 8. The capacity data was determined by putting the column in the hydroxide form using sodium hydroxide, rinsing the column with sodium chloride and then titrating the recovered sodium hydroxide with standardized hydrochloric acid.

Table 8. Column Specifications.

Column	Resin	Volume (ml,)	Length (cm,)	Capacity (meq,)
1	IRA-400	24	26	26.3
2	IRA-401S	28	30	21.8
3	AI-P	28	30	29.8
4	IRA-938	28	30	12.6
5	AGA-316	26	28	n.d.*
6	IR-45	25	27	n.d.*

* Not determined

Using Mississippi River water as the feed solution, the six columns were concurrently run to determine their effectiveness for organic removal. The resins were all initially in the chloride form. The Mississippi water was filtered through 3.0 micron filters, the purpose was to remove the sediment which would cause the column to clog. Characteristics of the filtered water are listed in Table 9.

Table 9. Mississippi River Water Characteristics*

Sample No.	1	2	3
Date	4-16-76	5-7-76	5-21-76
Chloride (mg/l)	5.4	6.8	12.0
Sulfate (mg/l)	7.0	11.0	29.5
TOC (mg/l)	9.1	6.2	7.8
TIC (mg/l)	23.8	36.0	36.8
Nitrate (mg/l)	0.1	0.1	0.1
pH	7.8	8.7	8.5

* Samples collected at University of Minnesota, Minneapolis, Minnesota

Two and a half liters of filtered Mississippi River water (Sample 1 of Table 9) were passed through the columns. The effluent was collected in 250 ml. fractions. These were then analyzed for TOC, TIC, pH, chloride and sulfate. Since there was very little variation between the samples of any individual column, average values for the ten fractions have been calculated and listed in Table 10.

Table 10. Ion Exchange Column Performance.

Resin	Raw Water Sample	TOC mg/l	TIC mg/l	Chloride mg/l	Sulfate mg/l	pH	Flow ml/min
IRA-400	1	1.6	0.7	110	0.0	5.7	4.1
IRA-401S	"	0.9	1.1	112	"	5.3	4.5
A-1P	"	0.4	0.7	107	"	5.7	4.6
IRA-928	"	0.5	3.7	95	"	5.9	4.3
IR-45	"	3.4	3.7	121	"	4.0	4.7
AGA-316	"	4.0	4.7	136	"	3.8	4.8
IRA-400	2	0.5	48.4	0.0	"	7.5	3.8
IRA-401S	"	0.4	47.1	0.0	"	7.7	3.8
A-1P	"	0.3	48.7	"	"	7.6	4.4
IRA-938	"	0.1	45.6	"	"	7.8	4.2

To remove the adsorbed anions, one normal sodium chloride was used as the regenerating solution (results are discussed below). A one normal solution of sodium bicarbonate was then applied to put the columns in the bicarbonate form. This was done, because bicarbonate ion is the major anion in the surface water used, and if the organic carbon can replace this anion (as the selectivity data suggests) the capacity of the columns for organics would be increased. The columns were then rerun, the procedure being the same as was used in the previous run, with the exception that water sample 2 (Table 9) was used.

The results of these two experiments show that the columns using strongly basic resins are better for the removal of organics than the weakly basic resins. The weakly basic resins removed from 40% to 50% of the TOC while a number of the strongly basic resins removed organics to levels below the detectable limits. There appears to be a trend toward increased removals with the use of the higher porosity resins. This effect is very pronounced in the columns using chloride as a replacement ion. The effluent in the columns using chloride goes from 1.5 mg/l for the medium porosity resin to 0.4 mg/l for a high porosity resin. The effect is less pronounced for the same resins using bicarbonate as the replacement ion, where the range is from 0.5 to 0.1 mg/l for the medium and high porosity resins respectively. As was anticipated, bicarbonate was in fact displaced by the incoming organics. In fact, it appears that the removal of organics by the resin is enhanced when bicarbonate is the replacement ion. This would be unexpected based on the previously discussed selectivity data obtained from the batch tests which showed that the attraction of the resin for the chloride or bicarbonate ions should be approximately equal at these concentrations. However, the removals for organics are high for both sets of experiments and the concentrations found in the column effluents are at or near the lower limits of detection. So, although the inorganic carbon is definitely displaced by the organics, whether or not it's displaced faster or easier than the chloride cannot be completely determined at this time.

Because of the promising results from the tests on the strongly basic resin, extended runs were conducted on these columns. These columns were as previously described and in the chloride form. Water sample 3 of Table 9 was used in this experiment as the raw water. One liter fractions were taken and these were analyzed for the major ions as previously described. The results of these analysis are shown in Figures 13 to 16.

For these runs, the inorganic carbon begins to break through the column after only 2 to 3 liters of water have been treated. As the concentration of inorganic carbon slowly rises to the amounts that are slightly higher than those contained in the incoming water, the concentration of chloride in the exchanged sample concurrently decreases. With the exception of column 4 which contains IRA-938, sulfate does not appear in the effluent and the TOC stays near or below 0.5 mg/l which is the lower limit of detection.

mg/l
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L
A
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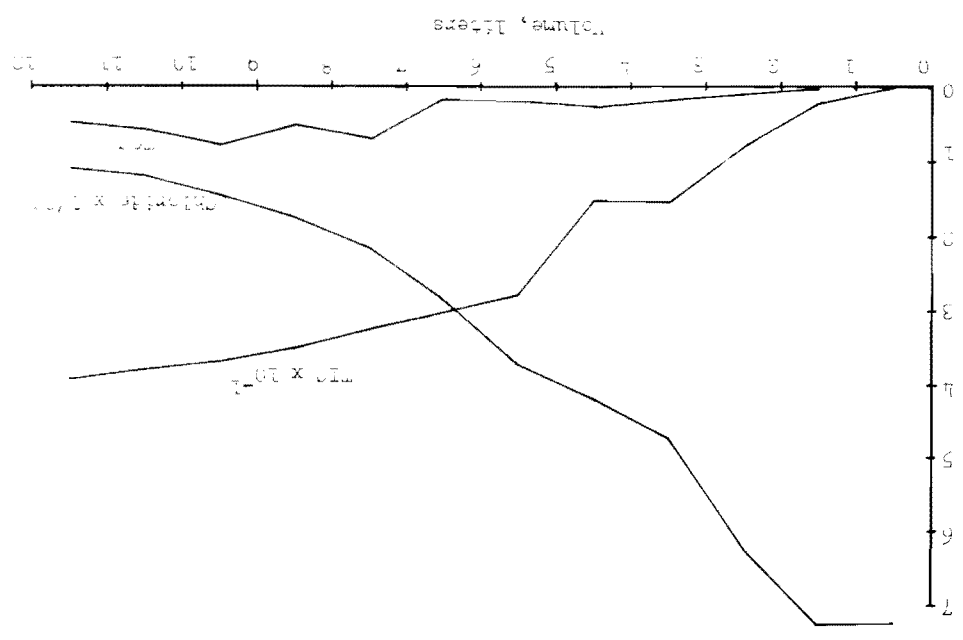


Figure 12.

mg/l
N
O
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L
A
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O
N
C

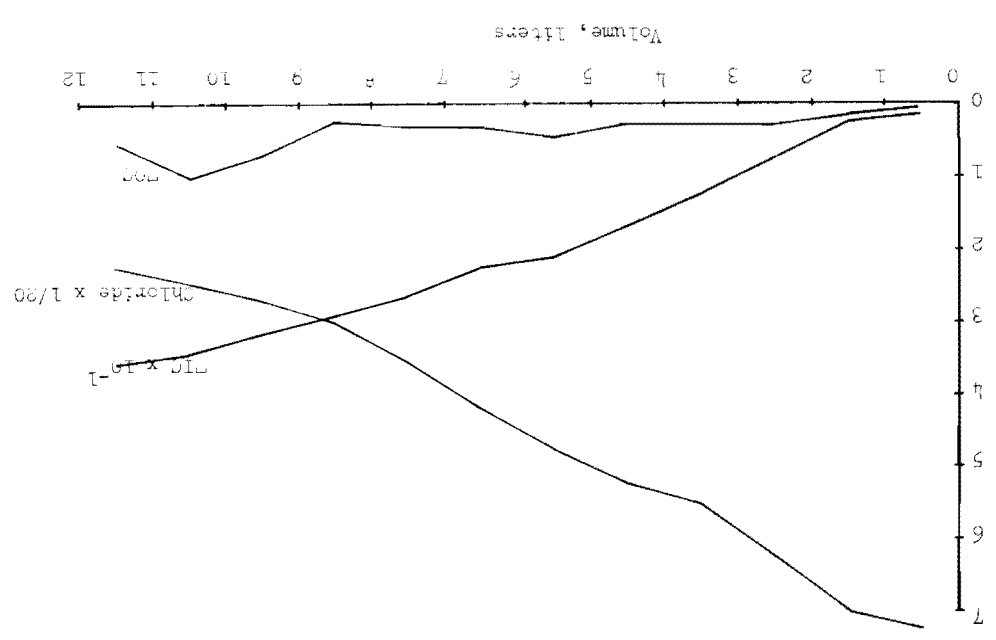


Figure 13.

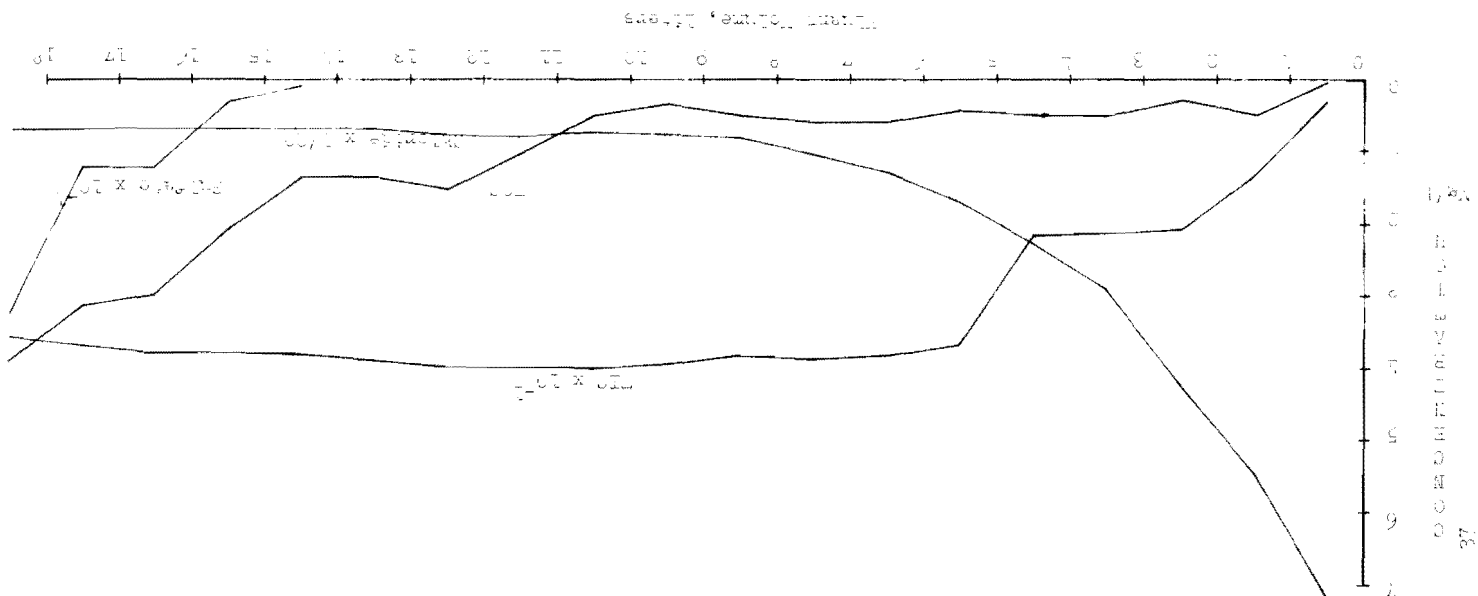


Figure 17.
 Column Result Bed 10A-03
 Flow rate = 4.0 ml/min.

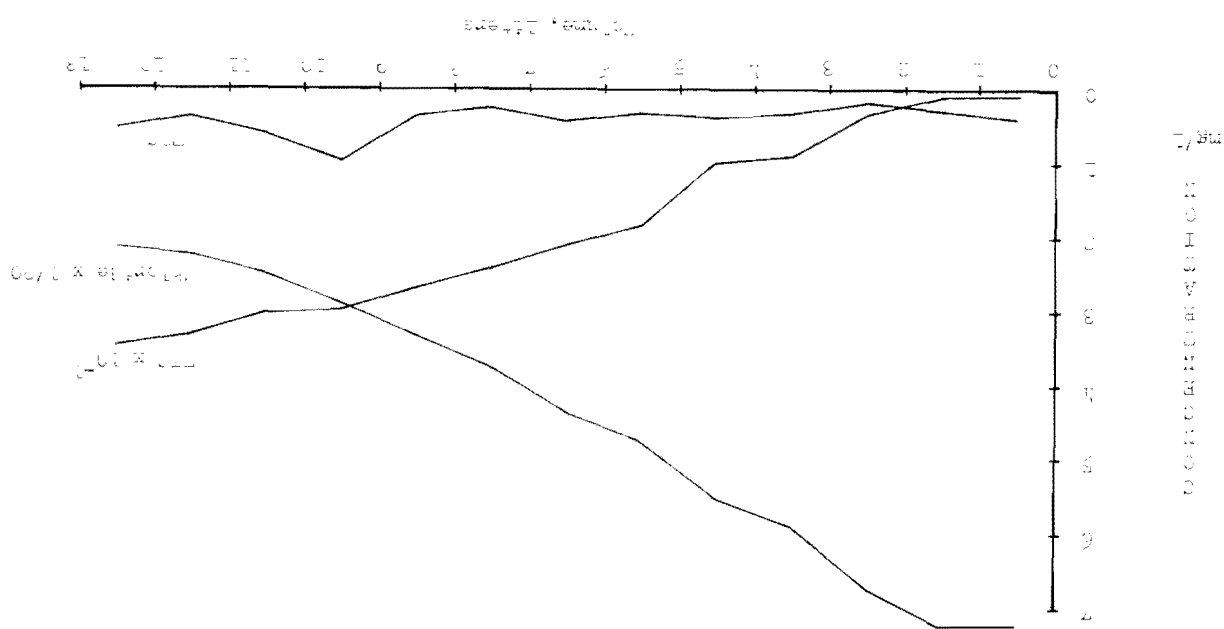


Figure 18.
 Column Result
 Bed 10A
 Flow rate = 4.0 ml/min.

Column 4 however does show a very definite breakthrough of TOC. The breakthrough begins after about 10 liters of sample have been used and continues at a very slowly increasing rate for the remainder of the test. Sulfate also breaks through this column, with the beginning at about the 15 liter mark. This breakthrough profile is considerably sharper than that obtained from the organics. The reason that organic breakthrough begins with this column before the others is due mainly to its lower capacity which is about one half of the capacity of the other columns.

The amount of each ion removed during the duration of the run of column 4 is summarized in Table 10A. The inorganic carbon does not affect the organic removal since it displaces the chloride, but then can be displaced by other ions. The amount of organics removed on a mass basis is fairly significant, however only about 4% of the capacity of the column is used by the organics at breakthrough, with most of the resin being in the sulfate form.

Although the selectivity coefficient of this particular resin is about ten times higher for the organic carbon than for the sulfate ion, sulfate begins to breakthrough after the organic breakthrough has begun. The reason is probably due to the drastic differences between these ions, differences which the selectivity test cannot take into account. The first of these is the large size of the organic molecules in relation to the sulfate ions. Thus it may be that although the equilibrium may favor the organic molecules, the kinetics of the ion exchange process may not allow access of the relatively large organics to the ion exchange sites, even for the high porosity resin that is being considered in this case. Another likely possibility is that because of the diverse nature of aquatic organics there are a variety of organics each with different selectivity coefficients, and what was measured in the batch test was a cumulative or overall selectivity coefficient. This would mean that what is being observed in the ion exchange column is a summation affect of a number of different organics each with its own breakthrough curve. Any of these considerations would of course also tend to widen the overall organic breakthrough curve, which is also experimentally observed.

Table 10A. Column Capacity.

	Resin IRA-938	
	Removals ($\frac{\text{mg. TOC}}{\text{ml resin}}$)	Removals ($\frac{\text{meq. TOC}}{\text{meq. Resin}}$)
TIC	5.46	1.02
TOC	4.56	0.04
SO	18.0	0.84

Regeneration of Ion Exchange Columns

The previous portions of this section have been concerned with the removal of the organic materials from a water supply. This is of course an important item of concern. However, the attractiveness of the ion exchange process is in its ability to be completely regeneratable by a reversible process which removes the contaminates from the resin to produce a highly concentrated waste stream. To whatever extent this is true, a great deal of the potential usefulness of this process will depend. In order to evaluate this parameter of the resins used, a mass balance was done comparing what was removed by the resin with what was found in the regenerating solution.

Sodium chloride was used at a one normal concentration. This particular salt is often used for ion exchange regeneration because of its high solubility and relative economy along with the fact it is a relatively 'safe' compound to use or handle.

The results of a mass balance for run number 2 are shown below in Table 11. The results show that the resins were regenerated completely with the exception of the low porosity resin IRA-400, which still shows fairly good recovery of organics. The results from the high porosity resins are not surprising since in fact these were developed and are noted for their ease of regeneration, especially when dealing with the large organic ions. The fact that IRA-400 is not completely regeneratable indicates it would not be suitable for this type of organic removal.

Table 11. Regeneration of Ion Exchange Columns.

Resin	Percent Recovered
IRA-400	82
IRA-401S	102
IRA-938	108
A-1P	101

PRELIMINARY DESIGN AND COST ESTIMATE

Although good removals of the organics found in natural waters was achieved by the use of strongly basic anion exchange columns, the practicality for its use on an existing plant or the possibility for its inclusion in a treatment plant depends on the cost of the project versus the benefits received. In order to evaluate the costs, it is necessary to design a particular facility and estimate its cost.

The important costs in any system, including ion exchange facilities would be, 1) capital costs which include the column facility, regeneration storage tanks, pumps, and the associated piping, valving and control equipment, 2) operating costs which would include labor, salt, resin, maintenance, power and brine disposal costs. The capital costs are set primarily by the design flow rate and flow velocity. These are set by the design engineer and through his choice of loading parameters the size of the facility is established. The operating costs are of course also affected by the volumes and rates of flow, but included are effects due to flow quality along with resin capacity and durability. These being of major importance through their influence on the salt and power requirements along with waste disposal costs.

Ion exchange is generally noted as a fairly expensive water treatment process. It is stated that for waters with over 100 mg/l TDS ion exchange is generally uneconomical (37).

To determine if this process would be economical a cost estimate was done which would pertain to a municipality that wants to expand its facilities to include organic removal with the use of a strongly basic anion exchange resin. The proposed plant would be in the Twin Cities area in Minnesota and would have a design capacity of 10 mgd and use surface water as its source of raw water.

As previously stated, the water's chemical characteristics are a very important cost consideration. For this reason costs will be evaluated for the average water quality along with what would be the consequences if the expected high values for the year in fact became the average values for a year due to a change in water quality. The water quality data used is given in Table 12 and is typical for the Mississippi River in the Minneapolis-St. Paul area. This data was obtained from the Minnesota Pollution Control Agency, the National Water Quality Network publications with the TOC and TIC estimates coming from data obtained by a long term study done by the University of Minnesota Department of Civil and Mineral Engineering which was done in cooperation with the MPCA. The equivalent weight of the organics was estimated as discussed in Section 1.

To evaluate the amount of resin that is required it must be recalled that as stated in Section II all the exchange capacity is not utilized in a column run before regeneration is required. In order to determine the fraction of the column that can be actually utilized for ion exchange it is necessary to estimate the size of the exchange zone in the column.

This zone has some finite length and is dependent on the selectivity, particle size and porosity of the resin as well as the operating conditions which include flow rate, initial concentration of ions and temperature. An estimate of the size of this zone has been given at 3 to 4 inches (25). However, it is also possible to estimate the length based on the previously discussed column experiments.

Table 12. Predicted Water Quality Data.

Chemical Parameter	Average		Maximum	
	mg/l	meq/l	mg/l	meq/l
Total Organic Carbon	10	0.083	30	0.250
Total Inorganic Carbon	30	2.5	50	4.17
Nitrate	0.2	0.0032	1	0.016
Sulfate	30	0.625	90	1.88
Phosphate	0.1	0.0032	1	0.032

An examination of the breakthrough curve of column 3 reveals that as a first approximation a linear breakthrough profile could be satisfactory as an estimation of the unused capacity. Taking the organic breakthrough profile as a linear function beginning after 11.0 liters of sample were exchanged, the length of the exchange zone is 18.6 cm. (7.3 in.). This is slightly higher than the previously referenced values and is likely due to a combination of the effects which have been previously discussed.

For the design of this system, loading parameters that were typical of those used in the bench scale column tests were chosen. The volumetric loading rate of 0.25 m³/minute/m³ resin was used. A depth of 150 cm. was chosen based on recommended depths for anionic columns used on a commercial scale (26). Based on these parameters the columns would have the following dimensions:

Utilizable depth = 141 cm.
Utilizable capacity = 94% of total
Resin volume required = 107.6 m³
Area = 71.73 m²
Flow velocity = 0.61 cm. per sec.

In order to provide a certain amount of versatility in operation and to ensure some margin of safety six ion exchange units will be used, five of which will handle the total design flow. This would allow one spare unit to be used during the regeneration cycle during peak flow conditions. A summary of the tank dimensions is below.

Table 13. Summary of Physical Characteristics.

Number of tanks	6
Individual tank area	14.35 m ²
Tank diameter	4.27 m
Tank height*	2.62 m ³
Total tank volume	226 m ³
Resin required (6 tanks)	129.2 m ³

* Total height includes resin height plus space for bed expansion during backwashing.

Cost Estimate

Equipment and Facilities:

These costs include ion exchange equipment, pumping equipment, controls and their installation along with the buildings to house these facilities. These cost estimates were based on a number of sources (12,25,26), with all prices adjusted to 1976 dollars.

The fixed costs have been summarized in Table 14. The total amount of the facility is estimated at one million, which would require an annual cost of \$94,540 if financing was provided over a twenty year period at an interest rate of seven percent.

Operating Costs:

The operating costs are the yearly costs that are incurred during the operation of the facility. These include resin costs, salt for regeneration, labor, maintenance, power and brine disposal costs.

The resin costs are based on a five year life of the resin, which is usually the life estimate chosen for anion exchange resins (25). The resin cost used was typical of strongly basic resins bought in bulk quantities in 1976. The cost for 129.2 m³ of resin at \$3530/m³ would total \$455,000. This would result in a yearly cost of about \$91,100.

Salt costs are directly proportional to the equivalents that have to be removed from the ion exchange column and the efficiency with which the salt can do this. Therefore salt costs depend not only on the flow rate, but also on the concentration of the ions removed. This means sulfate, TOC, nitrate and phosphate ions in this example. A regeneration efficiency of 80% on an equivalent basis will be assumed. With an average use of 2275 kg/day and a cost of \$0.044/kg., the cost of salt would be \$100/day (\$36500/year) for the average ion concentration or \$300/day (\$109,500/year) if the maximum concentration of ions considered was present.

Table 14. Ion Exchange Units.

	Unit Price \$/10 ³ CF	Volume 10 ³ CF	Cost 10 ³ dollars
Equipment	40,000	1.3	52
Controls	18,000	1.3	23.4
Installation	20,400	1.3	26.5
Total/unit			101.9
Total (six units)			611.4

Buildings	Unit Price	Size	Cost
Shell Cost	\$430/m ²	164 m ²	70,600
Concrete costs	\$235/m ³	82 m ³	19,270
Total Building Cost			89,870

Pumps

Total pump costs 100,000

Miscellaneous Costs

Estimated at 20% of total 200,300

TOTAL FIXED COSTS, DOLLARS 1,001,600

Yearly financing costs, 20 yrs., 7% 94,540

In this case a manually operated ion exchange unit was used. It may however, be desirable to have automated units in a process of this magnitude. This choice would have to be evaluated by a more detailed study. The amount of labor required is estimated to be about two hours per unit for each cycle (25). The length of the cycle run will vary depending on the water quality of the incoming water and the available resin capacity. For the average water quality the cycle run was estimated at 1.37 days while for the worst quality it was estimated at 0.45 days. Taking labor costs at a rate of \$6.00/hr. the costs would be \$43.80/day (\$16,000/year) at average conditions or \$132.00/day (\$48,000/year) at the maximum concentration of removable anions.

Power costs will be due mainly to the cost of the head loss through the ion exchange columns. This depends on the resin and the flow rates through the column. For 10 mgd going through the five columns and a cost of \$.02/kwh the electricity would cost \$10.29/day or \$3,750/year.

Maintenance costs are variable throughout the life of the project. They are usually negligible during the first years of operation, increasing as the equipment ages. For this project an annual value of 2% of the capital cost per year will be assumed to be the maintenance cost. This would amount to a yearly cost of \$20,000.

Disposal of the waste brine is a crucial portion of the overall project since it is here that the organic portion of the raw water is concentrated for final disposal. In addition to the organics, the brine will also contain a considerable amount of inorganics such as chlorides and sulfates, with sodium being the predominate cation present. The actual disposal process used would depend on the plant size and location. For small plants discharge into a sanitary sewer, brine disposal wells, or dilution with surface waters may be possible. For larger plants evaporation ponds or a recovery and reuse system may be utilized. Using a one normal sodium chloride solution for regeneration the average volume of brine would be 38.9 m³/day (10,300 gpd) while if the higher concentration of ionic species was present the flow rate would be 117 m³/day.

Disposal costs would vary depending upon which methods of disposal are used. If trucking the wastes to a site is necessary the costs for disposal could become very high. For this plant, disposal of the brine into the sanitary sewer system was proposed. The costs were estimated by the use of the strength charged system that is currently being proposed by the Metropolitan Waste Control Commission in Minnesota (27). The cost of discharging this waste into their collection system would be \$0.13/1000 gal. based on the estimated brine quality. This would correspond to average costs of \$23.94/day or \$8,000/year and maximum costs of \$65.60/day or \$23,900/year. If however some alternate form of brine disposal is deemed necessary the costs may go up dramatically. The effect of more expensive brine disposal is discussed later in this section.

The costs are summarized below in Table 15. It is apparent that the bulk of the cost goes into the facility and resin costs. At average estimated water quality the other operating costs only account for a relatively minor fraction of the total cost. However, the cost is very sensitive to the chemical quality of the water since these costs increased dramatically at the higher concentrations of ions causing a 40% increase in the total cost.

Table 15. Cost Summary.

	Average Cost Dollars	Maximum Cost ** Dollars	Percent **
Facility	94,540	94,540	35
Resin	91,100	91,100	34
Salt	36,500	109,500	14
Labor	16,000	48,000	6
Power	3,750	3,750	1
Maintenance	20,000	20,000	7
Brine Disposal	8,000	23,900	3
Total (1 year)	269,890	390,790	
Cost/m	.020	.028	
Cost/1000 gal	.076	.106	

* Cost computed with higher ion concentrations given in Table 11.

** Using the average yearly cost figures.

The cost of \$0.076/1000 gal. is a fairly expensive unit process and would probably increase the cost of water by about 20 to 30% of current costs. It is however in the same range of other EPA processes which have been proposed for organic control. A recent EPA study estimated that to remove organics by activated carbon adsorption for a 10 mgd plant would cost \$0.12/1000 gal and to remove volatile organics by aeration would cost \$0.07/1000 gal (34).

An analysis was also done on some of the assumed parameters other than water quality (which has been done) to determine their effect on the price of this process that has been previously calculated. This has been summarized in Table 16.

Table 16. Variation of Costs.

Item	Used Parameter	New Parameter	Change in Cost (cents/1000gal)
Loading Rate	0.26min. ⁻¹	0.2 min. ⁻¹	+ .6
Resin Life	5 yrs.	3 yrs.	+ 1.7
Interest Rate	7%	9%	+ .4
Brine Disposal per 1000gal	\$0.13	\$0	+ 1.8

This shows that water quality is the most important single parameter with respect to total costs. However, it must be remembered that it required a 300% increase in the ion concentrations to produce a 40% increase in the cost of treatment. The resin life and the brine disposal method used will also have an affect on the total cost, although to a lesser extent than water quality. Generally however it appears that this is certainly an economically feasible alternative for the removal of the organics that now go through conventional treatment and appear in the drinking waters of this country.

SUMMARY AND CONCLUSIONS

This study was initiated to provide quantitative information on the use of anion exchange resins for organic removal. It was shown that the organics that are present in surface waters which currently pass through conventional treatment could be removed by anion exchange with the use of strongly basic anion exchange columns. It was observed that the organics were removed to the lower limits of detection of the total organic carbon analysis with the use of the high porosity strongly basic resins. These resins were also found to be easily regenerated with the use of sodium chloride.

The selectivity and kinetics of the chloride versus organic exchange process was briefly investigated. The reason being that this is a new approach to this problem and no data was available in the literature to provide information which could be used for preliminary design of a full scale treatment plant.

A preliminary plant design was done, the result showed that the process would be economically feasible and certainly competitive with alternate methods of organic removal, assuming that they would also prove to be as effective at organic removal as ion exchange. So, ion exchange could prove to be an effective, reliable and economical method to provide for the removal of organics for drinking water.

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