ORGANIC-IRON REMOVAL FROM

WATER SUPPLIES

by

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ABSTRACT

The purpose of the study was to determine if resins or activated carbon presently used to remove organic color from water supplies would also remove organically bound iron. The resins studied were Amberlite IRA 904, Duolite S-37, Dowex 11 and Amberlite IRA 498. The activated carbon used was Atlas Darco. Solutions of fulvic acid, fulvic acid-iron and humic acid-iron were passed through the resin columns. Amberlite IRA 904, Duolite S-37 and Atlas Darco activated carbon effectively removed (100% removal) fulvic acid but little fulvic acid-iron or humic acid-iron (35% and 5% respectively). Dowex 11 and Amberlite IRA 498 were less effective in removing fulvic acid than IRA 904, Duolite S-37 and activated carbon, and would not remove fulvic acid-iron or humic acid-iron.

A simple test for organically bound iron was developed and it was found that iron-organic interactions were time dependent. Humic acid-iron reactions were very quick (approximately 4 hours) while fulvic acid-iron reactions were much slower (15 days required for 57% of the iron to be strongly bound). It was found that a strongly bound fulvic acid-iron solution acts very much like a humic acid-iron solution precipitating at a pH of less than 4.7 and that the color increases considerably as the solution ages and the organic-iron binding becomes stronger.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGMENTS

SECTION 1

INTRODUCTION

For many centuries, dissolved iron has created a problem in municipal and industrial water supplies. The iron may be present as a ferrous or ferric complex, with water or some substituted ligand. The United States Public Health Service sets a recommended maximum limit of 0.3 mg/l of iron as being essential to make water aesthetically acceptable and potable. Iron concentrations above this value cause the deterioration of water quality due to the formation of ferric hydroxide by the oxidation of ferrous to ferric iron in the presence of dissolved oxygen. Color and rust-staining problems may occur as a result. Iron bacteria are also encouraged to grow at concentrations above 0.3 mg/l, and this growth may result in water quality problems such as:

1. Taste and odor caused by decaying bacteria.

2. Rust staining problems caused by the precipitation of ferric hydroxide by the iron bacteria.

3. Fouling and clogging of water lines due to the mass of biological growth.

4. Formation of red or black biological sludge which may break free of pipes and come out the user's water taps.

Generally, iron bacteria are thought to oxidize the ferrous iron to ferric iron and effect the precipitation of ferric hydroxide. This oxidation procedure is thought to provide the energy for growth of the iron bacteria. The strictly autotrophic iron bacteria such as Gallionella ferruginea are believed to depend totally on this reaction, while the facultative iron bacteria such as Leptothrix or Crenothrix polyspora can apparently grow by the above reaction or by the decomposition of organic compounds. The exact mechanism by which iron bacteria derive their energy from the oxidation of ferrous to ferric iron is not understood. Iron bacteria are typically aerobic, filamentous water organisms which accumulate large amounts of ferric hydroxide around their cells. This ferric hydroxide may be present in amounts many times greater than the bacterial cell material. Starkey (3) found that iron bacteria were able to survive in water ranging in temperature from $0^{\circ}C$ to $32^{\circ}C$, could live at very low dissolved oxygen levels and were relatively insensitive to light. Thus, they were very adaptable to living in pipes. The bacteria have been observed growing in water with an iron content as low as 0.3 mg/l.

Clark, Scott, and Bone (1) have carried out experiments which indicate that at least three of the heterotrophic bacteria normally encountered in water (Aerobacter aerogenes, Serratia indica, and Bacillus pumilus) have the capability of using an

organic acid-iron complex as a food source and will precipitate the iron out as a rusty stain. Starkey (3) has presented the results of Molisch and Cataldi which show that many iron bacteria are able to grow on organic materials and that there is reason to believe that these bacteria destroyed the organic acid, which then led to the precipitation of the iron as ferric hydroxide.

From the foregoing discussion, it can be seen that bacteria can exist in the presence of ferrous iron and organically-bound iron and that either may act as the energy source for the bacteria. By maintaining a chlorine residual, the problems caused by bacterial growth can be removed. The water is still aesthetically displeasing, however, due to color, rust staining, and an iron content which is higher than that recommended by U.S.P.H.S. standards. Problems caused by ferric hydroxide and bacterial growth can be controlled by removing the ferrous iron and the organic-iron from the water supply.

There are several successful methods for removing iron in the ferrous or ferric form from water supplies. Aeration of the water followed by sedimentation and filtration is the most common method. The high dissolved oxygen content attained by aeration causes the ferrous ion to be oxidized to the ferric ion which is relatively insoluble in water and precipitates as ferric hydroxide. The ferric hydroxide is allowed to settle

and the water is then filtered to remove the remaining suspended particles of ferric hydroxide.

Cation exchange resins have been used to remove ferrous iron, especially when the removal of calcium and magnesium is also required. When the ion exchange process is used, it is important that the water be kept at a low dissolved oxygen content to ensure that the ferrous ion is not oxidized to the ferric form, as precipitated ferric hydroxide tends to foul the resin beds.

A third method commonly used to remove ferrous iron is a contact filtration method using manganous zeolite or greensand. In this method the iron is removed by oxidation and filtration while passing through a bed of manganous greensand.

When organic acids are present in water together with iron, an organic acid-iron complex is formed which is much more soluble than ferric iron. This complex is often referred to as organically-bound iron. Iron in this form cannot usually be removed by any of the above methods. The removal of organically-bound iron from water supplies has been found to be very difficult, and many communities and single dwellings live with the organic-iron problem because they cannot afford to rectify the situation.

It is the purpose of this study to determine whether activated carbon or the newly-developed organic scavenger resins will remove the organic acid-iron complex from water supplies.

SECTION 2

LITERATURE REVIEW

2.1 WATER SOLUBLE ORGANIC ACIDS

Colored organics in water are thought to originate from
a multitude of organic materials present in forest vegetation
and soil. The classification of organic acids in colored water
as given by Black and Christman (2) and other investigators (39)
are fulvic acid, humic acid and hymatomelanic acid. The
fractionation procedure is shown in Appendix 1, and provides
the following fractions:

1. Ether-soluble fats and waxes are removed in a separatory funnel.

2. Fulvic acid is described as being that portion of
organic color which is water soluble at pH=1.

3. Humic acid and hymatomelanic acid are water insoluble
at pH=1. Therefore they precipitate at pH=1 and can be
separated from the water soluble fulvic acid portion.

4. Hymatomelanic acid is described as being soluble in
ethyl alcohol, while humic acid is not.

This fractionation procedure is quite crude, but is the
procedure most widely reported in the literature.

Black and Christman (2) found that fulvic acids are
aromatic polyhydroxy methoxy carboxylic acids. The equivalent

5

weight of fulvic acid was determined as being between 89-133 per equivalent. Shapiro (4) has reported an average molecular weight of 456 on the basis of isothermal distillation data. Titration in aqueous systems indicated an average equivalent weight of 228. Oldham (5) reports a molecular weight of 640 for the humic and hymatomelanic acid portions, with the average equivalent weight being 222. In later work with the use of Sephadex gel separation columns, Christman (43) discovered molecular weights ranging from 700 to 10,000 for the majority of color molecules. Hall (15) reports molecular weights from 700 to 50,000 for the colored organics in Lake Mary, Wisconsin. He used Sephadex gel columns to separate the various molecular weight fractions and found that only about 4% of the colored organics in Lake Mary had a molecular weight of less than 700.

From this discussion, it may be seen that the molecular weight of the water soluble organic acids varies widely. In part, this may be due to the amount of microbial degradation of the organic molecule that has occurred before sampling.

A widely-reported property of colored water is the variation of color intensity with a variation in pH. Singley, Harris and Maulding (6) have developed a nomograph which converts units of color at any pH to units of color at pH=8.3. As the pH increases so does the color intensity. This is also documented by Christman and Ghassemi (7), although they state that pH and color variations are not the

same for every colored water.

The chemical formulae of fulvic, humic and hymatomelanic acids appear to be rather elusive. Some authors such as Burges (8) believe that humic acid is either a single chemical substance or a group of very similar substances. Most authors believe that the composition of these color molecules is dependent on the source, the manner of extraction and the formation time of the organic substances. There may be a great many different chemical formulae for the various organic molecules in each of these acid groups.

Christman and Ghassemi (7) subjected colored organics in several natural streams to degradative chemical studies using oxidation with alkaline CuO as the degrading technique. Seven degradation products of natural organic color were identified: Vanillin, Vanillic acid, Syringic acid, Catechol, Resorcinol, Protocatechnic acid and 3,5-dihydroxy-Benzoic acid. According to Christman and Ghassemi (7), other investigators (9,10) have found the same products in degraded soil humic acid. Hall (15) subjected both colored organics from Lake Mary and soluble leaf extract to chemical degradation studies. Both the alkaline CuO oxidation procedure and the Na-Hg reductive procedure were used in these studies. He discovered the same degradation products as Christman and also seven more, consisting of p-Methylphenol, o-Methoxyphenol, Benzoic acid, 3-4-Dehydroxybenzoic acid, p-Hydroxybenzoic acid, dibutyl

Phthalate and p-Hydroxyacetophenone. He also discovered that different molecular weight fractions of organic color (separated by Sephadex gel columns) were chemically similar compounds, differing mainly in molecular size. Hall concluded that better degradative techniques and more understanding of these techniques would be required before one could identify all the chemical subunits and the groups which participate in linking the subunits to form the organic molecules.

Since organic color molecules are of a very complex chemical nature and their identification and separation is at present impossible, the separation techniques used to classify them as fulvic, humic, and hymatomelanic acids appear to be all we can do at present.

Of the three groups, Wilson(11) states that fulvic acid is the most water soluble fraction of natural soil humus and would be expected to be found in natural waters in higher concentrations than either humic or hymatomelanic acids. This is borne out by Black and Christman (2) who found that for 10 different water samples, the average percentage of acids was fulvic 87%, humic 2% and hymatomelanic 11%. Christman and Ghassemi (7) have indicated that no relationship between organic carbon content and color could be found for the several waters examined. Black and Christman (12) performed chemical analyses on nine different waters and found no correlation between organically-complexed iron and color, and no correlation between C.O.D. and color. They also found that B.O.D. values

were extremely low in all samples, which suggests that if the organic substances causing color in water are products of microbiological decomposition, they are in their final state or may only be further decomposed by specialized bacteria.

In an analysis of 32 lake waters, Christman (17) found that all color colloids were negatively charged. Making use of this phenomenon, Black and Christman (12) used electro-dialysis cells and membrane filters to determine that most color colloids ranged between 3.5 mμ and 10 mμ in diameter. They used light-scattering experiments which indicated that the color in their water was in the form of color colloids.

Other investigators have concluded that the color in water is made up of organic molecules in true solution. At such a small size range, it is probably quite difficult to tell whether the color is made up of large organic molecules in true solution or an organic colloid.

2.2 ORGANIC ACID-IRON COMPLEXES

Many different complexing possibilities have been put forward by various authors. Babcock (13) believes that iron can be held in solution by "protective organic colloids". In studies of the oxidation rate of iron in aerated ground waters, Ghosh (14) indicates that organic matter may chelate ferrous and ferric ions. In Faust and Hunter's book (39), p. 245, it is suggested that metal chelates with organic ligands

are much more stable in dilute solutions than are metal organic
complexes.[1] Shapiro (4, 16, 39) in a series of experiments
concludes that iron precipitates may be peptized by adsorption
of organics. Oldham (5) indicates that the organic molecules
and ferric iron are in true solution with an equilibrium
constant of 1.46×10^4 at pH=2. In Faust and Hunter's book
(39), Schnitzer p. 308 found that 1:1 molar solutions of
Fe^{+3} or Al^{+3} to fulvic acid complexes were completely water
soluble, 2:1 complexes were less soluble and 6:1 complexes
were water insoluble.

Thus it may be seen that much experimental work has been
done. However, when considered as a whole, the results are
inconclusive. The mechanism of complexation may be any one
or a combination of all the above methods.

2.3 ORGANIC COLOR AND IRON REMOVAL FROM WATER

There appear to be four distinct methods for removing
organic color from water supplies. These methods are co-
agulation, oxidation by a strong oxidant, and ion exchange
or adsorption by resins or activated carbon. The following

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[1] Metal organic complexes are formed by the normal
exchange of electrons and electrostatic bonding and the
stability of the complex is measured by its equilibrium
constant.

Metal chelates were described as organic complexes in
which metal chelate rings were formed and the stability of the
complex depended on the number of metal chelate rings present.

discussion will make apparent why these methods would be considered in the removal of organically bound iron from water supplies.

In the coagulation method, ferric and aluminum salts are used as the coagulants to remove color. From the Joint Report on Coagulation and Color Problems (24), there appear to be two basic theories of coagulation for color removal. The first is a physical mechanism based on double layer compression. It is thought that the Al^{3+} or Fe^{3+} or their hydrolysis products act on the negatively charged color colloids to destabilize them and neutralize the negative charge. By this theory, organically bound iron should be removed with the coagulant as the organic iron colloids should carry a smaller negative charge than the original organic colloids.

In recent studies, however, this theory has been found to break down in several cases. A second theory has been put forward supporting specific chemical reactions at the color-solvent interface between the coagulant and the organics. In this case, the iron may cause interference with this chemical reaction and the efficiency of color and organic-iron removal may be affected.

Organic color has been removed from water supplies by the use of a strong oxidizing agent which oxidizes the organic to CO_2. When organically bound iron is present, this method has also been used with subsequent filtration of the oxidized ferric compound by either sand filters or manganous greensand filters.

The strong oxidizing agents which have been tried are potassium permanganate, chlorine and ozone.

The ion exchange or the adsorptive properties of various resins and activated carbon have been used to remove color from water supplies. Fouling problems occurred in the past, but with the development of new organic scavenger resins, this method is becoming practical. It has been suggested that these resins will also remove organically bound iron.

All the above methods have their own particular problems and these will be discussed in detail in the following pages.

2.3.1 COLOR REMOVAL BY COAGULATION

The use of coagulants to remove color-causing organics has been quite thoroughly investigated. This method appears to be the most widely used in practice at the present time.

A report by the Research Committee on Coagulation and Color Problems (24) states that

> "the choice of coagulant is generally based
> on individual preference and economics, but
> is particularly limited to aluminum and
> ferric salts."

These salts include aluminum sulfate, sodium aluminate, ferric sulfate, ferric chloride, and ferric chlorosulfate. The effective ions are the Al^{3+} and Fe^{3+} and their hydrolysis products. The pH range required for optimum color coagulation has been established by many investigators (25, 26, 24, 27) as being between pH=5 to 6 for Alum and pH=3.2 to 4.5 for the ferric salts. At the optimum pH, the best color removal is

obtained for the smallest amount of coagulant used.

Maulding and Harris (27) have shown that the optimum pH
for ferric coagulants changes significantly with temperature
and ionic environment. Calcium and sodium in concentrations
up to 200mg/l increase the effectiveness of color removal
with ferric sulfate and extend the pH range of good coagulation
upwards. In no case, however, is the optimum pH extended past
4.5. The presence of the chloride ion has no effect on the
coagulation of color, while the presence of the sulfate ion
has a deleterious effect on color removal. The optimum pH
for color removal depends on the water temperature as well as
the raw water color. At a water temperature of $0^{\circ}C$ the optimum
pH will be 0.5 higher than it will at $24^{\circ}C$. Hall and Packman
(28) state that different ratios of humic and fulvic acid
fractions for various waters require different ratios of coagulant
to raw water color. It is generally agreed that the use of
coagulants for color removal on soft, unbuffered surface waters
is quite practical. The cost of color removal increases
substantially as the waters become more buffered, due to the
larger amount of acid required to adjust the pH to the optimum
value. This cost does not appear to be offset by an increase
in coagulation efficiency caused by increased hardness in the
water.

Vilaret (29) has shown that although organic color can be
removed by the use of a cationic polyelectrolyte, it would
be uneconomical, as the amount required is proportional to the

the total surface area of the species being removed. For organic
color, the amount required is relatively great due to the very
small particle size. Cationic, anionic and nonionic polymers
have been used successfully as coagulant aids to strengthen
the floc formed with iron or aluminum salts.

In summary, although coagulation is at present considered
the best method for color removal, it has many problems and
may be quite expensive.

2.3.2 Oxidation and Filtration

As mentioned previously, the use of a strong oxidant to
change the organically bound iron complex to either CO_2 and
$Fe(OH)_3$ or CO_2 plus organic and $Fe(OH)_3$ has been suggested by
several authors.

Wiley and Jenning (18) used a permanganate solution and
a manganous greensand filter to oxidize and remove the organic
iron complex. To achieve effective color and iron removal they
found that a contact time of 5 to 20 minutes with the
permanganate was necessary before the water was filtered through
the manganous greensand. The dosage of potassium permanganate
and the contact time must be adjusted to suit the particular
conditions of the water.

These authors also experimented with chlorine as an
oxidizing agent but found that the process was not efficient
enough to be considered as a treatment process for the removal
of organically bound iron.

According to Welch (19), if an overdose of permanganate is added to the water supply it tends to regenerate the manganous greensand, thus increasing the length of filter runs. He also suggests that if used correctly, there is no possibility of any potassium permanganate reaching the distribution system. Added benefits in the use of permanganate as noted by Welch are removal of a portion of taste and odor and the destruction of bacteria and viruses by the oxidation process. As a disinfectant however, it has a disadvantage in that the manganous greensand removes the residual and therefore post-chlorination is required.

O'Donovan (37) found that ozone could be used economically for color removal. The ozone apparently oxidizes the color particles and breaks them down and in so doing leaves a clear effluent. Several large and small installations in Europe are using ozone for this purpose. O'Donovan writes that other investigators (41 and 42) have discovered that iron and manganese in other than very small amounts have a deleterious effect on the removal of color by ozonation. It is thought that the ozonation process oxidizes the iron and manganese to their insoluble hydroxides, therefore increasing the colloidal color in water. Other investigators are of the opinion that if ozonation is followed by filtration through manganous greensand, the iron and manganese will be removed from the solution. The ozonation is thought to break down the organic iron complex and oxidize the iron with subsequent removal of the iron in the manganous greensand.

2.3.3 Ion Exchange and Adsorption Resins

In the past, ion exchange resins have been used to soften
and demineralize water by the removal of cations and anions.
In these systems, problems have always been encountered with
organics such as humic and fulvic acid fouling the resin beds.
According to Frisch and Kunin (20), the accumulation of these
acids on the resins limits the capacity of the resins to further
exchange inorganic ions. Over a period of time, the acids
diffuse in the resin gel and are tightly bound by Van der Waal's
forces in addition to the normal ion exchange forces. These
organic acids were found to be very difficult to remove from
the resin, the best elutant solution being warm brine. However,
even this was not particularly efficient. More recently, it
has been found that some of the anion exchange resins could
elute the organic acids more efficiently than others. This has
led to the development of organic trap or scavenger resins which
are capable of removing organic acids from solution and can be
regenerated with considerable efficiency.

Abrams (21) indicates that weakly basic macroporous phenolic
anion exchange resins have good organic scavenging properties
and will probably have application in the removal of color from
water supplies. In later reports (22) (23), Abrams has run
laboratory and field tests which appear to confirm that color
may be removed from water by reversible sorption on macroporous
hydrophilic resins.

In Faust and Hunter's book (39) p. 236, Gustafson and Paleos
indicate that they obtained 76% removal of fulvic acid from a

solution by using an Amberlite XAD-2 anion resin. Their studies indicated that:

1. adsorption increases with increasing resin surface area;

2. adsorption increases as water solubility of the organic compound decreases; and

3. adsorption via hydrophobic bonding increases as the length of a hydrocarbon chain increases or as the number of aromatic rings increases.

Several investigators have used resins to concentrate the color in water before they fractionated it into humic, fulvic and hymatomelanic acids to be used in laboratory analysis.

No direct evidence has been found regarding the use of such resins for the specific purpose of removing organically bound iron from water supplies. It seems, however, that it may be feasible and economical, especially in small installations.

2.3.4 Activated Carbon

Activated carbon has long been used to remove organics and decolorize a variety of solutions. Activated carbon can be made from many carbonaceous starting materials. Some of these include coconut shells, peach pits, sawdust, wood char, fish, lignite coal, coffee grounds, molasses, rice hulls, carbon black, peat, kelp and sugar (4). The nature of the manufacturing processes used in the production of activated carbons remains

a closely guarded secret within the industry and is made up of
the following variables: the nature of the starting material;
the composition of the activation atmosphere (O_2, CO_2 or H_2O);
and, the time and temperature of the activation process.

With so many variables available to the manufacturer of
activated carbon, it is not surprising that a great many types of
activated carbons exist and that all have different carbon
adsorption surfaces. Many carbon users in the chemical industry
appear to have adopted the philosophy of trying out various
activated carbons, until they found one which suited their
purpose best and then adopting this particular carbon and fore-
going further investigation. One of the activated carbons most
used in removing organics from water supplies appears to be made
from lignite coal and is produced by Atlas Chemicals under the
trade name of Darco.

Abrams (30) mentions using activated carbon to remove
color from water and compares the results obtained using
activated carbon with results using Duolite S-37, an organic
scavenger anion exchange resin. Duolite S-37 was found to be
much more efficient in color removal. Driscoll (33) also used
activated carbon from Atlas Chemicals in comparison with Amberlite
IRA-458. Amberlite IRA-458 was found to be much more efficient
in color removal. Hager and Flentze (36) found carbon filtra-
tion effective in removing detergents, insecticides, viruses,
specific chemical pollutants and taste and odor pollutants.

SECTION 3

PROBLEM APPROACH AND MATERIALS USED

3.1 PROBLEM APPROACH

Upon reviewing the problem of removing organically bound
iron from water supplies, it appeared that two approaches were
possible:

1. determination of the chemical nature of the organic
acid-iron complex and then trying to develop a chemical
or physical process which would remove this complex: or
2. use of a trial and error procedure involving the
presently popular water treatment methods for remvoing
colored organic acids from water supplies.

During the literature review it became clear that the
chemical nature of the natural organic acids in water is at
best only partially known. The variability of the organic
compounds makes their chemical determination very complicated
and difficult. The addition of iron would probably increase
this complexity. Another problem which would present itself
even if one were able to determine a chemical formula for the
organic acid-iron complex, would involve finding a removal
mechanism. The mechanisms of substance removal by adsorption
and absorption are not well understood and it would probably be
these mechanisms by which removal of organic iron from water occurs.
This approach to the problem was thought to be very time-consuming
and difficult due to the chemical complexity of the materials
and removal mechanisms.

For the above reasons, and since at present there are
only a certain number of water treatment processes which would
be considered economically feasible, the trial and error
approach to the problem was selected. The literature review
on water treatment processes showed that activated carbon and
ion exchange resins might be used to remove organically bound
iron from water supplies quite economically on a small scale.
It was decided to test some of the ion exchange resins and
activated carbons presently used in treating water supplies
in North America to see what levels of success could be achieved.

3.2 RESINS AND ACTIVATED CARBON USED

It was previously noted in the literature review on ion
exchange resins that organic scavenger resins have recently
been developed which are capable of removing organic acids
from aqueous solutions. These particular resins have also
been found to efficiently elute the organic acid when a regener-
ation solution is passed through them. The exact mechanism
of organic acid removal appears to be in some doubt.

In an attempt to find organic scavenger resins which might
remove organically bound iron efficiently from water supplies,
the following companies were contacted:

1. Diamond Shamrock Chemical Company

2. Rohm and Haas Company of Canada Ltd.

3. Alchem Ltd.

4. Ionac Chemical Corporation.

These companies were requested to submit test samples of their resins which they considered most likely to be successful. The following resins were received in accordance with that request:

1. Duolite S-37 (Diamond Shamrock Chemical Co.)

2. Amberlite IRA-458 (Rohm and Haas Co.)

3. Amberlite IRA-904 (Rohm and Haas Co.)

4. Dowex 11 (Alchem Ltd.)

In the search for activated carbon, Atlas Chemicals was contacted and they agreed to supply Granular Darco activated carbon for the purpose of this experiment.

Duolite S-37

Duolite S-37 is a highly porous phenolic weak base adsorbent resin specifically designed to remove "organics" from water. Abrams (30) mentions that more than forty operating field installations are using Duolite S-37 to remove harmful organic matter prior to the deionization of the water by other resins. The organics are removed in order to avoid fouling problems in their ion exchange resins. This organic removal is achieved without significant change in the inorganic composition of the water. Duolite S-37 is said to be highly effective in the removal of humic, fulvic and hymatomelanic acids and their iron complexes. Some tests conducted in East Germany (31) indicate that the resin is more effective in its removal of color when iron is associated with the color. The

presence of iron resulted in a three to sevenfold increase in
the capacity of the resin to remove organics.

The resin matrix consists of crosslinked phenol-formalde-
hyde with the functional groups being secondary and tertiary
amines and phenolic hydroxyl. It has a service pH range of 2 to
8 and is regenerated with a 4% sodium hydroxide solution. The
resin is made up of light brown granules and adsorbs the organics
rather than removing them by an ion exchange process. Water with
high alkalinity should not tend to shorten the life of this
resin as bicarbonate will not be exchanged when the resin is
in the hydroxide form.

Amberlite IRA-458

Amberlite IRA-458 is a strongly basic anion exchange resin
which derives its exchange activity from quaternary ammonium
groups. This resin differs from other styrene-divinylbenzene
resins in that its acrylic-based structure is more hydrophilic.
Recent studies have revealed that ion exchangers with a relatively
hydrophilic resin structure show a lower affinity for organics
than do those with a more hydrophobic structure. Thus the
increased mobility of organics within the resin, resulting from
a decrease in affinity, permits more rapid organic diffusion into
the resin during the service cycle, and more rapid removal of
organics during the regeneration cycle.

The mechanism by which the color bodies are removed
is thought to be one of adsorption rather than ion exchange.
Due to its excellent adsorption and desorption properties,
Amberlite IRA-458 in the chloride form is considered to
be an excellent organic scavenger resin (32). Amberlite IRA-458

is regenerated in this form by a 10% NaCl solution and has no
pH limitations.

In an unpublished study comparing the effectiveness of seven
different sorbents as organic scavengers, Driscoll (33) found
that Amberlite IRA-458 was more effective in removing organics
than either Duolite S-37 or Amberlite IRA-904. In his experiment
the colored organic solution was prepared from fulvic and humic
acids and passed through the resin columns. Organic removal
efficiency as measured by C.O.D. removal was as follows:

	% REMOVAL
Amberlite IRA-458	80
Duolite S-37	72
Atlas Chemical Activated Carbon	65
Amberlite IRA-904	60

It should be pointed out that Amberlite IRA-458 is also
an anion exchange resin and can be used as such in a conventional
deionization system; in this case the regenerant is NaOH.
Abrams (30) indicates that when a strong base anion exchange
resin is used on colored water with a high concentration of
anions, the capacity to remove color is decreased due to
competition of the anions for the exchange sites. This may
indicate that Amberlite IRA-458 may be more successful on waters
of low alkalinity if the color is not removed by sorption alone.

Amberlite IRA-458 has not yet been approved by the United
States Food and Drug Administration for treatment of foods
and beverages. It can be used, however, if it is followed by
a cation exchange resin.

Amberlite IRA-904

Amberlite IRA-904 is a macroreticular polystyrene strongly
basic anion exchange resin containing quaternary amine active
groups. It is produced in the bead form with a high degree of
crosslinking of the resin matrix. It is very stable both
chemically and physically and is designed to be used as an
organic scavenger resin in the chloride form. The resin is
regenerated with a 10% NaCl solution and has no pH limitations.
It shows extremely high resistance to organic fouling due to
high porosity and a high degree of crosslinking. The resin has
a low ion exchange capacity in its chloride form due to its
high affinity for that anion. Thus, there is relatively little
change in the influent water composition after passage through
the scavenger resin. IRA-904 has U. S. Food and Drug Administra-
tion approval and so may be used by itself for removal of
organics from municipal water supplies.

Dowex 11

Dowex 11 anion exchange resin is a strong base resin
with a special styrene divinylbenzene copolymer matrix having
a high capacity and porosity.

When used as an organic scavenger the resin is regenerated with a mixture of 10% NaCl and 1% NaOH regeneration solution. Dowex 11 is said to be operable in the pH range from 0 to 14. In field tests conducted by Horembala and Feldt (34), Dowex 11 was used as an organic scavenger resin in front of other deionization resin beds to remove the organics which were fouling the beds. The resin was successful in removing the organics responsible for fouling the ion exchange beds, thus extending the length of the runs and the life of the beds. It has been suggested that as an organic scavenger, Dowex 11 may replace clarification by sedimentation and filtration in the removal of organics in some water supplies containing low organic content and low dissolved solids.

Granular Darco Activated Carbon

The activated carbon was supplied by Atlas Chemicals and is made from lignite coal. Grade 12 x 20[1] was used in this experiment. This activated carbon has been used to remove colored organics from water supplies in several commercial installations.

---

[1] Note: Grade 12 x 20 refers to the size of the granular activated carbon particles. The granules will pass through a number 12 sieve but will be retained on a number 20.

3.3 DEFINITION OF ORGANICALLY BOUND IRON

Since the trial and error method has been chosen, it is not considered important to determine whether or not the organically bound iron exists as a complexed compound or as a chelated compound. No attempt has been made to define the chemical nature of the organic-iron complex. Instead it has been assumed that the iron exists in an organically bound state if all the following conditions are met.

1. No iron is removed when the solution is passed through a diatomaceous earth filter or another kind of filter which would normally remove $Fe(OH)_3$ colloids.

2. No iron is removed by passing the solution through a manganous greensand filter. This would normally remove Fe^{3+} and Fe^{2+} ions and $Fe(OH)_3$ by an oxidation and filtration process;

3. No iron is removed by the passage of the solution through a cation exchange resin. This would normally remove the Fe^{3+} and Fe^{2+} ions.

4. The iron must remain dispersed in the solution for several months at a pH between 5 and 8 with no evidence of precipitation of ferric hydroxide.

It should be pointed out that iron could be held in solution by the organics but still be removed by manganous greensand or a cation exchange resin. In this case the iron complexation with the organics is weak and for the purpose of this report is not considered to be organically bound.

3.4 PREPARATION OF THE ORGANICALLY BOUND IRON SOLUTION

The development of a solution which was concentrated and remained relatively stable constituted a problem. When testing resins, the solution should be fairly concentrated so that a mass balance of organic acid and iron can be easily calculated. Also, in order to obtain relatively accurate results using the Total Carbon Analyser, the solutions had to be fairly concentrated.

Two solutions were prepared for testing, one consisting of a humic and hymatomelanic acid-iron complex, the other consisting of a fulvic acid-iron complex. Since these acids cover the full range of colored organic acids in water, it was considered that the solutions were sufficient for testing the removal efficiencies of the various resins and the activated carbon chosen. Appendices 1, 2, and 3 explain the preparation of the two solutions. There were various problems associated with the preparation, some of which are pointed out in the following sections and some of which are presented in the Appendices.

3.5 TEST PREPARATIONS

Equipment Required

The equipment used in this experiment was set up according to the Dow Chemical Laboratory Manual on Ion Exchange. One hundred milliter burrettes were used as ion exchange columns.

These burrettes were converted to ion exchange columns by the
insertion of a resin bed support in the bottom of the burrette.
The support consisted of 4 mm glass beads under which was
placed 1" of glass wool to support the beads. Separatory funnels
were attached to the top of the burrettes by the use of a
rubber stopper through which the tube from the funnel passed
into the top of the burrette. Figure 1 shows the apparatus
arrangement. The rubber stopper made a tight seal so that the
flow rate through the resin could be adjusted by the burrette
valve at the bottom. The resins were placed in the burrette
to a depth of approximately 2/3 the height of the burrette.

Some advantages and disadvantages of using the 100 ml.
burrette as a resin column are as follows:

Advantages

1. Very simple to set up.

2. Requires small volumes of resins and liquids to be
processed.

3. Complete apparatus is of convenient size for a
laboratory.

Disadvantages

1. Limits maximum resin depth to approximately 23 inches.

2. Small diameter creates a wall effect which may cause
small errors in resin volume measurements.

3. Burrette is fragile.

Separatory Funnel

Rubber Stopper

100 ml Burette

Resin

Rack
Stand ·

4 mm Glass Beads
Glass Wool

Bottle
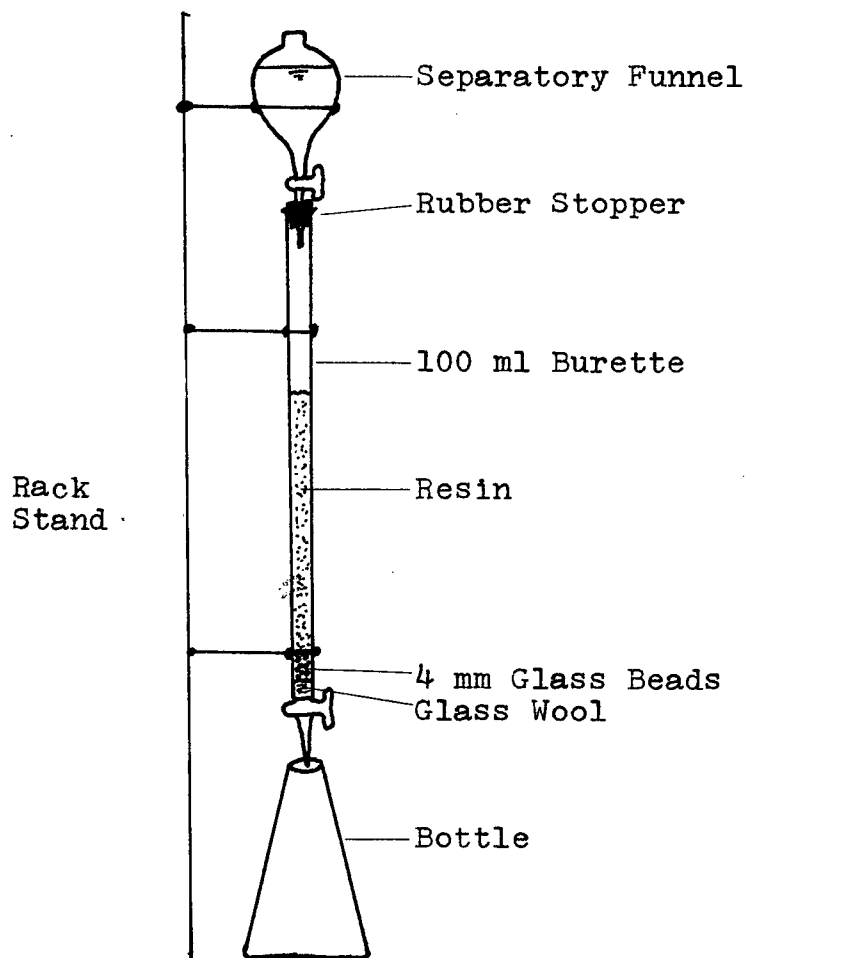
Fig. 1 Resin Column Apparatus

Generally speaking, the advantages of using a 100 ml burrette as an ion exchange column far outweigh the disadvantages and the equipment and arrangement as indicated worked very well.

Tests and Instruments Used

Total Carbon Analyzer.

A T.O.C. Analyzer (Beckman Model 915) was used to measure the total organic carbon removed from the solution and the total organic carbon eluted from the resins by the various washes and regeneration solutions.

Iron Analyses

An Atomic Absorption Spectrophotometer (Jarrel Ash 82-500) was used to measure iron in the solution, the effluent and the regenerated elutant.

Color Analyses

Color was measured in the visible range from 300 nm to 700 nm using a Bausch and Lomb Spectronic 600 spectrophotometer.

Chemical Oxygen Demand

The test was performed according to Standard Methods for the Examination of Water & Wastewater, 13th Edition 1971. The C.O.D. of the solution and effluent was used to check the T.O.C. values obtained.

Resin Preparation

After placing the resins in the burrettes, they were back-
washed to remove all air bubbles and to allow the resin beads
to settle into a compact unit in which channelling effects would be
minimized. The resins were then regenerated into the
proper form for use as organic scavengers. The regeneration
procedures laid out in the manufacturers' specifications were
followed. In all cases, at least 40 minutes of contact time
between the resin and the regenerating solution was allowed.
The flow rates as outlined in the manufacturers' specifications
were followed--this was normally 0.25 to 0.5 gal/ft ^{3}/min.
The resins were then washed with distilled water as the final
preparatory step. In addition, some of the resin columns were
washed as per Duolite Tech Sheet 105 (supplied by Diamond
Shamrock Chemical Co.) to condition the resins and remove the
small amounts of soluble organics on the resins. This condi-
tioning procedure was as follows:

> After resin has been placed in a column, backwashed,
> settled and drained (leaving one inch of water above the
> bed)--
>
> 1. Flow two bed volumes of 1.5N NaOH through resin
> (ten minutes).
>
> 2. Wash out caustic with five bed volumes of distilled or
> deionized water (thirty minutes); drain water from resin
> leaving one inch above top of bed.
>
> 3. Flow two bed volumes of 2N HCl through the resin
> (ten minutes).

4. Wash out the acid with five bed volumes of distilled water
(thirty minutes); drain water from resin to within one
inch of top of bed.

5. Repeat the caustic-rinse-acid-rinse cycle outlined in
steps 1 - 4.

6. If maximum purity is necessary, rinse the resin with
two bed volumes of polar solvent such as acetone or
ethanol.

In the presentation of data in later chapters any resin
noted as "washed" has been washed from steps 1 to 6 using
acetone in the sixth step.

HUMIC-IRON REMOVAL FROM AQUEOUS SOLUTION

A solution of humic acid-iron complex was prepared as out-
lined in Appendices 1 and 2. The humic residue used to prepare
the solution consisted of: humic acid 42%, ether soluble fats
and waxes 28%, fulvic acid 16%, hymatomelanic acid 14%. Since
the majority of the colored organic acids present were humic, the
solution is called the humic acid solution.

4.1 EXPERIMENT #1 HUMIC-IRON REMOVAL WITH RECOMMENDED REGEN-
ERATING SOLUTION.

Procedure:

The resin columns were prepared according to the instructions
in the Dow Chemical Laboratory Manual on Ion Exchange. The
equipment required and its method of preparation was discussed in
Section 3. Before any of the iron complex was allowed to pass
through the scavenger resins, they were generated into their proper
form by the use of the following solutions.

Resin	Solution
Amberlite IRA-904	10% NaCl in Distilled Water
Amberlite IRA-458	10% NaCl in Distilled Water
Dowex 11	10% NaCl and 1% NaOH in Distilled Water
Duolite S-37	4% NaOH in Distilled Water.

The final preparatory step was a distilled water wash.
The humic acid-iron solution was then applied to the columns at
a flow rate which varied between 0.75 and 1.0 gal/ft ^{3}/min.

The resins and activated carbon used in this experiment
included:

1.   Amberlite IRA-904
2.   Duolite S-37
3.   Manganous Greensand
4.   Dowex 50W-X8 (cation exchange resin)
5.   Dowex 11
6.   Amberlite IRA-458
7.   Atlas Chemical Activated Carbon (Granular Darco)

Results:

The results of this experiment are presented in Table I.
Very little of the iron was removed in passing through the
manganous greensand filter or through the Dowex 50W-X8 cation
exchange resin. After preparation, the solution was passed
through a diatomaceous earth filter and no removal of iron
was measured (see Appendix 2). By periodically measuring the
iron in the solution over several months, it was noted that
the iron remained dispersed throughout the solution. Since
these conditions fulfil the requirements of organically bound
iron by the definition given in Section 3, the humic acid-iron
solution was considered to be in the organically bound state.

The number of values averaged to obtain the results shown
in Table I are indicated in Column 7. The accuracy of the iron
data is considered to be very good because of the precise and
accurate nature of the Atomic Absorption Spectrophotometer. In
averaging the T.O.C. results, judgement was used to pick results

Table I

Humic-Iron Removal by Resins, Activated Carbon and Manganous Greensand.

	T.C. mg/l	T.I.C. mg/l	T.O.C. mg/l	Fe mg/l	pH	No. of Values averaged	Total [1]B.V. passed
Humic Iron Influent	38	22	16	15.4	8.0		
IRA 904 Reg. 10% NaCl	14	2	12	13.8	6.1	7	22
IRA 904 washed Reg. 10% NaCl	14.5	1.5	13	13.6	6.1	5	17
Duolite S-37 Reg. 4% NaOH	34	22	12	15.0	10.0	4	14
Manganous Greensand	30	14	16	14.6	7.5	5	27
Dowex 50W-X8 Reg. HCl	--	--	--	14.6	--		5
Dowex 11 Reg. 10% NaCl 1% NaOH	19	3	16	13.5	9.1	5	16
Dowex 11 Washed Reg. 10% NaCl 1% NaOH	18.5	3.5	15	14.0	9.1	6	18
Darco Activated Carbon	31	19	12	14.6	8.3	5	13

[1]B.V. indicates Bed Volumes of solution passed through the column.

which appeared to be most stable and representative. The T.O.C. results must therefore be treated with caution.

Generally the data presented in Table I indicates that very little of the organics were removed. This is also borne out by the iron data which indicates very little removal of iron. It might be noted that the Amberlite resins do remove the total inorganic carbon or the bicarbonate ions, thus removing the buffering capacity of the water. Upon reviewing the manufacturers' literature, this would not have been expected as these resins were in the chloride form. As a general rule the resins in the chloride form were thought to pass bicarbonate ions. The Duolite S-37 resin in the hydroxide cycle did not remove the bicarbonate ions. This was expected as Duolite S-37 in this form is said to achieve organic removal without significant change in the inorganic composition of the water.

By comparison of influent to effluent in Nessler tubes, it was noted that some color was removed in the first few bed volumes by the IRA-904, the activated carbon, and the Duolite S-37. The amount of color removal varied in that order, with the IRA 904 resin removing more color than either the activated carbon or the Duolite S-37. In no case, however, was much color removed from the solution. This visual indication of color removal is substantiated by the T.O.C. data which indicated that approximately 4 mg/l of organic carbon was removed by each of the above three columns. Thus, it appears that some of the humic acids are removed by Ira 904 Activated Carbon and Duolite S-37. Comparison of influent to effluent of all other resins and

manganous greensand showed no removal of color. This was also borne out by the T.O.C. data which indicated that no organic carbon was removed from the solution in any of the other cases.

None of the resins were effective in removing the iron present in the solution. Since this was the primary goal, none of these resins could be considered useful in removing the humic acid-iron complex from water supplies.

Results were not obtained for the Amberlite IRA 458 as the pH of the resin was so low that the humic acid precipitated in the resin column. It was noted that when the humic acid was precipitated and removed from solution in the column, so was the iron. This was taken as another indication that the iron was in fact bound to the organic acid.

Due to these problems with the IRA 458 resin, another experiment was performed, in which different regeneration techniques were tried.

4.2 EXPERIMENT #2 HUMIC-IRON REMOVAL WITH EXPERIMENTAL REGENE-RATING SOLUTIONS

Procedure:

The resin columns were prepared and setup using the same method as Experiment #1. The three resins used in this experiment were generated with the following solutions:

1. Amberlite IRA 458   1% NaOH and 10% NaCl in Distilled Water.

2. Amberlite IRA 458   10% NaCl in Distilled Water

3. Amberlite IRA 904   1% NaOH and 10% NaCl in Distilled
                          Water.

4. Duolite S-37   4% NaOH

The IRA 458 was generated with NaOH and NaCl solution in
order to raise the pH of the resin so that the humic acid would
not precipitate in the resin column. Another column of IRA 458
resin was regenerated in the NaCl form to see if the precipitation
of humic acid would occur again. The IRA 904 resin was regenerated
with the NaOH and NaCl solution to determine the effect of the
NaOH on the removal efficiency of the iron complex by the resin.
The Duolite S-37 resin was left in the same base form as was used
in the previous test. The humic acid-iron solution was applied to
the column at a flow rate which varied between 0.75 and 1.0
gal/ft ^{3}/min.

Results:

The results of the second experimental run are shown in Table
II. Due to problems encountered in determining the Total Inorganic
Carbon and Total Organic Carbon on the Total Carbon Analyser, the
T.I.C. and T.O.C. data must be treated with caution. In general
little or no organic carbon was removed by any of the resins. It
can be noted again that the Amberlite resins remove the inorganic
carbon or bicarbonate ions from the solution. The Duolite S-37
resin appears to have had some organics leached from it, but no
increase in color was noted. Very little iron was removed by
any of the resins. During this run it was found that the humic
acid did not precipitate in the IRA 458 resin column which had been
regenerated with salt only. No explanation can be given for the
discrepancy between IRA 458 results in Experiment #1 and Experiment #2.

Table II

Humic Iron Removal by Experimentally Regenerated Resins.

	T.C. mg/l	T.I.C. mg/l	T.O.C. mg/l	Fe mg/l	pH	No. of Values Ave.	Total B.V.[1] Passed
Original Sample Influent	28-30	17-19	10-12	15.4	7.0		
Effluents From Resins							
IRA 458 Reg. 10% NaCl,1%NaOH	12	1	11	13.8	7.8	12	57
IRA 458 Reg. 10% NaCl	11	2	9	13.0	-	13	46
IRA 904 Reg. 10% NaCl,1%NaOH	12	4	8	12.6	6.9	12	54
Duolite S-37 Reg. 4% NaOH	30.5	16.5	14	13.3	8.7	10	42

1 B.V. - indicates Bed Volumes of solution passed through the column.

In conclusion, these resins cannot be considered satisfactory for the purpose of removing humic acid-iron complexes from an aqueous solution.

Section 5

FULVIC-IRON REMOVAL FROM AQUEOUS SOLUTION

A dark amber-colored solution of water was obtained from Burns Bog south of Vancouver. Since no precipitate was noted when the solution's pH was reduced to 1 it was concluded that all the organic acids present were fulvic acids. Iron was added to this fulvic acid as described in Appendix 3.

5.1 EXPERIMENT #1 FULVIC ACID-IRON REMOVAL EFFICIENCY

Procedure:

The following columns were used with the resins being prepared according to Dow Chemical Laboratory Manual on Ion Exchange:

1. Amberlite IRA 904
2. Atlas Activated Carbon (Granular Darco)
3. Duolite S-37
4. Manganous Greensand
5. Dowex 11
6. Dowex 50W-X8 (Cation)
7. Amberlite IRA 458

Resin regenerating solutions were:

1.	Amberlite IRA 904	1% NaOH and 10% NaCl in distilled water.
2.	Amberlite IRA 458	1% NaOH and 10% NaCl in distilled water.
3.	Dowex 11	1% NaOH and 10% NaCl in distilled water.
4.	Duolite S-37	4% NaOH in distilled water.
5.	Dowex 50W-X8	15% NaCl in distilled water.

The fulvic acid-iron solution was then passed through the resins, activated carbon and manganous greensand at a flow rate of

41

approximately 1 gal/ft^3/min. The T.O. C. was not measured due to problems with the Total Carbon Analyser. Color was measured with the Spectrophotometer.

Results:

Fig. 2 shows the transmission of light vs. wave length as determined by the Spectrophotometer for the effluents from the various columns.

It may be clearly seen that Amberlite IRA 904 removed almost all of the color present in the solution. The transmission of light in this case was very close to that for distilled water. Activated Carbon and Duolite S-37 also removed much of the colored organics from the water. As indicated, all other resins and manganous greensand removed very little organic color from the solution.

From Table III it can be observed that the removal of organic color did not correspond to the removal of iron from the solution. Amberlite IRA 904, for instance, is seen to remove almost all of the color but very little of the iron. The Dowex 50W-X8 cation exchange resin and the manganous greensand are found to remove most of the iron but very little of the colored organics. Thus, it may be concluded that the iron is not in an organically bound state as previously defined.
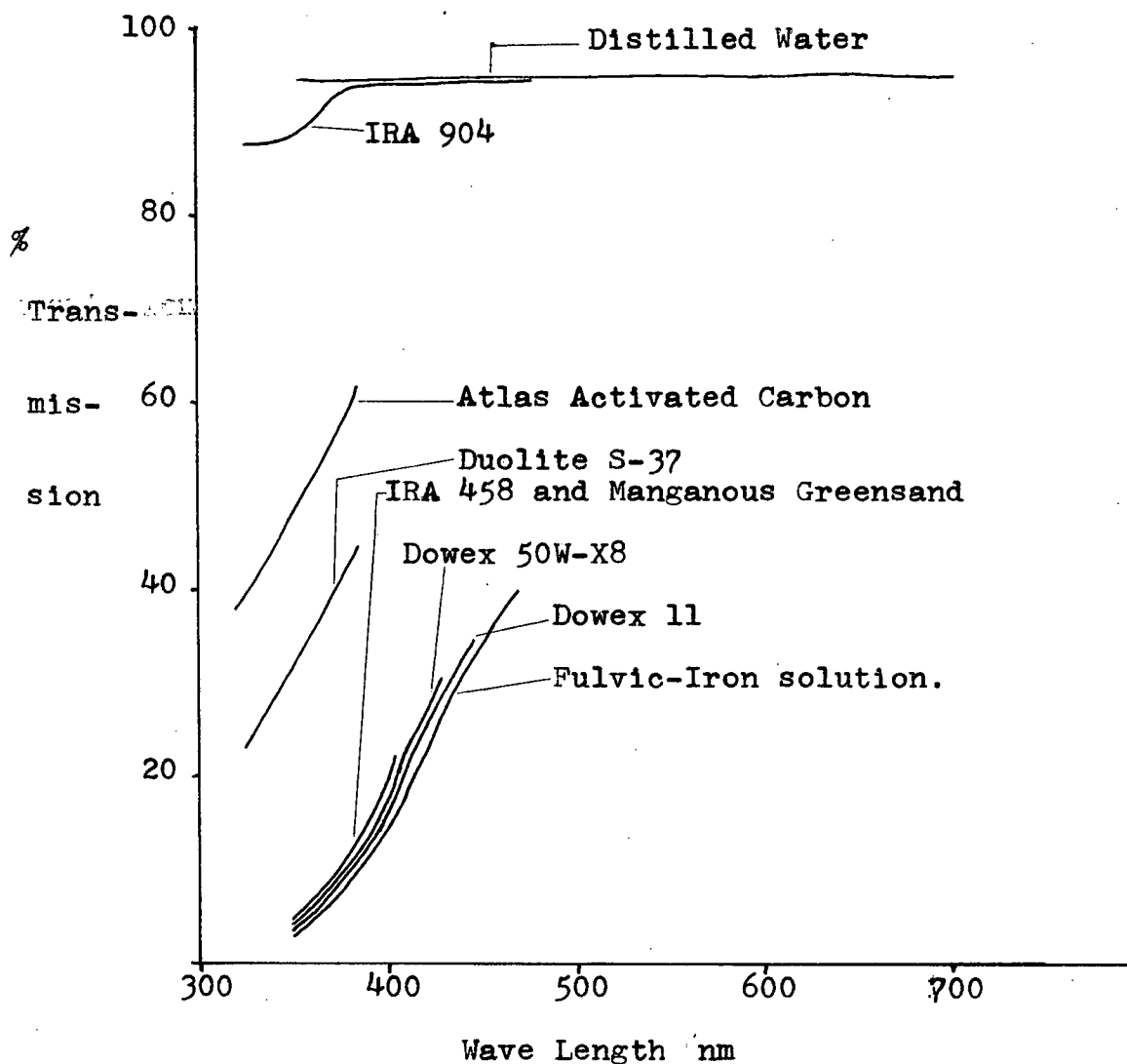
Fig. 2 FULVIC-IRON COLOR REMOVAL BY RESINS,
ACT. CARBON AND MANGANOUS GREENSAND.

Table III

Iron Removal from Fulvic-Iron Solution

Effluent	Bed Vol. Passed	No. of Samples Averaged	Fe mg/1	pH	% Fe Recovered From Column
Fulvic-Iron Influent			15	4	
IRA 904 Reg. 1% NaOH, 10% NaCl	32	6	12	4	30
Atlas Activated Carbon	22	6	1	8.2	
Duolite S-37 Reg. 4% NaOH	27	6	0.5	9.9	16
Manganous Greensand	20	5	3.4	6.7	
Dowex 11 Reg. 1% NaOH 10% NaCl	21	4	14	4	16
Dowex 50W-X8	20	5	2	6.2	
IRA 458 Reg. 1% NaOH 10% NaCl	29	5	8	8.2	5

Atlas activated carbon and Duolite S-37 resin are shown
to remove almost all the iron and much of the organic color
from the solution. Very little of the iron was regenerated
from the Duolite S-37, however. It was thought that the hydroxyl
ions present in this resin might be precipitating the iron as
ferric hydroxide within the resin matrix and that this precipi-
tation could cause iron fouling of the resin. It is not known if
the activated carbon could be reactivated when the iron was
present.

Dowex 11 and Amberlite IRA 458 are seen to pass the iron,
with the Dowex 11 having essentially no effect on the iron
concentration, while Amberlite IRA 458 passed about one half of
the iron.

A combination of resins and manganous greensand or activated
carbon could be used to remove both color and iron from the
fulvic acid-iron solution if the solution were to remain un-
changed. The solution characteristics changed with storage time,
however, and the colored organics and iron become increasingly
difficult to remove as the solution aged.

The effects of this change are shown in Figure 3. As the
solution changes, the percent transmission of light decreased
(Figure 3), indicating an increase of color. The increased
color was also noted visually and the solution was seen to
darken considerably. As indicated in Figure 4, the Amberlite
IRA 904 resin effectively removed all the color from the fulvic
acid-iron solution initially. After the original solution had
aged for three weeks, however, the resin removed much less color
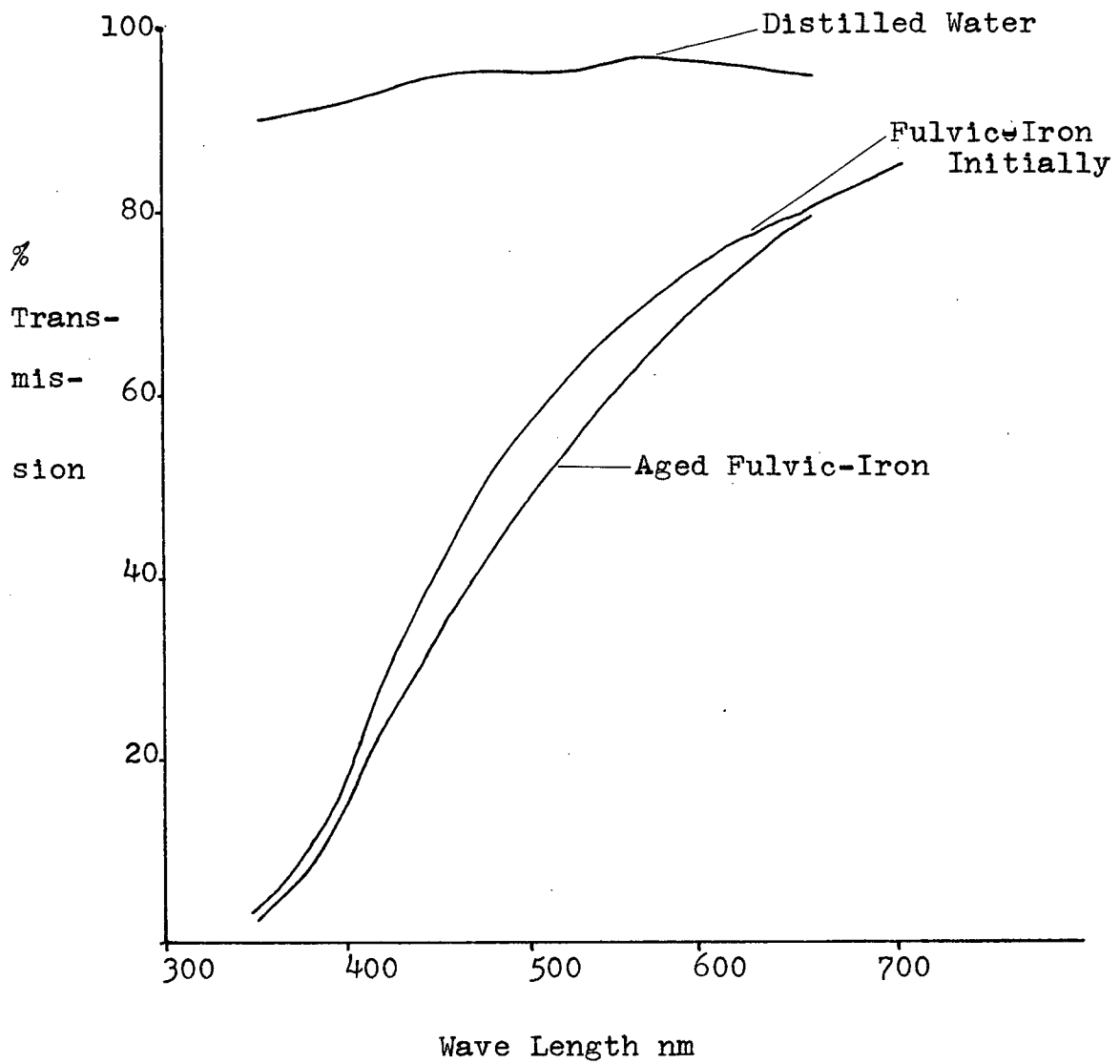
Fig. 3 COLOR CHANGE AS FULVIC-IRON SOLUTION AGES
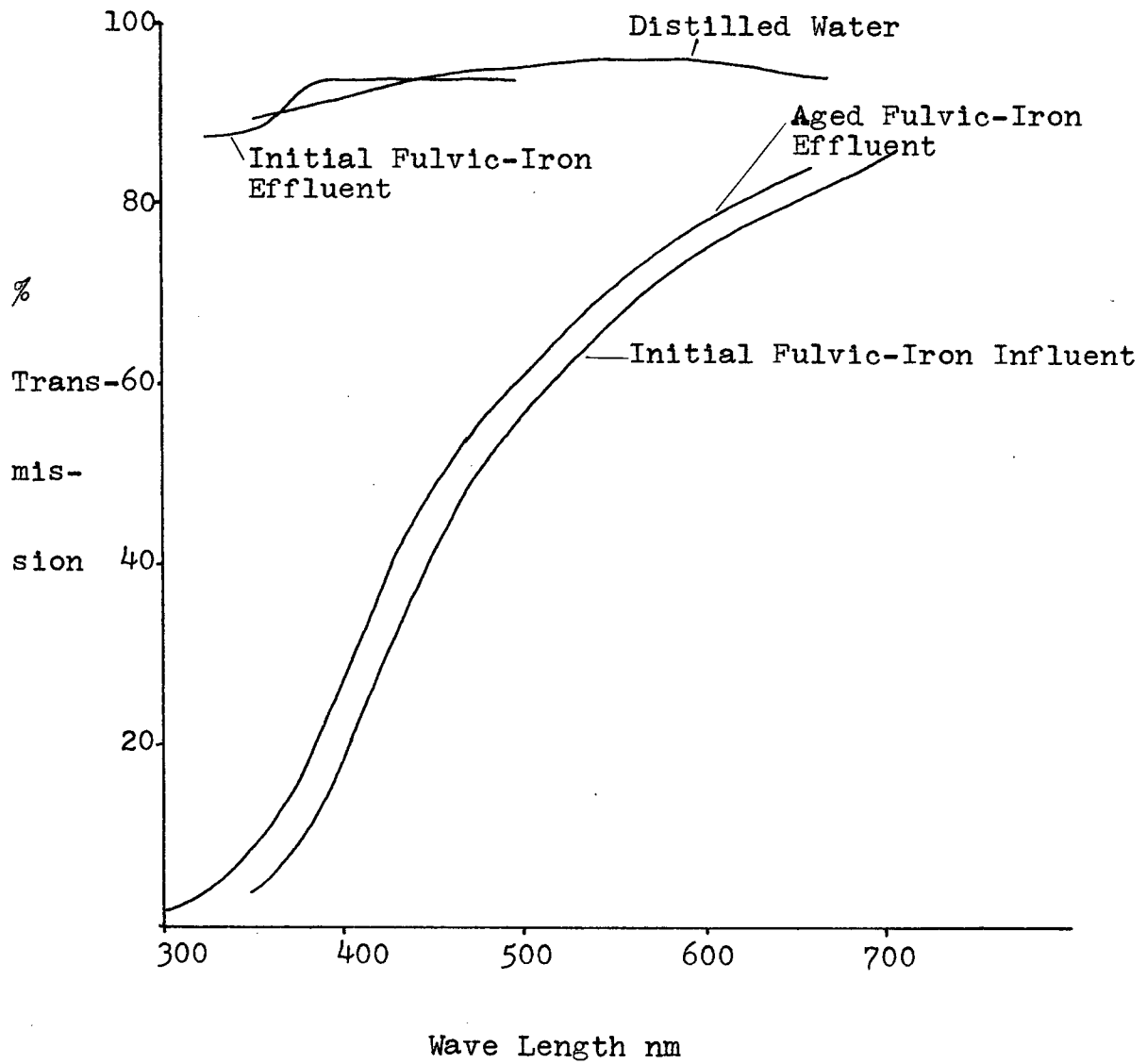
Fig. 4 COLOR PASSED BY IRA 904 RESIN AS FULVIC-IRON AGES

from the solution. Figure 4 also shows the difference in color between the initial fulvic acid-iron solution and the effluent from the resin after the fulvic acid-iron solution had been aged. This color difference was observed to be relatively small. It should be stated here that the resins were completely regenerated before the three-week-old fulvic acid-iron solution was passed through them.

In order to be sure that it was the addition of iron to the fulvic solution that was causing this change in characteristics, a solution of just fulvic acid which was $1\frac{1}{2}$ months old was passed through the IRA 904 resin. These results are presented in Figure 5 and it may be seen that the removal of color is the same as the removal obtained passing the initial fulvic acid-iron solution through the resin. This result indicates that the iron is in fact changing the characteristics of the organic solution.

It is thought that the iron becomes more strongly bound to the organics as the solution ages. In the natural environment the strength of these organic-iron bonds may be strong or weak depending on the conditions present. The removal characteristics of both weakly and strongly bound organic-iron are important from a water purification standpoint; thus it was decided to trace these removal characteristics as the fulvic iron solution ages.
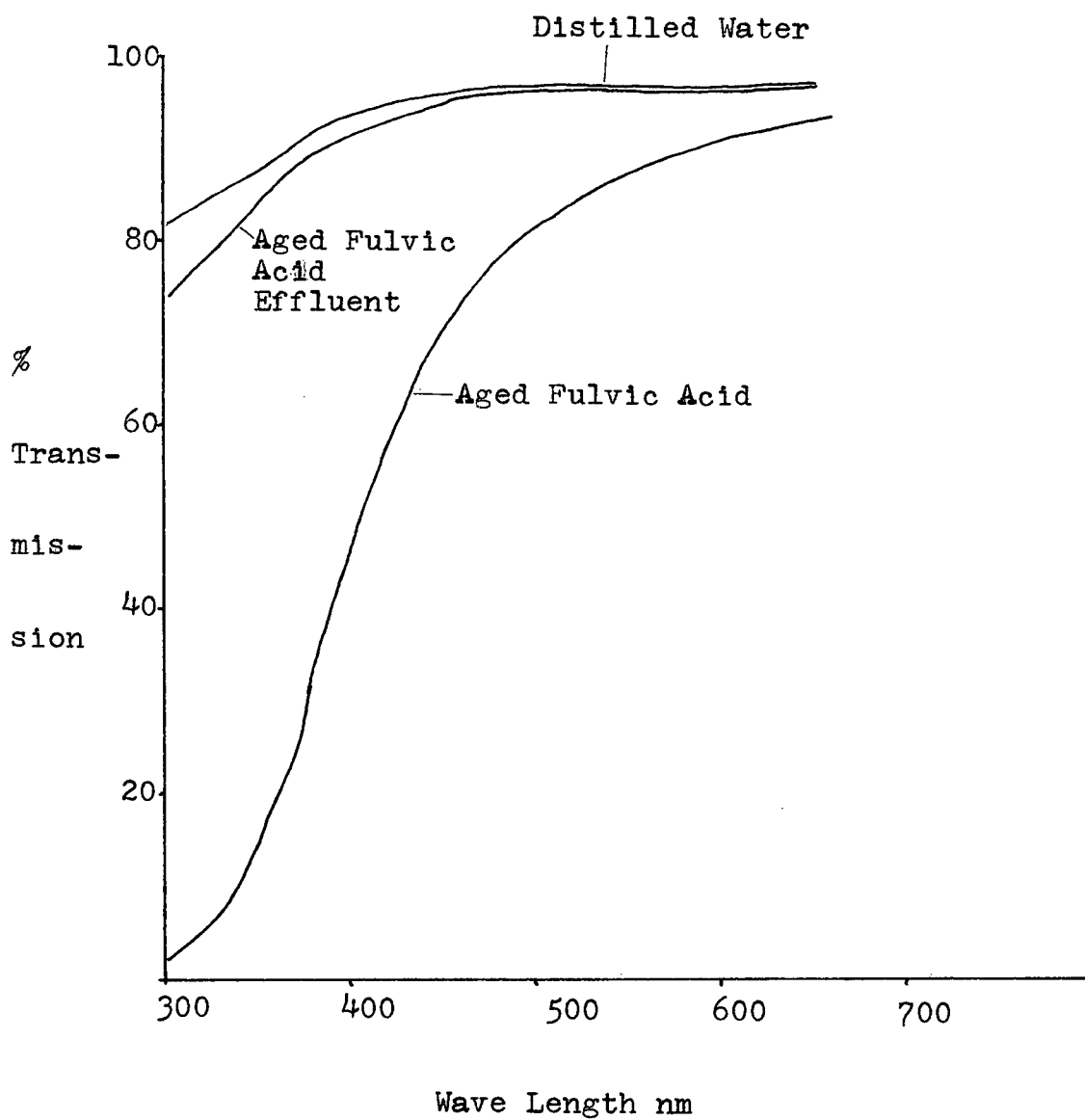
Fig. 5 AGED FULVIC ACID AND IRA 904 EFFLUENT COLOR.

It was previously noted that the Duolite S-37 removed the iron from solution and that this iron could not be eluted; thus, iron fouling is indicated in this resin. Therefore, the Duolite S-37 resin was not considered satisfactory for tracing the fulvic acid-iron removal characteristics over the period of time. Dowex 11 was previously seen to pass most of the iron and remove little of the colored organic acids, so it could not be considered satisfactory for the experiment. Amberlite 458 was unsatisfactory as it removed very little color and any iron removed could not be eluted from the resin. Amberlite IRA 904 was therefore chosen for the experiment as it removed all the colored organics and allowed most of the iron to pass through. Of the iron which was removed by the resin, 30% could be eluted, thus reducing the risk of iron fouling.

Section 5.2 describes the experiments which were undertaken to develop the best regeneration cycle for this resin.

5.2 EXPERIMENT #2 REGENERATION CYCLE SUITABLE FOR FULVIC-IRON REMOVAL.

Procedure:

Due to the findings presented in the previous experiment, it was decided to use IRA 904 and a cation exchange resin in series to remove both color and iron from the fresh fulvic acid-iron solution. The cation exchange resin chosen was Dowex MSC-1, as it was understood that this resin could be economically used to purify water supplies and was resistant to organic fouling.

This experiment was intended to determine the most efficient regenerating cycles for the combination of the IRA 904 and Dowex MSC-1. It was decided to try three types of regeneration processes.

Method 1. The IRA 904 and Dowex MSC-1 were both regenerated with NaCl. It was thought that if both resins could be regenerated with the same solution it would minimize the operating costs of the process.

Method 2. The IRA 904 was regenerated with 10% NaCl and 1% NaOH solution, and the Dowex MSC-1 by NaCl. It was hoped that the NaCl might first be used to regenerate the Dowex resin and then used in conjunction with the NaOH to regenerate the IRA 904 resin.

Method 3. The IRA 904 regeneration cycle consisted of an HCL wash first to remove the iron and some of the organics. Then a 1% NaOH and 10% NaCl solution would be used to regenerate the resin and remove the rest of the organics. Finally, an HCL wash was used to remove all the hydroxyl ions present so that ferric hydroxide could not form in the resin. In this case, the Dowex resin was regenerated by HCl.

The equipment used was the same as described in Section 3. The regeneration procedure was as per the manufacturers' specifications and Section 3. A final distilled water rinse was used in all three methods.

Results:

The results of the three regeneration methods are shown in Table IV. The first regeneration process posed a problem when the NaCl regenerating solution would only remove a small portion (approximately 34%) of the organic carbon present in the IRA 904 resin. The iron removed by the NaCl regeneration solution was also rather limited (approximately 57%). Therefore, this method of regeneration was considered unacceptable.

The regenerating solution used in Method 2 is seen to work very well in eluting the organics from the IRA 904 resin. The total recovery of organic carbon is 110%, as seen in Table IV. The iron removal achieved by this method is not very great, however, with only (25%) of the iron being recovered.

Iron fouling problems would likely develop if this method of regeneration were used. It is thought that the hydroxyl ions present on the resin exchange sites precipitate the iron causing ferric hydroxide to form within the resin matrix. It was concluded that method 2 should not be used to regenerate the resin.

The regeneration efficiencies using Method 3 were very good, with 94% of the iron and 91% of the T.O.C. being eluted from the resins. As both the IRA 904 and the Dowex MSC-1 were placed in the same column, the iron and T.O.C. recoveries are only shown under the IRA 904 column in Table IV. It will be noted that the great majority of the iron was removed by the HCl wash at the beginning of the regeneration cycle. Due to the superior performance of the resins when regenerated by Method 3, it was concluded that this should be the regeneration

TABLE IV

Fulvic-Iron Elution Efficiency

Methods	1st Wash mg	IRA 904 2nd Wash mg	Dowex MSC-1 1st Wash mg	Total Rec. mg	Total Fe or T.O.C. Removed From Sol.	Total Recovery %
Method 1 NaCl			NaCl			
Fe Recovered	4.2		28.2	32.4	56.6	57%
T.O.C. Recovered	100			100	291	34%
Method 2 NaOH NaCl			NaCl			
Fe Recovered	9.5		6.1	15.6	63.0	25%
T.O.C. Recovered	338			338	308	110%
Method 3 HCl	NaOH NaCl					
Fe Recovered	34.2	1.6	Dowex MSC-1 in same column as IRA 904	35.8	38	94%
T.O.C. Recovered	105	70		175	193	91%

method used to trace the changing organic acid-iron solution.

The fulvic-iron removal efficiency of the IRA 904 and Dowex MSC-1 resins in series is presented in Table V. It can be seen that the iron removal is excellent; even after 88 bed volumes, the iron removal efficiency is 93%. T.O.C. removal is also very good, as the removal efficiency is 82% after 88 bed volumes of solution have passed through the resin. Color was measured by the transmission of light at a wavelength of 350 nm. The color of the final effluent was much less than that of the feed solution.

It is thought that this constitutes a satisfactory removal efficiency, considering the concentration of organics and iron in the original solution.

Table V

Fulvic-Iron Removal Efficiency

	Bed Vol.	T.O.C. mg/1	%T.O.C. Removed	Fe mg/1	%Fe Removed	Trans. Light @350 nm
Fulvic-Iron influent		83		15		4
Method 1	0-33	4	95	0		85
	33-61	9	89	0.25	98	65
Method 2	0-31	4	95	0.25	98	85
	31-56	10	88	0.5	97	62
Method 3	0-18	3	96	0.25	98	89
	18-42	9	89	0.5	97	72
	42-70	11.6	86	1.0	93	49
	70-88	15	82	1.0	93	42

SECTION 6

FULVIC-IRON SOLUTION CHANGE WITH AGE

6.1 EXPERIMENT DESCRIPTION

An experiment was designed to measure and observe the changes which time produced in a fulvic acid-iron solution. The experimental results were gathered over a 33 day period. Amberlite IRA 904 resin was used to determine how much of the organic acid-iron complex could be removed by an organic scavenger resin as the time allowed for organo-iron complexation increased from 6 to 33 days.

Dowex 50W-X8 was used to determine how much iron could be removed by a cation exchange resin as the time allowed for complexation increased to 33 days. In order to relate changes in the fulvic-iron solution to the original solution, the same fulvic acid solution without any iron added was used as a control solution throughout the experiment. It was assumed that this solution would not change its chemical characteristics. This assumption was based upon past experimentation in which a similar solution from Burns Bog did not change significantly in a two month period.

At the end of 33 days, the fulvic-iron solution was passed through a column of Atlas activated carbon to determine how much of the fulvic acid-iron complex could be removed by this process. The fulvic acid-iron solution was also passed through a manganous greensand column to determine what amount of iron would be removed.

Finally, both the fulvic acid-iron solution and the fulvic acid solution were subjected to the organic acid fractionation test at intervals throughout the month to determine if either solution was changing to a humic-hymatomelanic acid solution.

6.2 EXPERIMENTAL PROCEDURE.

A solution of fulvic acid obtained from Burns Bog was split in half, with one fraction being used to prepare a fulvic acid-iron solution as per Appendix 3. At first the color in both solutions was the same. This was not surprising as past experimentation had indicated that initially very little of the added iron is strongly complexed to the fulvic acid and the fulvic acid-iron solution is very similar to the fulvic acid solution in pH, T.O.C. and color.

Four Amberlite IRA 904 and one Dowex 50W-X8 resin columns were prepared. These particular resins were chosen because of good previous performance. The Dowex 50W-X8 was regenerated with a solution of 2N HCl . Two of the Amberlite IRA 904 resin columns were regenerated as per method 3 in the previous section. The other two were regenerated in the same manner except that the final acid wash was deleted. This was done in order to determine if the final acid wash was actually required.

The fulvic acid-iron solution was passed through the

Dowex resin and through one of each type of IRA 904 column. The control solution of fulvic acid was passed through the remaining two IRA 904 columns.

For clarification purposes the following numbers have been assigned to the respective resin columns:

Resin Column	Resin Used	Feed Solution	Regeneration Procedure
#1	IRA 904	Fulvic Acid	Method 3
#2	IRA 904	Fulvic Acid	Method 3 deleting final acid wash.
#3	IRA 904	Fulvic Acid-Iron	Method 3
#4	IRA 904	Fulvic Acid-Iron	Method 3 deleting final acid wash.
	Dowex 50W-X8	Fulvic Acid-Iron	HCl

Effluent testing was carried out 6, 10, 15 and 33 days after sample preparation. On each test date ten bed volumes of fulvic acid control solution were passed through resin columns number 1 and 2. Similarly ten bed volumes of fulvic acid-iron solution were passed through resin columns numbers 3 and 4 and the Dowex 50W-X8 resin column. The Dowex resin was used to determine how much of the iron was actually organically bound on any of the testing dates (as per the definition in Section 3). On day 33, the fulvic acid-iron

solution was passed through a column of manganous greensand to check the results from the Dowex resin and to complete the test for organically bound iron. The fulvic acid control solution and the fulvic acid-iron solution were also passed through columns of activated carbon (Atlas Granular Darco) on day 33, to determine the removal of each by the activated carbon.

All of the former solutions and the effluents were tested for iron, C.O.D., T.O.C., pH and the transmission of ultraviolet and visible light. The resins were regenerated twice during the test period.

In addition to the above tests, the organic acid fractionation test was carried out on each of the testing dates. The pH of both the fulvic acid control solution and the fulvic acid-iron solution was lowered to pH=1. Observations were made as to how much precipitate was formed. This precipitate would normally be classified as humic or hymatomelanic acid by definition if found in a natural water supply.

6.3 EXPERIMENTAL RESULTS

Fulvic Acid Removal by Resins

Both #1 and #2 resin columns removed the fulvic acid effectively from the solution. Figures 6 and 7 show the percent transmission of ultraviolet and visible light through the fulvic acid solution and the effluent from the resins. In a visual
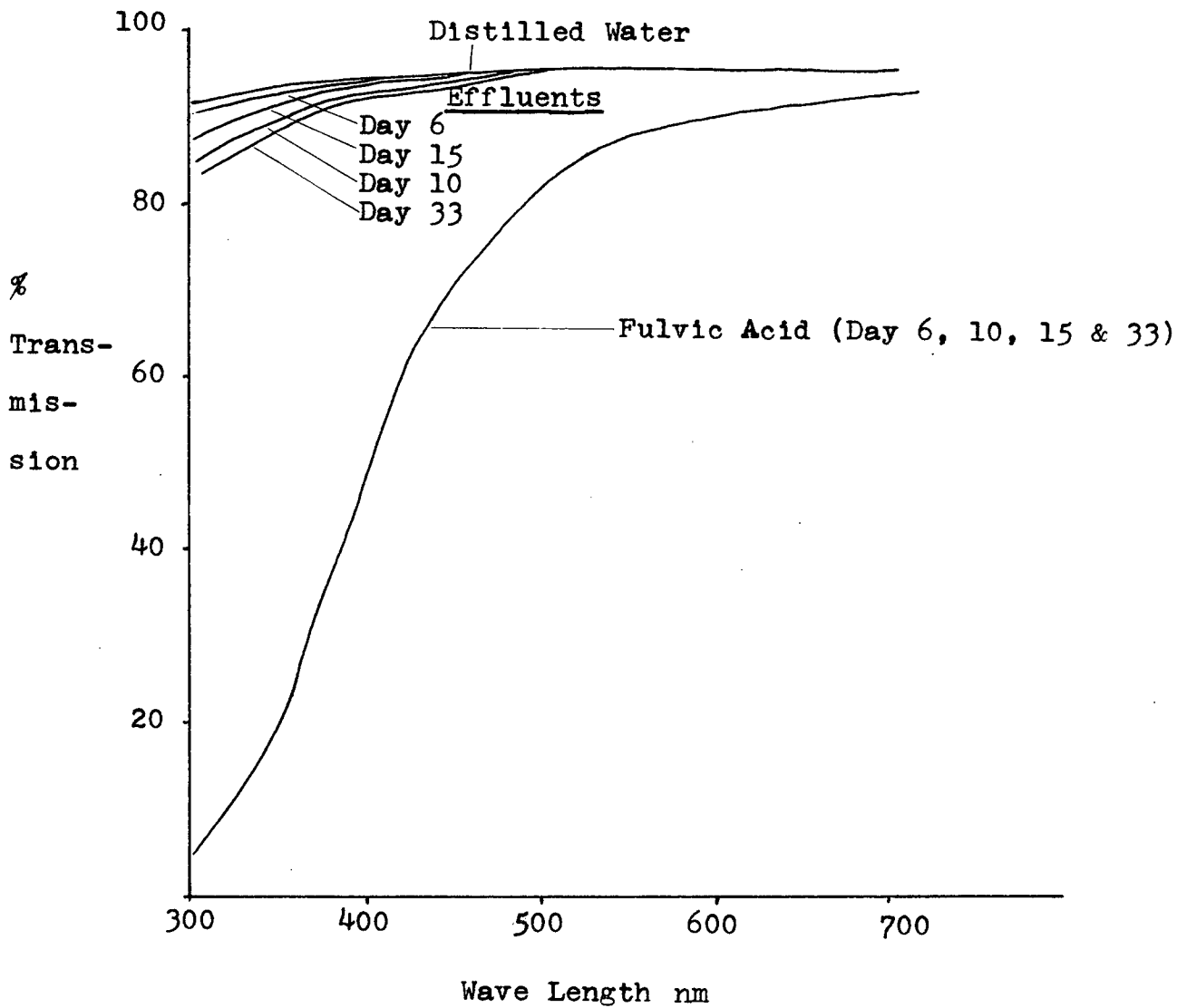
Fig. 6 FULVIC EFFLUENT COLOR

FROM RESIN #1

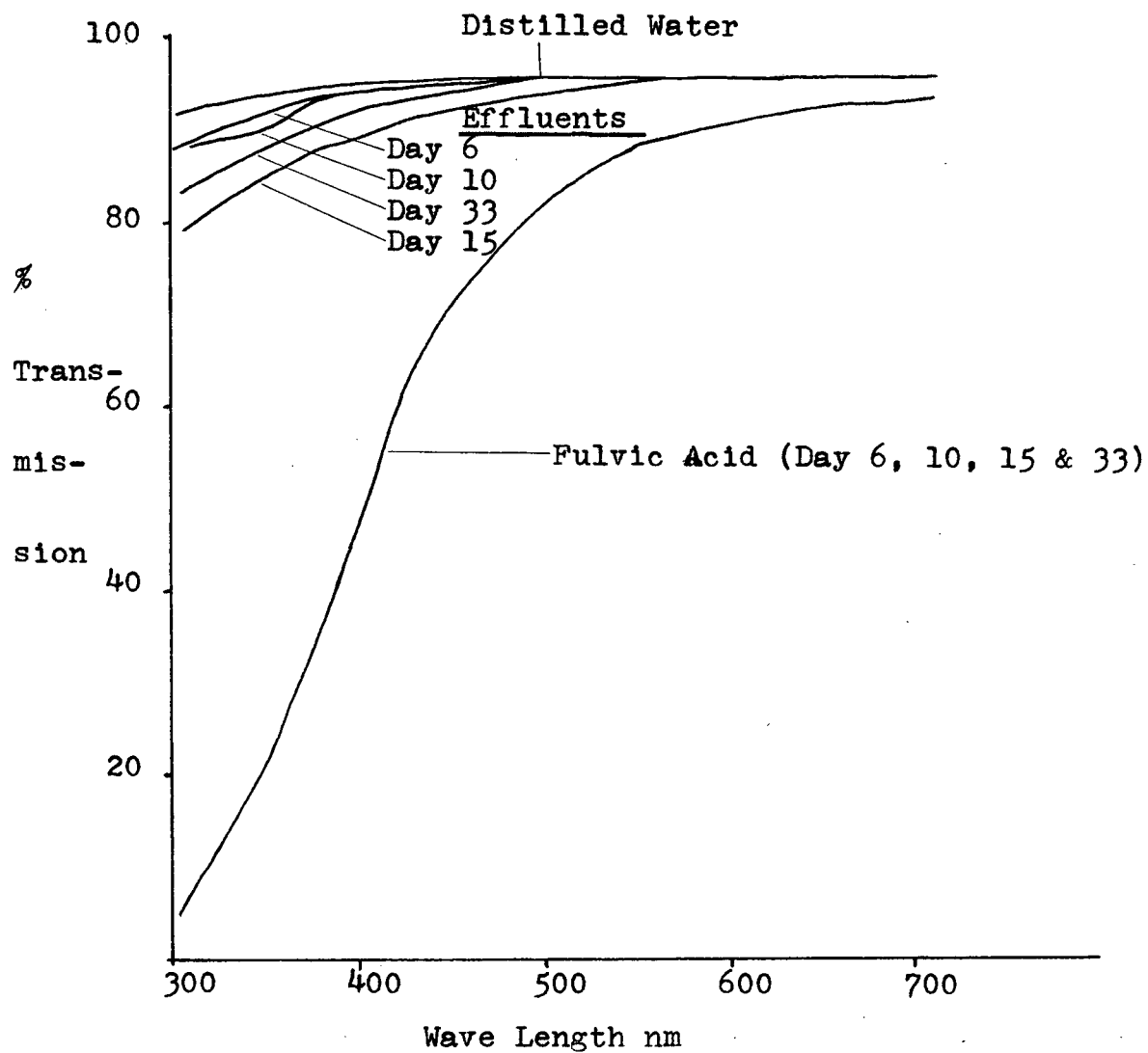Note: For actual colors on Day 33 See Fig. 8

Fig. 7 FULVIC EFFLUENT COLOR

FROM RESIN # 2

Note: For actual colors on Day 33 See Fig. 8

inspection of the effluents, no difference could be noted between distilled water and the effluents of these resins. Figure 8 is a photograph of the effluents on day 33 and shows that both resins totally removed the organic color from the fulvic acid solution.

Table VI shows the T.O.C., C.O.D., and pH of the fulvic acid control solution on the four testing dates. It can be noted that the solution stays relatively constant with regard to the characteristics given and from Figures 6 and 7 it can be noted that the color of the fulvic acid solution does not change with time.

As indicated in Table VII, the T.O.C. remaining in solution after passing through Resin #1 is very low. This supports the results obtained from the light scan shown in Figure 6. It may also be observed that the pH of the effluent is very similar to the pH of the fulvic acid control solution. This shows that the acid wash removed essentially all the hydroxyl ions present in the resin after regeneration with NaCl and NaOH.

Table VIII shows the characteristics of the effluent from Resin #2. The T.O.C. values are very low and in keeping with the results from the light scan presented in Figure 7. It will be noted that the day 15 sample has a much higher T.O.C. than the others. It is thought that the resin was not rinsed well enough following the regeneration cycle and that this caused it to pass some organics it would otherwise have removed. Most of the color was removed, even though a T.O.C. content of 8 mg/l remained. The pH of the effluent from Resin # 2 is
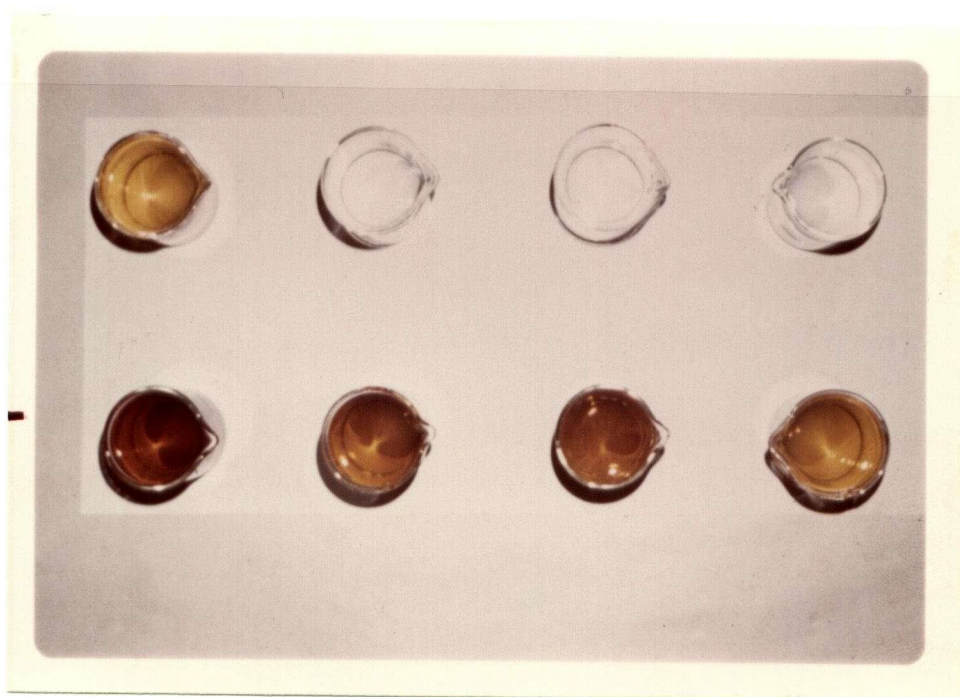
Figure 8 FULVIC EFFLUENT AND FULVIC-IRON EFFLUENT ON DAY 33

Top Row, Left to Right: Fulvic Acid, #2 Resin Effluent,
#1 Resin Effluent and Activated Carbon Effluent.

Bottom Row, Left to Right: Fulvic-Iron, #4 Resin Effluent,
#3 Resin Effluent and Activated Carbon Effluent.

Table VI

Fulvic Acid Feed Solution.

	Day 6 mg/l	Day 10 mg/l	Day 15 mg/l	Day 33 mg/l
T.O.C.	41	-	42	40
C.O.D.	105	-	100	90
pH	3.9	3.9	4.0	3.9

Table VII

Resin #1 Fulvic Effluents

	Day 6 mg/l	Day 10 mg/l	Day 15 mg/l	Day 23 mg/l
T.O.C.	0	2	2	1
C.O.D.	-	-	-	0
Fe	0	0	0	0
pH	4.1	3.8	4.2	3.9

10 B.V. of solution were used in all cases.

Table VIII

Resin #2 Fulvic Effluents

	Day 6 mg/l	Day 10 mg/l	Day 15 mg/l	Day 33 mg/l
T.O.C.	0	1	8	2
C.O.D.		-	16	5
Fe	-	-	-	-
pH	6.2	4.5	7.0	4.9

10 B.V. of solution were used in all cases.

seen to be higher than the pH of the feed solution. This indicates the presence of hydroxyl ions in the resin. The pH of the effluent is seen to decrease from 6.2 to 4.5 as more bed volumes of solution are passed through the resin. (The resin was regenerated on day 12). This was expected to happen as the resin will tend to give up the hydroxoxyl ions first before giving up the chloride ions.

In conclusion, the fulvic acid control solution remained quite constant in its characteristics and the two IRA 904 resin columns continued to remove the organic acid effectively throughout the experiment.

Fulvic Acid-Iron Removal by Resins

Both #3 and #4 resin columns removed color and T.O.C. quite effectively on days 6 and 10. By day 15, however, the solution had changed to such an extent that very little organic color or T.O.C. removal was taking place, as may be observed in Figures 9 and 10. The photographs (Fig. 8 and 12) show the color of the effluents on day 33. From Table IX it can be noted that the T.O.C. and C.O.D. decrease as the solution ages. The pH of the solution was adjusted to 4.5 on day 13 and then to 6.0 on day 17 because it was found that the fulvic-iron complex precipitated at lower pH values. This phenomenonis discussed in detail on page 82. Since the pH of the solution in the latter part of the experiment was more conducive to microbial activity, it is thought that such activity resulted in the decrease of T.O.C. and C.O.D.
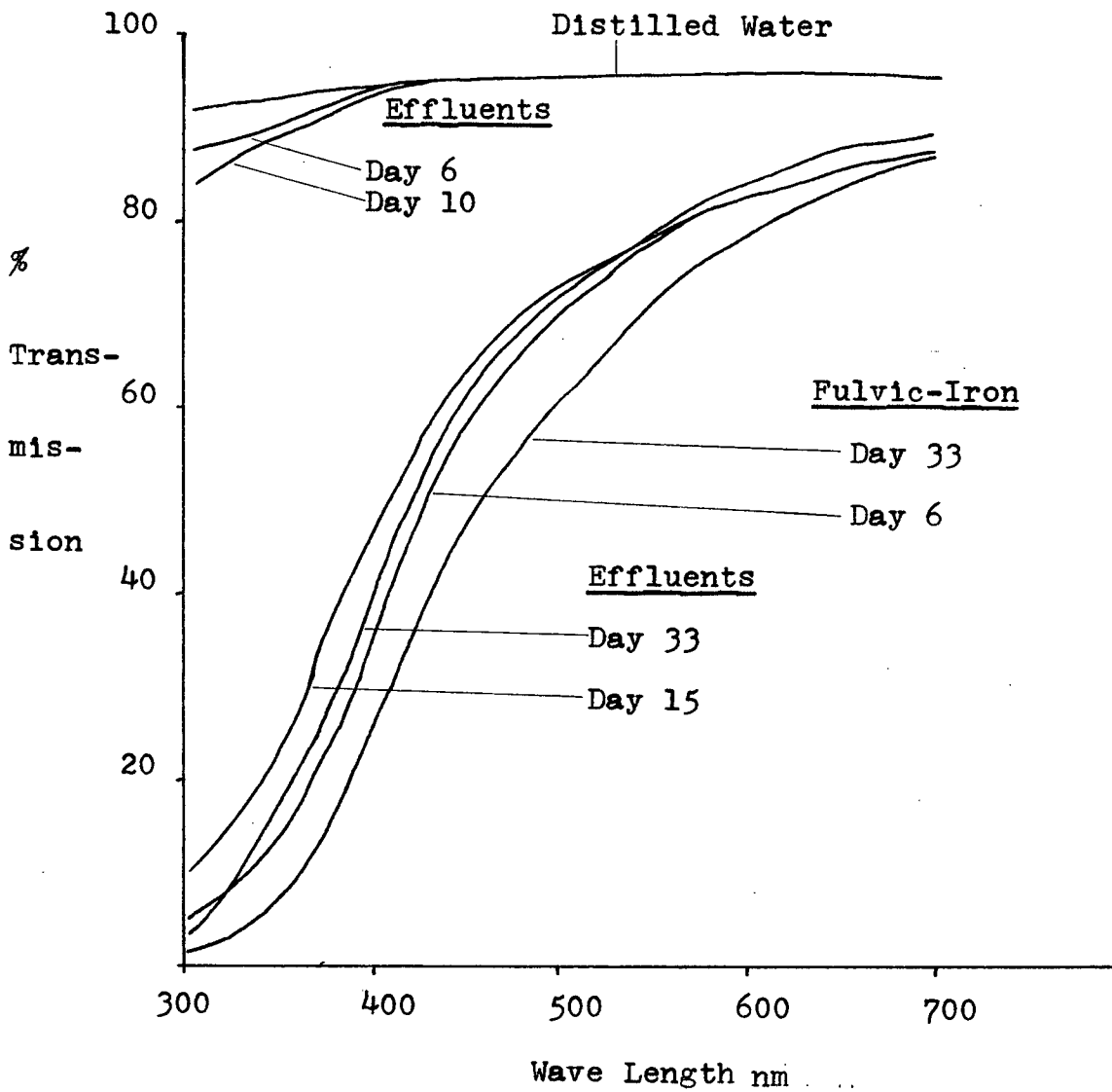
Fig. 9 FULVIC-IRON EFFLUENT COLOR

FROM RESIN #3
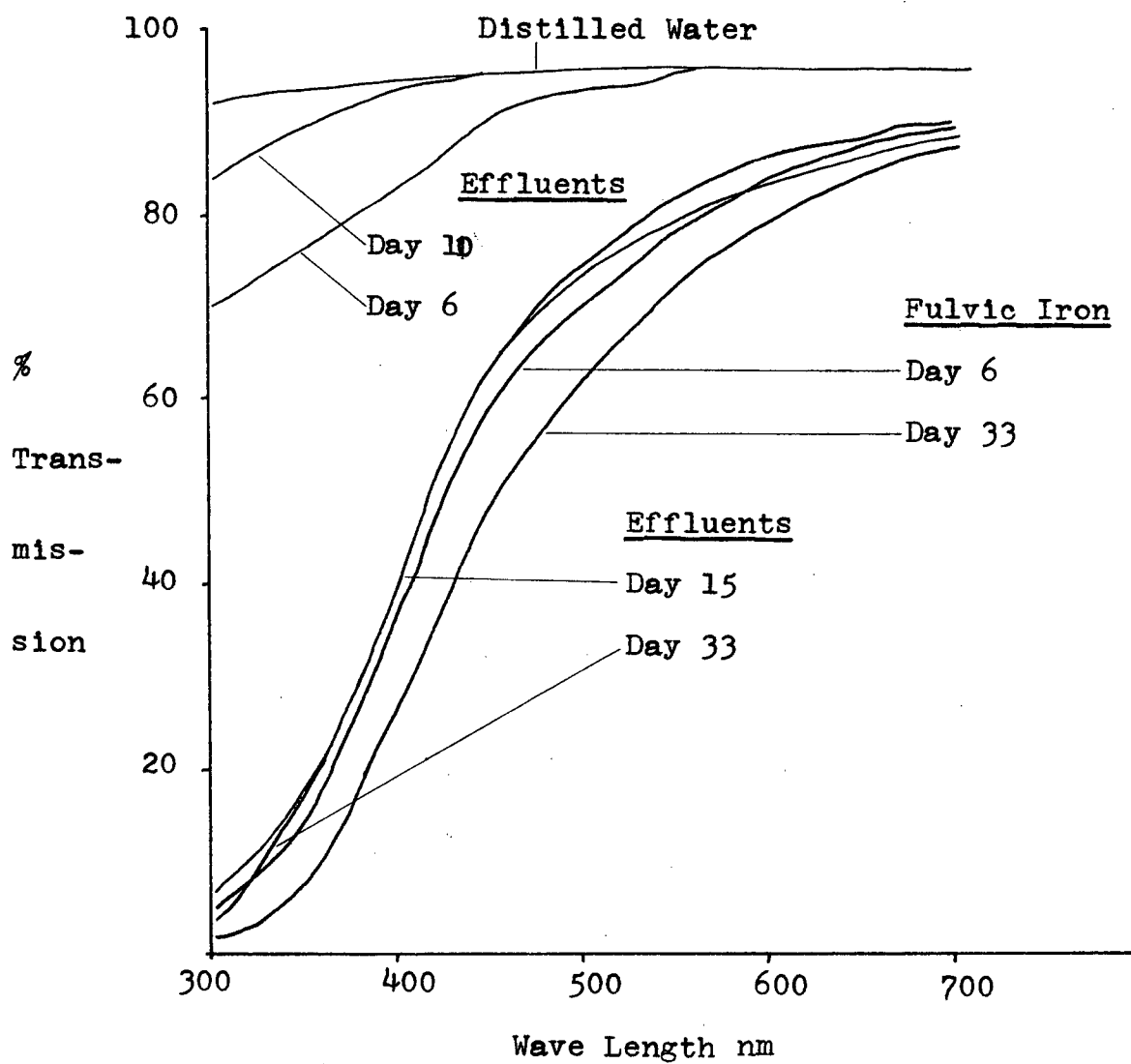
Fig. 10   FULVIC-IRON EFFLUENT COLOR
          FROM RESIN #4

Table IX

Fulvic-Iron Feed Solution.

	Day 6 mg/l	Day 10 mg/l	Day 15 mg/l	Day 33 mg/l
T.O.C.	41	-	38	35
C.O.D.	103	-	85	76
Fe	14.5	15	14	14
pH	3.8	3.8	4.5	5.8

Table X

Resin #3 Fulvic-Iron Effluents.

	Day 6 mg/l	Day 10 mg/l	Day 15 mg/l	Day 33 mg/l
T.O.C.	0	2	17	16
C.O.D.	-	-	66	43
Fe	12	12.75	6.75	10.0
pH	4.3	3.9	5.3	5.4

The values in Table X for the effluent from Resin 3
confirm the light scan shown in Figure 9. The T.O.C. in the
effluent is very low on days 6 and 10. However, on days 15
and 33, the T.O.C. jumps to much higher values (approximately
50% of the concentration in the influent fulvic acid-iron
solution). The pH values of the effluent are not significantly
changed from those of the influent. This is as expected, since
no hydroxyl ions should be present in this resin. The iron
data indicates that less iron is passed through the resin on
days 15 and 33 than on days 6 and 10.

The data shown in Table XI for the effluent from Resin
4 confirm the light scan data presented in Figure 10. Only
the day 6 T.O.C. value does not agree with the color indi-
cation in the light scan; however, since the water was still
relatively free of color (as observed visually), the dis-
agreement was not considered too important. Generally, the
T.O.C. and C.O.D. values of the effluent are very low for days
6 and 10. On day 15 and 33, however, these values increased
a great deal. This is reflected in the change of color of
the effluent as indicated in Figure 10.

It may be noted in Table XI that the presence of hydroxyl
ions in the resin is reflected in the pH of the effluent,
which is higher than the pH of the inflowing fulvic acid-iron
solution.

Table XI

Resin #4 Fulvic-Iron Effluents.

	Day 6 mg/l	Day 10 mg/l	Day 15 mg/l	Day 33 mg/l
T.O.C.	1	2	21	17
C.O.D.	4	-	59	-
Fe	7.5	12.75	8.5	10.0
pH	4.8	4.1	7.2	6.2

Table XII

Fulvic-Iron Effluent from Dowex 50W-X8 & Manganous Greensand

	(Dowex 50W-X8			)	Fulvic Iron Feed Solution	Manganous Greensand
	mg/l Day 6	mg/l Day 10	mg/l Day 15	mg/l Day 33	Day 33	Day 33
T.O.C.	29	-	32	30	35	31
C.O.D.	-	-	104	-	76	
Fe	1.0	1.5	8.5	10.0	14	12.75
pH	3.0	3.0	3.1	3.1	5.8	6.1

Table XII shows the amount of iron passed by the Dowex 50W-X8 on all four testing dates. It may be noted that the Dowex cation resin removes much less iron on days 15 and 33 than on days 6 and 10. This data is taken to indicate that the iron is becoming more bound to the organics as the solution ages. On day 33, very little iron was removed from the solution by manganous greensand. This was further confirmed by the data on Figure 11. Thus the iron may be said to be in the organically bound state from our definition presented in Section 3. A photograph of the Dowex 50W-X8 and manganous greensand effluents is shown in Figure 12.

In conclusion, it appears that as the fulvic-iron solution ages, the iron-organic bonds become stronger and the IRA 904 resins begin to pass much more color, T.O.C., and C.O.D.. Thus while IRA 904 will remove fulvic acid from water it will not effectively remove the fulvic acid-iron from water.

Iron Elution Efficiency for Resins #3 and #4

As may be seen from Table XIII regeneration by method 3 was effective as long as the iron was not strongly bound to the fulvic acid.
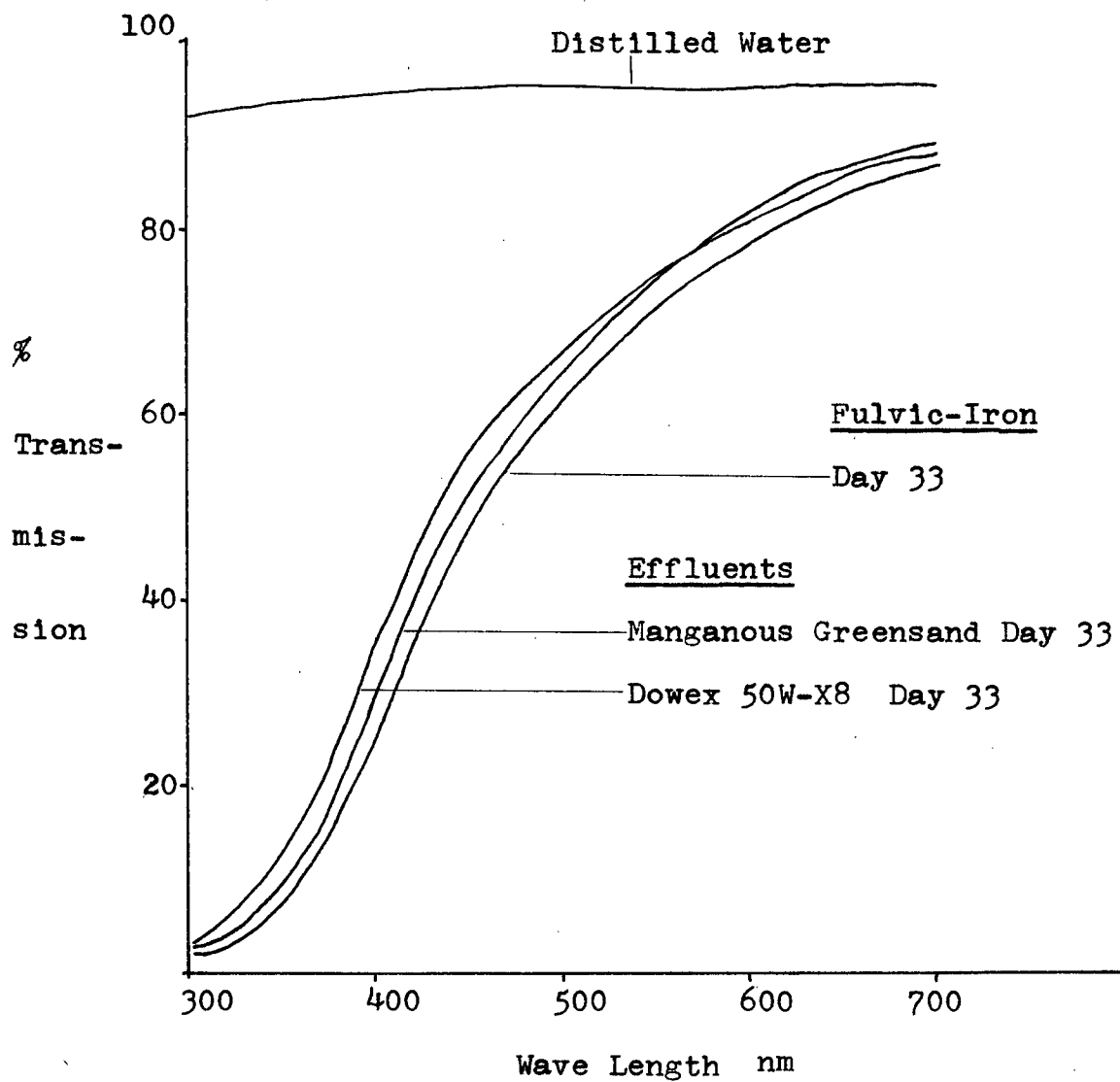
Fig. 11 FULVIC-IRON EFFLUENT COLOR BY
DOWEX 50W-X8 & MANGANOUS GREENSAND.

Fig. 12 FULVIC-IRON EFFLUENT COLOR ON DAY 33

Top, Left to Right:

1. Fulvic Acid-Iron Solution.
2. Effluent from Manganese Greensand.
3. Activated Carbon Effluent.

Bottom, Left to Right:

1. Effluent from #3 IRA 904 Resin.
2. Effluent from #4 IRA 904 Resin.
3. Dowex 50W-X8 Effluent.

Table XIII

Percent Iron Eluted from Resins #3 and #4.

	Regeneration Method	%Fe Eluted on Day 13	% Fe Eluted on Day 34
Resin #3	Method 3	100%	55%
Resin #4	Method 3 with final acid wash deleted	74%	69%

Note: Regeneration by Method 3 requires an HCl wash followed by regeneration solution of 10% NaCl and 1% NaOH followed by another HCl wash.

When the iron became more strongly bound to the fulvic acid only 55% of the iron could be removed from the resin by Method 3. Regeneration by method 3 with final acid wash deleted was less effective when the iron was weakly bound but more effective when the fulvic acid iron bonds became stronger.

As the fulvic-iron becomes more strongly bound regeneration becomes more difficult and neither method could be considered acceptable as 31 to 45% of the iron remains in the resin.

Fulvic and Fulvic-Iron Removal by Activated Carbon

On day 33, the fulvic acid control solution and the fulvic acid-iron solution were passed through columns of Darco activated carbon. Table XIV shows that the activated carbon removed almost all the T.O.C. and C.O.D. from the fulvic acid control solution.

This is confirmed by the light scan in Figure 13 and the photograph (Figure 8), which shows that very little color is left in solution. It is evident from the data in Table XIV that the activated carbon removes much less of the T.O.C. or C.O.D. from the fulvic acid-iron solution. This is also indicated in the light scan shown in Figure 14. The photographs (Fig. 8 and 12) show that the fulvic iron effluent is quite highly colored.

Thus it is concluded that activated carbon will remove almost all T.O.C. and color from an aged fulvic acid solution, but removes much less T.O.C. and color from an aged fulvic-iron solution.

Table XIV

Activated Carbon Effluents

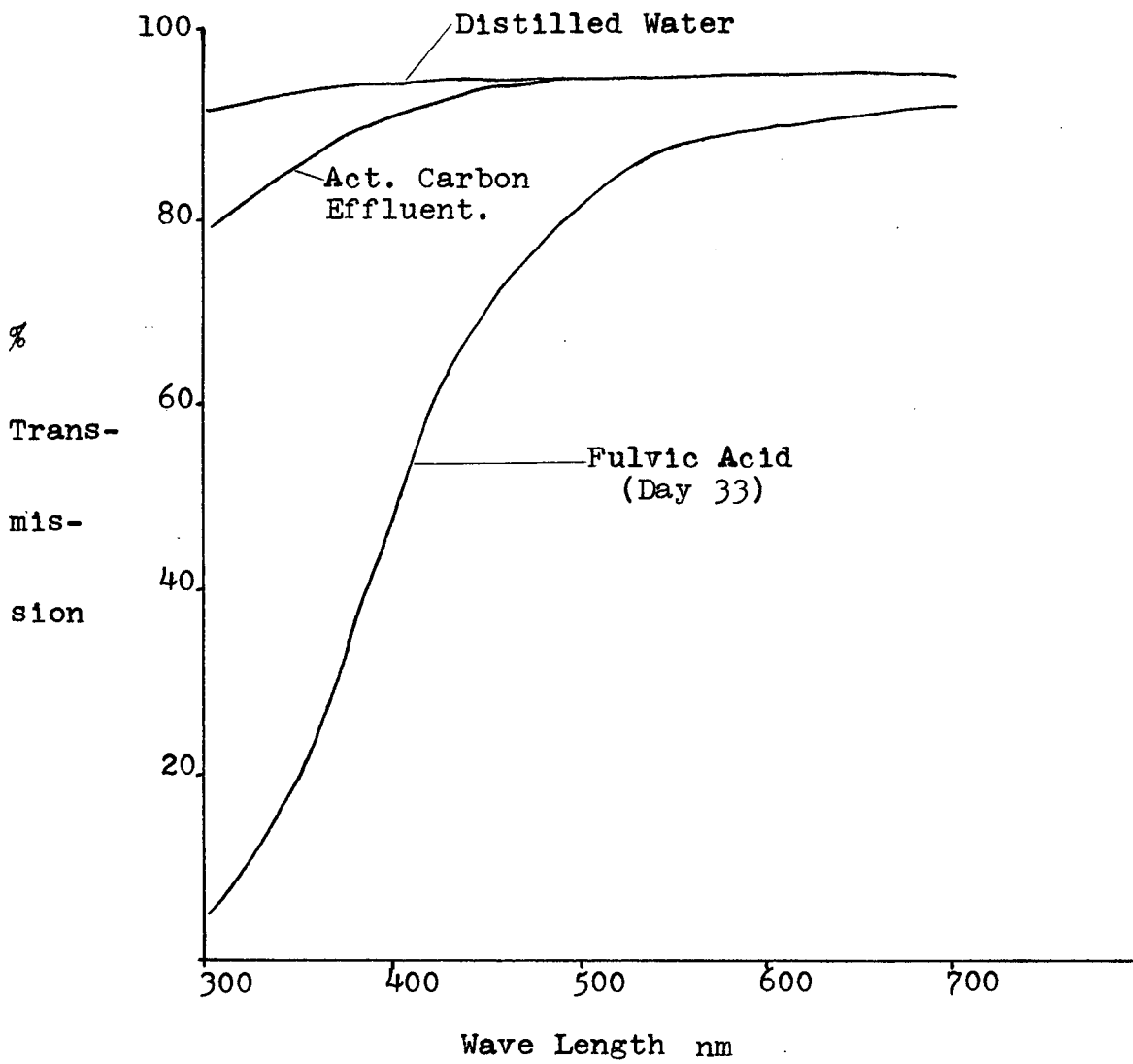|	T.O.C. mg/l	C.O.D. mg/l	Fe mg/l	pH
Fulvic Acid Feed	40	90	0	3.9
Activated Carbon Fulvic Acid	3	9	0	7.5
Fulvic-Iron Feed	35	76	14	5.8
Activated Carbon Fulvic-Iron	15	28	8.0	-

Note: All values taken on day 33.

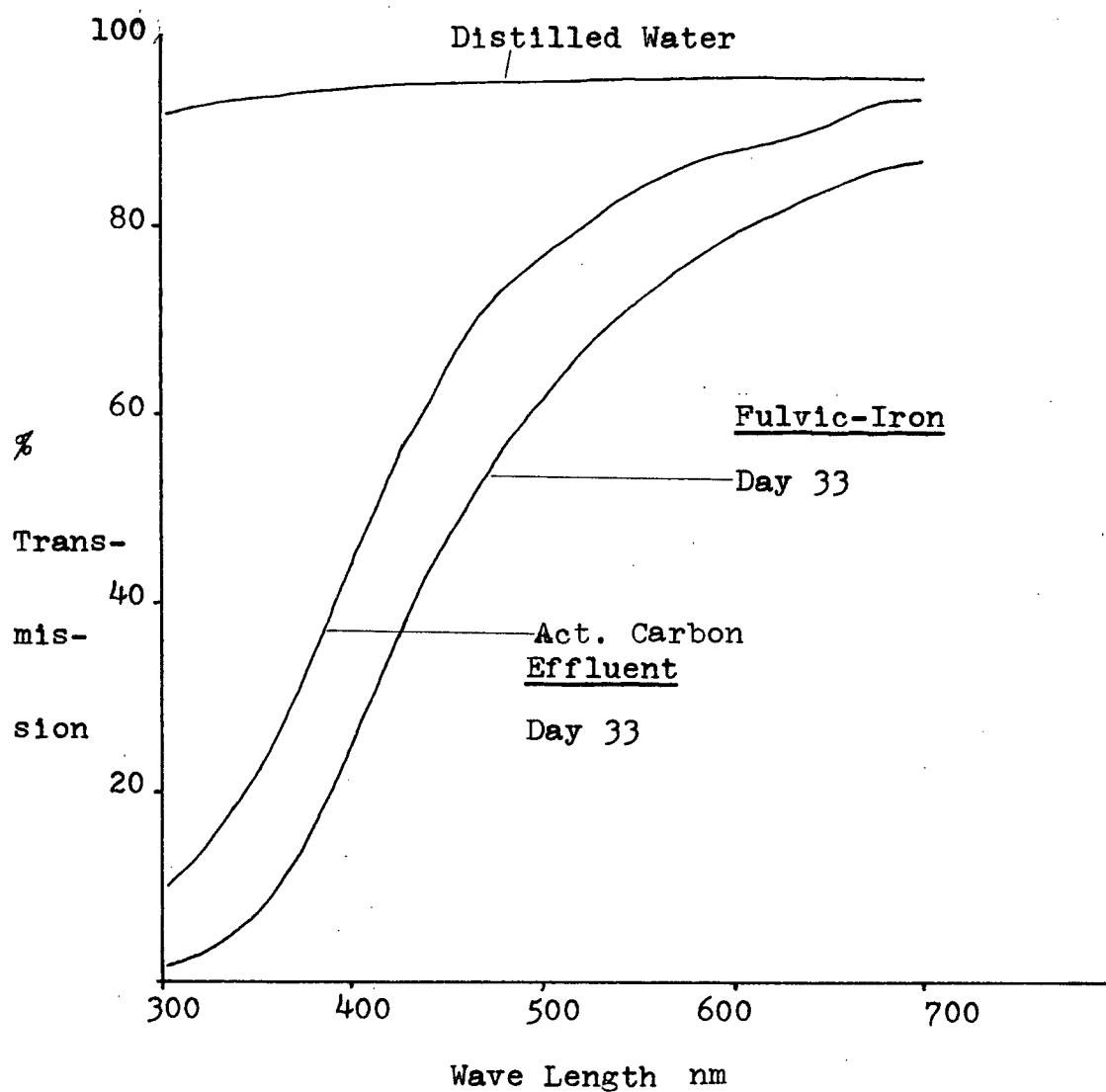Fig. 13 FULVIC COLOR REMOVAL BY

ACTIVATED CARBON

Fig. 14 FULVIC-IRON EFFLUENT COLOR BY
ACTIVATED CARBON

Fulvic Acid-Iron Color Increase

The color of the fulvic acid solution and the fulvic
acid-iron solution on day 1 were the same (Nessler tubes were
used for comparison). As the fulvic acid-iron solution aged,
the color was observed to deepen whereas the color of
the fulvic acid solution remained the same. Figure 15 shows
the color of the solutions on day 33. As may be seen, the
color has drastically increased.

Fulvic Acid Change to Humic Acid in the presence of Iron

The definition of fulvic acid is that it remains in
solution at a pH of 1, while humic and hymatomelanic acids
precipitate at a pH of 1 to 2. For the purposes of simpli-
fication, all organic acids which precipitate below a
pH=2 will be called humic acids in this report.

The original solution of fulvic acid from Burns Bog would
remain in solution at pH=1 or lower. Table XV shows the results
of the organic acid fractionation test on the fulvic acid
control solution and on the fulvic acid-iron solution for the
various testing days. As can be seen, the fulvic acid control
solution does not change; it remains, throughout the experiment
(by definition) totally fulvic acid. This is not the case with
the fulvic acid-iron solution. It only remains fulvic acid
until just after the 10th day. As has been previously shown,
the iron appears to become tightly bound with the fulvic acid
between day 10 and 15, and , once this occurs, the whole complex

Fig. 15 <u>COLOR OF FULVIC AND FULVIC-IRON SOLUTION</u> (Day 33)

Left: Fulvic Acid Control Solution.

Right: Fulvic Acid-Iron Solution.

Table XV

Organic Acid Fractionation

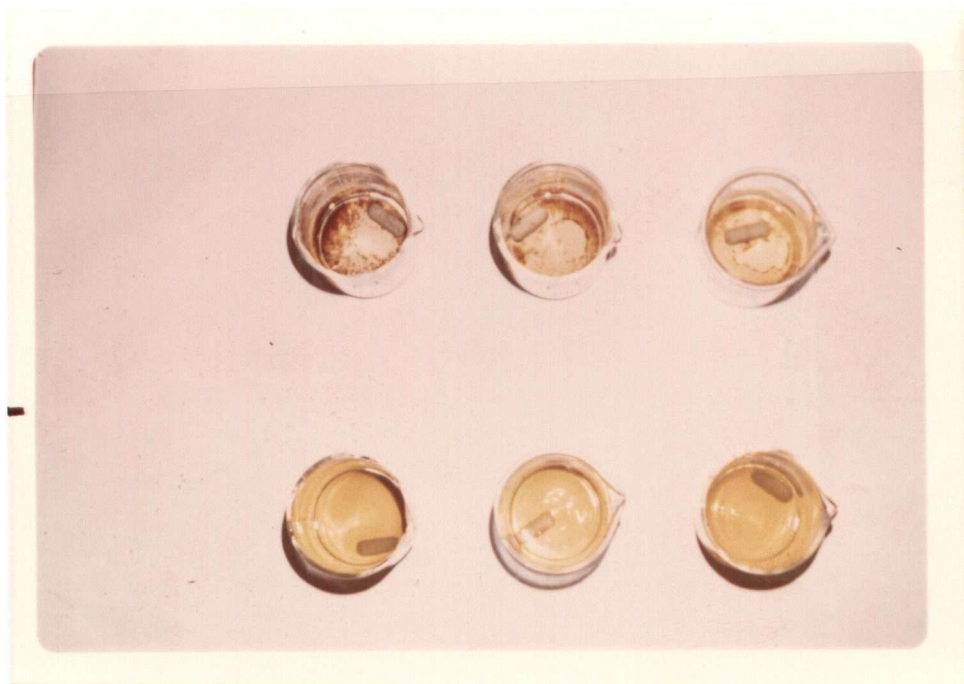|		Day 6	Day 10	Day 15	Day 33
Fulvic Acid Solution	pH=1	No Precip.	No Precip.	No Precip.	No Precip.
	pH=1.5	"	"	"	"
	pH=2	"	"	"	"
Fulvic-Iron Solution	pH=1	Very slight Brown Precip.	Very slight Brown Precip.	Brown Organic Precipitate	Brown Organic Precipitate
	pH=1.5	No Precip.	No Precip.	Dense Brown Organic Precipitate	Dense Brown Organic Precipitate
	pH=2	"	"	"	"

Figure 16 PRECIPITATED FULVIC-IRON AFTER 33 DAYS AGING

Top Row, Left to Right:

Precipitated Fulvic Acid-Iron pH=2 1.5 and 1.

Bottom Row, Left to Right:

Fulvic Acid pH=2, 1.5 and 1.

acts as a humic acid, precipitating as a dense brown organic precipitate at pH=2. It will, however, go back into solution at higher pH values. Figure 16 is a photograph of the precipitated fulvic-iron on day 33.

This phenomenon was observed in the carboy of fulvic acid-iron feed solution itself. On day 13, most of the organics in the solution were found to have precipitated, leaving a slightly colored supernatant with a pH of 3.6. This supernatant was found to have a T.O.C. = 9 mg/l and an iron content = 6.75 mg/l. Since the fulvic acid-iron solution had a T.O.C. = 40 mg/l and an iron content of 15 mg/l a few days before, it was assumed that the precipitated organics amounted to 31 mg/l and the precipitated iron amounted to 8.25 mg/l. It is thought that the 8.25 mg/l of iron could be considered to be organically bound to the 31 mg/l of organic acid. After some experimentation it was decided to raise the pH of the solution to 4.7 because the organic acid and iron went back into solution at this pH. It is interesting to note that on day 15 the Dowex cation exchange resin passed 8.5 mg/l of iron. The amount of organically bound iron in the solution on day 13 was calculated (above) at 8.25 mg/l. Since the Dowex cation exchange resin passes only organically bound iron, this was taken as further proof that the iron was binding with the fulvic acid to form an iron organic complex.

No further precipitating problems were encountered after raising the pH of this solution. It was noted on days 15 and 17 however, that the pH of the solution was decreasing, so on day 17 it was decided to adjust the solution to pH= 6.0. The iron and the color remained dispersed in the solution for the next $1\frac{1}{2}$ months without any noticeable precipitation.

Undoubtedly there are many chemical possibilities by which the iron might cause the fulvic acid to react like humic acid and to pass through the IRA 904 resins and activated carbon while the fulvic acid by itself would not. As stated previously, no attempt has been made to examine the chemical structure of the fulvic acid-iron complex.

SECTION 7

SUMMARY & RESULTS

Organically bound iron has posed problems in municipal water supplies for many years. An effort has been made in this study to solve the problem of its removal from these water supplies. After reviewing the literature the trial and error approach to solving the problem seemed most suitable.

Newly developed ion exchange resins and activated carbon appear to present a good solution to the problem, especially when dealing with very small communities and single dwellings. The literature review revealed that the resins commonly used in North America to treat water supplies are produced by three manufacturers:

1. Dow Chemical Co. Ltd. (Alchem Ltd. in Canada)

2. Diamond Shamrock Chemical Co.

3. Rohm and Haas

These companies were contacted and asked to supply resins which they 'thought would be most likely to remove organically bound iron from water. The resins received were:

1. Duolite S-37 from Diamond Shamrock

2. Amberlite IRA 904 and IRA 458 from Rohm and Haas

3. Dowex 11 from Alchem Ltd.

All of these resins have been used to remove organics and color from water supplies in commercial installations.

84

Atlas Chemicals were contacted and a sample of Granular Darco Activated Carbon made from lignite coal was received from them. This particular type of activated carbon has been used in several installations to remove colored organics from water supplies.

Two solutions of organically bound iron were used in the experiments:

1. Humic and hymatomelanic acids which were extracted from composted leaves formed the major portion of the organic acids present in the first solution.

2. Water from Burn's Bog containing only fulvic acids was used in the second solution. The ferrous iron was added to each solution under controlled conditions.

Experimentation revealed the following observations and results.

1. It was found that iron-organic interactions in solution were time dependent.

2. The reactions between humic acid and iron were quick as 95% of the iron became strongly bound to the humic acid within four hours.

3. Fulvic acid-iron reactions were much slower and a period of 15 days was required for 57% of the iron to become strongly bound to the fulvic acid.

4. A fulvic acid-iron solution in which the iron is strongly bound to the fulvic acid, behaves in much the same manner as a humic acid-iron solution. After 13 days of aging the fulvic acid-iron complex precipitated at a pH of 4.7 but went back into solution when the pH was raised above this value.

5. Amberlite IRA 904 and Duolite S-37 and Atlas Darco
    activated carbon were all effective (approximately
    100%) in removing fulvic acid from solution as
    evidenced by the low color and T.O.C. values
    in the effluent.

6. Amberlite IRA 904, Duolite S-37 and Atlas Darco
    activated carbon were not effective in removing
    fulvic acid-iron or humic acid-iron from solution
    as evidenced by the high color and T.O.C. values
    in the effluent.   (Amberlite IRA 904
    and Atlas Darco Activated carbon removed approx-
    imately 55% of the T.O.C. and approximately 35% of
    the iron from the fulvic acid iron solution which had
    aged for 33 days. Amberlite IRA 904, Duolite S-37
    and Atlas Darco Activated Carbon removed approximately
    25% of the T.O.C. and 5% of the iron from the humic
    acid iron solution)..

7. Dowex 50W-X8, Dowex MSC-1, and manganous greensand
    were effective in removing iron which was not
    organically bound to the fulvic or humic acid in
    the solution. Organically bound iron could not be
    removed by these resins nor would they remove any
    fulvic acid or humic acid from the solution.

8. IRA 458 did not remove fulvic-iron or humic-iron
    from solution.

9. Dowex 11 would not remove fulvic-iron or humic-iron
    from solution.

10. Fulvic acid is effectively eluted from Amberlite
    IRA 904 by a regenerating solution of 10% NaCl and
    1% NaOH.

11. Fulvic acid is effectively eluted from Duolite S-37
by a regenerating solution of 4% NaOH.

12. Iron fouling can occur if Amberlite IRA 904 or Duolite
S-37 are left in the hydroxyl form as the iron which
is not strongly bound to the organic acids precipitates
in the resin column. If Amberlite IRA 904 is acid washed
immediately before and after use this problem is
minimized.

13. Some of the strongly bound organic iron was removed by
the Amberlite IRA 904 resin (approximately 35%). This
organic-iron could not be effectively removed with an
acid wash or with the 10% NaCl and 1% NaOH solution (30-
45% of the iron remained in the resin). This indicates
that iron fouling might occur in the resin.

14. The color of the fulvic-iron solution became considerably
darker as the solution aged and the iron became more
strongly bound to the fulvic acid.

SECTION 8

CONCLUSIONS

It is concluded that:

- Neither the activated carbon (Atlas Darco) nor the organic scavenger resins (Amberlite IRA 904, Amberlite IRA 458, Duolite S-37, Dowex 11) will successfully remove aged fulvic acid-iron complexes or humic acid-iron complexes from water.

-Activated carbon (Atlas Darco) and the organic scavenger resins (Amberlite IRA 904, Duolite S-37) will successfully remove fulvic acid from water which has no iron present.

-Manganous greensand and the cation exchange resins (Dowex MSC-1, Dowex 50W-X8) will successfully remove iron from water which has no organic acids present.

- Activated Carbon (Atlas Darco) or a combination of Amberlite IRA 904 and Dowex MSC-1 resins will successfully remove both fulvic acid and iron from solution if the fulvic acid is not fully complexed to the iron. However, the fulvic acid-iron reactions are time dependent, therefore each situation would need to be examined independently and could vary throughout the year. It is not expected that any combination of resins or activated carbon would be successful in removing the fulvic acid and iron all of the time.

- Fulvic acid-iron which has had sufficient time to become fully complexed has the same precipitation characteristics as humic acid-iron complexes. Both organic-iron complexes will precipitate at a low pH (2 to 4.7) but will stay in solution when the pH is greater than 6.

BIBLIOGRAPHY

1. Clark, Francis M., Robert M. Scott and Ester Bone, "Heterotrophic Iron Precipitating Bacteria", Journal AWWA, August, 1967.

2. Black, A. P. and R. F. Christman, "Chemical Characteristics of Fulvic Acids", Journal AWWA, July 1963.

3. Starkey, Robert L., "Transformations of Iron by Bacteria", Journal AWWA, October 1945.

4. Shapiro, J., "Chemical and Biological Studies on the Yellow Organic Acids of Lake Water", Limnol Oceanog., 2:161 (1957)

5. Oldham, W. and E. F. Gloyna, "Interactions of Iron with Soil Organic Acids", Journal AWWA, November 1969.

6. Singley, J. E., R. H. Harris and J. S. Maulding "Correction of Color Measurements to Standard Conditions", Journal AWWA, April, 1966.

7. Christman, R. F. and M. Ghassemi, "Chemical Nature of Organic Color in Water", Journal AWWA, June 1966.

8. Burges, A. "The Nature and Distribution of Humic Acid", Sci. Proc. Roy Dublin Soc., Ser. A, 1:53 (1960).

9. Burges, N. A., H. M. Hurst, and B. Walkden, "The Phenolic Constituents of Humic Acid", Geochim. et Cosmochim. Acta, 28:1547 (1964).

10. Jakab, T., P. Dubach, N. C. Mehta and H. Devel, "Degradation of Humic Substances, III Degradation with Alkali", Z. Pflanzenernaehr. Dveng. Bodenk. (Ger.) 102:17 (1963).

11. Wilson. A. L., "Determination of Fulvic Acids in Water", Journ. Appl. Chem. 9:501 (1959).

12. Black, A. P. and R. F. Christman, "Characteristics of Colored Surface Waters" Journal AWWA, June 1963.

13. Babcock, R. H., "Iron and Manganese in Water Supplies and Methods of Removal", Water and Sewage Works, 98:442 (1951).

14. Ghosh, M. M., "A Study of the Rate of Oxidation of Iron in Aerated Ground Waters", Dept. of Civil Engineering, University of Illinois (1962.)

15. Hall, K., "Natural Organics Matter in the Aquatic Environment", Doctoral Dissertation, University of Wisconsin,1970.

16. Shapiro, J., "Yellow-Acid-Cation Complexes in Lake Water, Science, 127:702 (1958).

17. Christman, C.H., "Ultramicroscopic Studies of Colloids in Water", Journ. AWWA, 21:1076 (August, 1929).

18. Wiley, B. F. and H. Jenning, "Iron and Manganese Removal with Potassium Permanganate", Journ. AWWA, June, 1963.

19. Welch, W. A., "Potassium Permanganate in Water Treatment", Journ. AWWA, June, 1963.

20. Frisch, N.W. and R. Kunin, "Organic Fouling of Anion Exchange Resins", Journ. AWWA, July, 1960.

21. Abrams, I.M., "Scavenger Resins for Removal of Organics from Water", presented at the International Water Conference of the Engineers' Society of Western Pennsylvania, Sept. 30, 1964.

22. Abrams, I.M. and R.P.Breslin, "Present Studies on the Removal of Organics from Water", presented at the 26th Annual Meeting, International Water Conference of the Engineers' Society of Western Pennsylvania, Pittsburgh, Pa., Oct. 22, 1965.

23. Jayes, D.A. and I.M.Abrams, "Color Removal from a New England River Water":, International Water Conference, Engineers' Society of Western Pennsylvania, Nov. 7, 1966.

24. Singley, J.E., Chairman, A.W.W.A. Research Committee on Coagulation and Research Committee on Color Problems, "Coagulation and Color Problems", Journ. AWWA, May, 1970 (Joint Report).

25. Hale, F. E., "The relation between Aluminum Sulfate and Color in Mechanical Filtration", Journ. Ind. and Eng. Chem., 6:632 (1914).

26. Hedgepeth, L.L., N.C. Olsen, and W. C. Olsen, "Chlorinated Copper as a New Coagulant", Journ. AWWA, 20:167 (1928).

27. Maulding, J.S. and R.H. Harris, "Effect of Ionic Environment and Temperature on the Coagulation of Color Causing Organic Compounds with Ferric Sulfate", Journ. AWWA, April, 1968.

28. Hall, E. S. and R.F. Packham, "Coagulation of Organic Color with Hydrolyzing Coagulants", Journ. AWWA, 57:1149 Sept. 1965.

29. Vilaret, M.R., Doctoral Dissertation, University of Florida 1966.

30. Abrams, I.M., "Removal of Organics from Water by Synthetic Resinous Adsorbents", Chemical Engineering Progress, Vol. 65, No. 97, 1969.

31. Mucke, D. and R. Obenaus, Wiss. Z. Univ. Rostock, 12:103 (1963).

32. Data Sheet and Laboratory Tests for Amberlite as carried out by Rohm and Haas Company.

33. Driscoll, M., Unpublished data from tests performed for the Rohm and Haas Company, Southwest Medical Institute, Dallas, Texas.

34. Horembala, L. E. and C. A. Feldt, "Ion Exchange Screen for Organic Matter Improves Demineralizer Performance". Presented at the 28th meeting of International Water Conference of the Engineers' Society of Western Pennsylvania, Pittsburgh, Pennsylvania, Dec., 1967.

35. Bohnsack, G., "Tests on the Behaviour of Anion Exchangers Toward Humic Acids", Mitteilungen der VGB, 76: 53-8 (1963).

36. Hager, D.G. and M.E. Flentze, "Removal of Organic Contaminants by Granular Carbon Filtration", Journ. AWWA, 1440, Nov. 1965.

37. O'Donovan. D. C., "Treatment with Ozone", Journ. AWWA, 1167, (September), 1965.

38. Coogan, G.J., "Diatomite Filtration for Removal of Iron and Manganese", Journ. AWWA, 1507, Dec., 1962.

39. Faust and Hunter. Organic Compounds in Aquatic Environments. Marcel Dekker, 1971

40. Mattson and Mark. Activated Carbon-Surface Chemistry and Adsorption from Solution. Marcel Dekker, 1971

41. Rawson and Fuller, Manual of British Water Engineering, pp. 538-539.

42. Campbell, R. M., "The Use of Ozone in the Treatment of Loch Turret Water", Journ. Inst. Water Engrs., 17:333 (1963).

43. Ghassemi, M. and R.F. Christman, "Properties of the Yellow Organic Acids of Natural Waters", Limnology and Oceanography, Vol. 13, No. 4, Oct. 1968.

44. Menzel, D. W. and Vaccaro, R. F., "The Measurement of Dissolved Organic and Particulate Carbon in Seawater", <u>Limnol. and Oceanography,</u> 9, (1964).

APPENDIX 1

PREPARATION OF HUMIC AND HYMATOMELANIC ACIDS

These acids were extracted from leaves which had been
composting for two years. The method of extraction involved
soaking the composted leaf material in distilled water which
had its pH raised to approximately 11 by the addition of
NH_4OH. The composted material was soaked for eighteen hours.
This mixture was then filtered and the resulting liquid
acidified with HCl to a pH of approximately 2. Any pre-
cipitate was filtered and dried for two hours at $70^\circ C$. This
dark brown precipitated material was then stored in a dessicator.

In order to determine what percentage of the above material
was actually humic and hymatomelanic acid, the material was
fractionated as per Figure 17 and the following formula used.
Total residue weight=weight of ether soluble fats and waxes +
weight of humic acid + weight of hymatomelanic acid + weight
of fulvic acid.

The dark brown residue was weighed and dissolved in
distilled water which had its pH adjusted to 9 with NH_4OH.
This concentrate was then washed with diethyl ether in a sep-
arating funnel to remove the ether soluble fats and waxes.
The weight of the ether soluble fats and waxes was determined
by evaporating the ether and weighing the residue.

Concentrate (Diethyl Ether, Washed)

Solid Precipitate

Ethyl Alcohol

Liquid (Fulvic Acid)
Fraction 1

Soluble
(Hymatomelanic Acid)
Fraction III
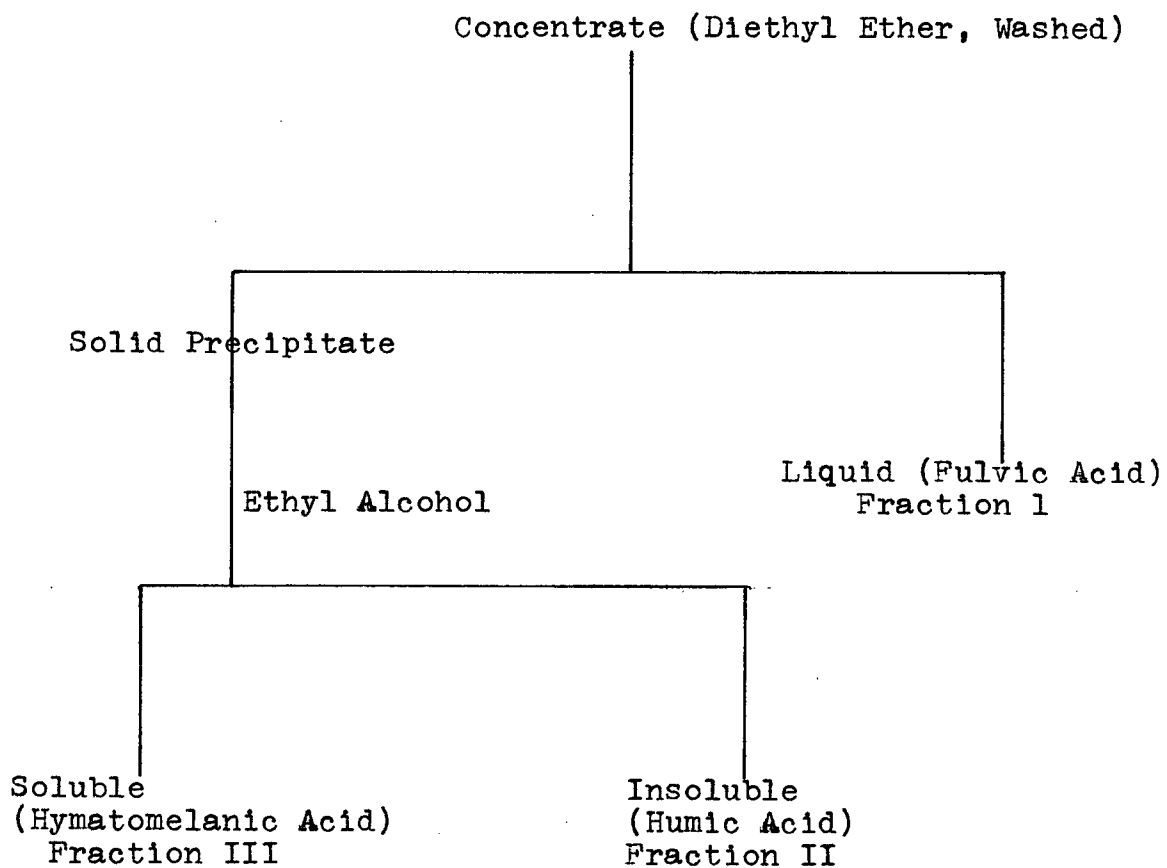
Insoluble
(Humic Acid)
Fraction II

Fig. 17 SCHEMATIC DIAGRAM OF FRACTIONATION
PROCEDURE.

The pH of the remaining solution was then adjusted to pH=1 by the addition of HCl, and the concentrate was filtered. The residue filtered from this solution was dried and weighed to determine the total weight of the humic and hymatomelanic acids. This residue was then washed with ethyl alcohol and refiltered. The filtered residue was dried and weighed to determine the amount of humic acid present in the concentrate. The weight of the fulvic acid present was determined by the previously given formula.

The percentages of the total for the different acid fractions in the concentrate were found to be:

Ether soluble fats and waxes = 28%

Fulvic Acid = 16%

Humic Acid = 42%

Hymatomelanic Acid = 14%

Total Residue wt. =100%

Since the humic acid makes up the greatest single portion of this solution, the solution is referred to as the humic acid solution.

APPENDIX 2

THE COMPLEXATION OF HUMIC ACID TO IRON

IRON SALT USED

Several experiments were performed to determine by what method the iron should be added and what iron salt should be used. $FeSO_4$, $FeCl_2$ and $Fe(NH_4)_2(SO_4)_2$ were tried in these experiments. The procedure consisted of purging a flask of distilled water with nitrogen for approximately one hour in order to remove all dissolved oxygen. The ferrous salt was then added to this distilled water and dissolved under a nitrogen purge to ensure that no dissolved oxygen would oxidize the ferrous iron to ferric iron. The pH of this solution was adjusted to between 8 to 9. Several solutions of each of the above ferrous salts were prepared in concentrations varying from 2 mg/l to 50 mg/l. These solutions were allowed to sit overnight exposed to air. It was found that the solutions containing $Fe(NH_4)_2(SO_4)_2$ had the best developed precipitate in the morning. All the solutions formed a precipitate which could be filtered. As a further check $Fe(NH_4)_2(SO_4)_2$ was added by the same procedure as above to a water which contained an alkalinity of 200 mg/l.

The samples were allowed to sit exposed to air overnight and in the morning they were centrifuged for 25 minutes at 2200 rpm to remove the precipitate. The supernatants of all the samples were found to contain no iron.

It was concluded that the ferrous ion would come out of solution forming $Fe(OH)_2$ or $Fe(OH)_3$ as a filterable precipitate at any concentration above 2 mg/l if exposed to air overnight at a pH of between 6 and 8.

Problems were encountered when a combination of alkalinity, hardness and iron were added to the humic acid solution. After several experiments it was decided to add only iron and alkalinity to the humic acid solution as when calcium hardness was added it tended to partially precipitate the humic acid and a very poor settling floc was formed.

PREPARATION OF THE HUMIC ACID-IRON SOLUTION

A solution of humic acid was prepared by dissolving 40 mg/l of dried humic acid, prepared as per Appendix 1, in distilled water of pH=9. Alkalinity (200 mg/l measured as $CaCO_3$) was added to this solution in the form of Na HCO_3. This adjusted the pH of the solution to 8.3. The solution was then purged with nitrogen for approximately 2 hours to remove all the dissolved oxygen. A ferrous iron solution of $Fe(NH_4)_2 (SO_4)_2$ was prepared under nitrogen purge as previously explained. After approximately two hours the

iron solution was withdrawn by a pipette and transferred to the humic acid solution taking care that none of the iron solution came in contact with air. The humic acid iron solution was left under a nitrogen purge for the next three hours in order to assure that the ferrous iron would link to the humic acid. Previous experiments had determined that this was the best procedure to use. After the iron and humic acid had been together under nitrogen purge for three hours, the nitrogen was shut off and the solution was aerated for 30 minutes. It was thought that any uncomplexed ferrous iron would be oxidized to ferric iron and would precipitate as $Fe(OH)_3$ if high dissolved oxygen levels were maintained. No precipitate was noticed in the solution nor was any noticed when the solution was passed through a number 41 Watman filter. A sample of the solution was also passed through a diatomaceous earth filter with no removal of iron. It was therefore concluded that no ferric hydroxide had precipitated after being aerated.

Problems occurred with this solution changing with time. However, the iron concentration of the solution remained relatively stable and the iron remained dispersed throughout the solution for several months. The T.I.C. and T.O.C. were seen to change as the solution got older. Both were found to decrease in concentration though the solution did not visibly change color. The T.O.C. was thought to decrease due to

bacterial action while the T.I.C. was thought to decrease
due to the acidic nature of the organic acids. It was noted in
several cases that as the organic acid-iron solution got older
the pH of that solution decreased.

Since the iron became complexed to the humic acid by the
definition in Section 3 very quickly and remained complexed for
several months this solution was considered to be quite good for
testing purposes.

APPENDIX 3

COMPLEXATION OF FULVIC ACID TO IRON

Highly colored water was obtained from Burns Bog (a peat bog area near the Fraser River south of Vancouver, B. C.). When tested by lowering the pH to 1 it was found that this water contained only fulvic acids. This solution was purged with nitrogen for four hours and a ferrous ammonium sulfate solution was added by the same procedure outlined in Appendix 2. The nitrogen purge was continued for another three hours to allow the organic acid time to link with the iron. The solution was then aerated for two hours to ensure a high dissolved oxygen content. Since the pH of the natural bog water was 4, it was not expected that the ferric hydroxide would form and precipitate out immediately. After a few days, the solution was passed through a diatomaceous earth filter with no removal of iron. Through experimentation with this solution it was found that it did not initially meet the definition of organically bound iron used in this research. The reaction between the iron and the organic acid was time dependent and the solution changed in color and characteristics as it became older. At no time, however, did the iron ever precipitate as ferric hydroxide and under the correct pH conditions it was found to remain dispersed throughout the solution for months. The details of this changing solution are given in Chapter 6.