"The Preparation and Oxidative Properties of Ferrate Ion (FeO_4^{2-}). Studies Directed Toward Its Use as a Water Purifying Agent. Phase I."

by

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The Preparation and Oxidative Properties of Ferrate Ion (FeO_4^{2-}). Studies Directed Toward Its Use as a Water Purifying Agent.

ABSTRACT

The use of FeO_4^{2-} in the treatment of deep-well and Missouri River water has been evaluated with respect to many variables. It is found that the addition of FeO_4^{2-} effectively reduces the amounts of iron, manganese, cadmium, mercury, lead, cobalt, nickel, arsenic, and boron to values less than the detectable quantities with our instrumentation. This is done with less than 50 ppm of added Na_2FeO_4. The presence of river silt has no effect and the reagent is effective above a pH of 7. In more acidic water some base such as CaO must be added to prevent the spontaneous FeO_4^{2-} decomposition but less than is presently being used in plants around the country. For iron removal, 1-2 ppm FeO_4^{2-} removes iron to less than .02 ppm giving an easily filterable precipitate.

Any excess FeO_4^{2-} decomposes in 15-20 minutes (depending on temperature and acidity) precipitating $Fe(OH)_3$ and giving O_2 to the system. No residual reagent remains. Many organic substances are oxidized to CO_2 and N_2 ultimately while H_2S goes to S_8 and NO_2^- to NO_3^- and NH_3 to a series of products.

FeO_4^{2-} is extremely deadly to many river water bacteria as well as to selected strains of laboratory bacteria. It approaches the effectiveness of OCl^- (Cl_2) in the tests so far conducted. (1-5 ppm) FeO_4^{2-} removes essentially all the test bacteria in laboratory studies. Test virus are also highly susceptible to

to its action and the damage is permanent. It has the further advantage of leaving no residue or residual action after a short reaction period and filtration. The time of contact need be only short, one minute or less for it to be effective at 5-25°C.

The preparation of Na_2FeO_4 can be carried out by electrolyzing scrap iron in 50% NaOH solution giving about 50% theoretical conversion to the ion. The by-product is H_2 which has many industrial uses. Thus there is reason to believe that Na_2FeO_4 can be prepared cheaply, shipped as a stable concentrated NaOH solution and metered as a liquid into water purification streams.

This study has shown that Na_2FeO_4 is extremely effective for removing transition metal ions and other foreign ions as well as killing bacteria and clarifying well water and river water. It may be the final treatment of choice when industrial production of the reagent is accomplished.

Key Words

Water, Purification, Iron, Sedimentation, Bacteria, Oxygen, Streams.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

INTRODUCTION AND OBJECTIVES

All of our water resources are gradually being contaminated by various man-produced or man-induced substances. Based on studies of past changes, it appears that the future will continue this trend and before long severe strains will be placed upon our ability to purify the water needed for human and animal consumption. The standard methods of treating river and well water have been improved in recent years primarily through closer control over the variables and better machinery to do the job more effectively. However, such continued improvement is not likely utilizing existing methods. Many are now suggesting that new chemical and physical methods be investigated as potential replacement for conventional ways. What appears to have significant potential is the FeO_4^{2-} ion which here-to-for has been thought to be too unstable for commercial use. We have begun studies on this ion and have shown it to be especially effective and highly useful at a moderate cost.

The objectives are:

a) To find new methods and evaluate old procedures for preparing solutions of Na_2FeO_4 and to study its stability and its properties in various media with an effort toward finding a cheap, simple method of producing a "time" stable substance.

b) To determine how it decomposes in pure water media and in stream and lake water with the objective of removal of objectional substances in a water treatment process. It is expected to compete favorably with Cl_2 due to its other useful properties.

c) To carry out some mechanistic and theoretical studies on the detailed steps by which simple ions as well as amino-acids are decomposed by FeO_4^{2-}.

d) To examine the fate of bacterial strains and virus when treated with FeO_4^{2-} and estimate the ability of the ion to kill common bacteria and virus found in water supplies.

STATEMENT OF PROBLEMS

1. To determine the cheapest method of making FeO_4^{2-} from inexpensive substances.
2. To evaluate its industrial cost and its physical and chemical properties.
3. To find out what organic substances are destroyed by it, at what rate and to identify the products.
4. To learn of the co-precipitating ability of the $Fe(OH)_3$ produced and to find out which ions are removed.
5. To carry out kinetic and ^{18}O studies to determine the mechanism of reduction of FeO_4^{2-} in pure water.
6. To estimate the ability of this ion to destroy biological living material in water.
7. To give an educated evaluation of the usefulness of Na_2FeO_4 to purify water for human consumption by removing organic substances, living organisms, and to remove itself and suspended material by co-precipitation precipitation phenomena.

METHODS OF INVESTIGATION

1. Two basic approaches were made:

   a. The use of Cl_2 in alkaline media on $Fe(OH)_3$.

   b. The electro-oxidation of scrap iron in 50% NaOH solution.

   The latter method is new and we found it to be cheaper than method (a). Therefore, the investigation went into the electrical efficiency of the process with respect to the presence of Cl^-. The concentration of OH^-, the temperature, current density, rate of stirring and metal type.

2. Based on the cost of electricity, NaOH, iron scrap and transportation, estimates of the cost of Na_2FeO_4 were made. Utilizing the amount necessary to purify water $\cong$5 ppm a cost per 1000 gallons was also made.

3. Various organic substances including many amino-acids, sugars, etc. were tested for their ability to react with FeO_4^{2-} in neutral solution. Their concentration was in the range $1\text{-}5\times10^{-4}$ m/l and reaction had to be noticed within 5 minutes for an oxidation test to be considered positive. Room temperature 29°C was used. The products were usually CO_2 and N_2 which were determined by gas chromatography and mass-spectralanalysis. Some other products were noted but it is clear that in many cases the main products were partially oxidized acids and nitro compounds. Very precise studies were made on the reaction with NO_2^- and NH_3. Complete stoichiometric relationships resulted.
4. Water from various sources (wells, river, tap) was collected,

refrigerated or used directly. Various other ions were added and then FeO_4^{2-}. The solution was allowed to stand until the precipitate was completely formed and then filtered or decanted into a new flask. It was analyzed for the element concerned usually by atomic absorption. Blanks were always run at the beginning and end of each day. It was generally found that the FeO_4^{2-} was completely decomposed in one hour and separation of the red-brown precipitate complete in 10 hours at room temperature. Sedimentation rates were evaluated.

5. These theoretical studies were carried out as described in the enclosed paper. We found the formula of the ion, the rate equation for its decomposition, the mechanism for reaction with SO_3^{2-}, NH_2NH_2, H_2O_2 and NO_2^- and an estimate of PO_4^{3-} as a stabilizing ion. A careful evaluation of FeO_4^{2-} usefulness in NH_3 removal was made.

6. This portion of the study was done in two parts. First to obtain bacterial growth curves two different strains of pseudomonis bacteria were grown for 24 hours at 37°C in a nutrient broth solution consisting of 5% beef extract in distilled water. The strains were diluted to 10^{-6} in a buffered nutrient salt solution and subcultured. Varying amounts of K_2FeO_4 were added to the subcultures which were allowed to incubate at room temperature for 1 hour. This was sufficient time for exponentially growing cells to go through one complete growth cycle. The subcultures were then agar-plated and incubated for 24 hours at 37°C. Before counting the plates which showed no growth, they

were allowed to sit at room temperature for a few days for any delayed growth. Missouri River water bacteria were also grown overnight and treated as above. E. Coli were reacted with FeO_4^{2-} in water and a growth medium to determine its effectiveness. Cl_2 was compared directly. A virus, $P_{(22)}$ was treated with FeO_4^{2-} and Cl_2 and then used to react with E. Coli Bacteria. The FeO_4^{2-} action on virus was directly compared with Cl_2.

7. Utilizing the results given above a general estimation of the potential usefulness of this reagent for water purification was made.

RESULTS

Preparation of Solutions of FeO_4^{2-}

The results of numerous attempts to produce Na_2FeO_4 from $Fe(OH)_3$ and OCl^- while successful led to several problems which did not lend themselves to inexpensive commercial production. OCl^- was prepared (with Cl^-) from Cl_2 and 50% $NaOH$-H_2O solutions. This reaction is rapid and quantitative. The NaCl produced has to be removed by filtration which is difficult since the liquid is so viscous. Several types of iron hydroxide were used: a) freshly prepared from Fe(III) X salt and NaOH where X was NO_3^-, Cl^-, ClO_4^-, and SO_4^{2-}, where it was purified by water extraction or used directly; b) aged perparations from the former; c) Fe_2O_3 commercial and $Fe(OH)_2$ was also used. The results seen below indicate that only freshly prepared hydroxide is effective and that only a portion of it is ever converted. Further, the presence of NO_3^-, Cl^- (large excess), ClO_4^-, and SO_4^{2-} dramatically alter the yield. Fe_2O_3 is highly ineffective presumably due to its insolubility and low surface area. $Fe(OH)_2$ is very good and perhaps even better than $Fe(OH)_3$, but, of course, it takes more oxident also. The time and temperature variables, were partially studied and in both cases a maximum was observed. This suggests, as has been noticed in other systems, that all variables will be a function of batch size, stirring rate and impurity levels as has been suggested by the data in Table I. It is concluded that this method of preparation is not highly desirable for commercial production, especially since it necessitates several filtrations of caustic material which have a high viscosity and molecular Cl_2 is an expensive starting material.

TABLE I

Formation of Na_2FeO_4

Temp	Iron Form	Theoretical % OCl^- Used	% Non-Used(Fe^{3+})
0°	$Fe(OH)_3$[1]	80	22[2]
10°	$Fe(OH)_3$[1]	90	35[2]
20°	$Fe(OH)_3$[1]	105	36[2]
25°	$Fe(OH)_3$[1]	140	28[2]
0°	$Fe(OH)_3 + NaNO_3$	92	15[2]
0°	$Fe(OH)_3 + NaCl$	90	20[2]
0°	$Fe(OH)_3 + NaClO_4$	90	20[2]
0°	Fe_2O_3	29	92
10°	$Fe(OH)_2$ pure	95	62
10°	$Fe(OH)_2 + NaCl$	98	55
10°	$Fe(OH)_2 + NaNO_3$	109	42
10°	$Fe(OH)_2$ pure[3]	110	28

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1. Freshly prepared free from salts
2. Contact time four hours--rapid stirred
3. Very mild stirring

The second method involved the oxidation of crude iron metal electrolytically in 30-50% NaOH solution. Using electrodes of 10-15 cm^2 with a separation of 2 cm, the resistance was about 2-5 ohms initially and rose as the bubbles were formed. Rapid stirring was employed and the compartments were separated by a sintered glass disk of high area. Various types of metal were used and it was found that mild sheet iron was somewhat better than the alloyed types, that low temperatures and high stirring rate facilitated the reaction and that 35-40% NaOH was the best base concentration. At the other electrode H_2 was produced (VPC) and quantitatively ±5%. Table II summarizes some of these results.

TABLE II

Type of Fe	Temp	%NaOH	% Dec. Efficiency	Amount $Fe(OH)_3$
Soft Sheet	0°	50	20	Small
Soft Sheet	10°	50	15	Small
Soft Sheet	25°	50	5	Large
Soft Sheet	0°	40	30	Small
Soft Sheet	0°	20	10	Large
Soft Sheet	-10°	40	41	Small
Cast Iron	0°	50	12	Small
Steel	0°	50	15	Small
Stainless	0°	50	2	Large
Pure Iron (low c)	0°	50	40	Small
Pure Iron (low c)*	0°	50	20	Small
Pure Iron (low c)**	0°	50	45	Small

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* No stirring

** Low Current Density

The product produced had very little $Fe(OH)_3$ in it when produced at low temperature with mild steel and was quite stable with time at room temperature. A sample of about 2 M Na_2FeO_4 in 50% NaOH decomposed only 5% in four days at room temperature. The rate of decomposition is markedly increased by the presence of $Fe(OH)_3$ in many cases which is likely a surface effect. The stability of FeO_4^{2-} is increased at low concentrations, at low temperatures in the presence of PO_4^{3-} or F^-, in the absence of $Fe(OH)_3$ and in the base regions of pH9 and 50% MOH.

Using crude commercial NaOH solution, scrap iron from junkyards - a 40% efficiency in the oxidation and a complete loss of the hydrogen and the oxygen produced, we estimate a cost of about \$1.50-\$2.00 per pound of Na_2FeO_4 if obtained in 1 gallon of 50% NaOH not including the excess NaOH cost or the cost and maintenance of equipment. This value could be lowered by high volume preparation and by the sale of H_2 and O_2.

Reaction with Substrates

A study has been made of the products of and the rates of reaction of FeO_4^{2-} with various reductants. Almost all common reducing agents are rapidly ($t_{1/2}$ 1 min or less) oxidized by FeO_4^{2-} in neutral or basic media. Those ions oxidized which have simple stoichiometry and are rapid are given in Table III.

TABLE III

Fe^{2+}
Sn^{2+}
Cr^{2+}
N_3^-
SCN^-
SO_3^{2-}
$S_2O_3^{2-}$
NO_2^- (slower)
H_2O_2
H_2 (Under certain conditions) $N_2O_2^{-2}$

All the amino acids tested (5) including cystene and glycine reacted at measurable rates. In the latter case the products included CO_2 and N_2 with excess FeO_4^{2-}. However the reactions were not stoichiometric and many other more complex compounds were formed especially when the amino acid was in excess. Ethylene glycol, sugar and glycerine were oxidized to acids but the former only slowly. It does not behave as OsO_4 or IO_4^{3-} with olefins. No evidence for reaction with fatty acids or soaps was found. More specific information on the exact rate expressions, the ^{18}O transfer studies and the mechanisms of some of the more simple ions and molecules is given in the paper "Studies on the Mechanism of Isotopic Exchange and Reduction of Ferrate (VI) Ions (FeO_4^{2-})", by H. Goff and R. K. Murmann, American Chemical Society enclosed.

The coprecipitating ability of the $Fe(OH)_3$ produced has been found to be very great. As a preliminary to this the clarification of Missouri River water was attempted utilizing 5 ppm of K_2FeO_4. This water contained about 0.8 g of sediment per liter which did not deposit overnight when untreated and was cloudy to the eye. The addition of 5 ppm $K_2FeO_4^{2-}$ produced a tan precipitate which "carried down" the finely divided day and overnight the solution became perfectly clear to the eye and to a spectrophotometer. A one-micron filter did not show any rust color from the water drawn from the middle of this solution. Thus the FeO_4^{2-} removed the suspended material satisfactorily.

A study of the time necessary for 1/2 settling estimated on several water suspensions showed that the time was lowered by a factor of about 4-8 by the addition of 5-50 ppm FeO_4^{2-}.

Tables IV and V contain data on the purification of water of natural type by coprecipitation with the $Fe(OH)_3$ produced. Several points are immediately apparent:

a) Although iron is added, less than .02 ppm remains in solution after clarification. The added FeO_4^{2-} even takes out existing iron which probably is in the +2 state.

b) Pb^{2+} is effectively reduced with 50 ppm or less of FeO_4^{2-} to the limit of the analytical method = < .1 ppm. On the other hand, CrO_4^{2-} is hardly affected at all.

In table V is given the data on two types of well water obtained in Columbia, Missouri. It should be pointed out that both had a "sulphur" odor probably due to H_2S. (One water had a stronger odor than the other. The addition of 1.5-3 ppm of FeO_4^{2-} completely removed this odor from these water samples in the presence and the absence of air.

Again it is seen that practically no Fe^{2+} remains, that the iron originally present is gone and that the ions Cu^{2+}, Pb^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, and Fe^{2+} are very effectively removed. Cr^{3+} is only partially effected. Recent studies have been confirmed by an outside laboratory that PO_4^{3-} is effectively removed.

The theoretical studies are described in the American Chemical Society Paper (enclosed). Using $H_2{}^{18}O$, we were able to prove for the first time that the formula of the negative ion was FeO_4^{2-}, that the oxygens exchange with solvent slowly, that the rate of oxygen exchange is positively acid dependent and that it competes

TABLE IV

Co-Precipitation of Metal Ions with Iron Hydroxide Denied From FeO_4^{2-}

Missouri River Water pH = 7.6 Clay Sediment Present

Metal Ion	Amt. Added (ppm)	Amt FeO_4^{2-} Added (ppm)	[Metal Ion] (in solution) ppm
----	----	0	.03Fe; <.1 Pb
----	----	20	<.02Fe, <.1Pb
----	----	50	<.02Fe, <.1Pb
(Pb(II)	4.8	0	0.31Pb
"	4.8	50	<0.1Pb
"	4.8	100	<0.1Pb, <.02Fe
"	4.8	200	<0.1Pb
"	4.8	20	<0.1Pb
"	9.6	50	<0.1Pb
"	9.6	100	<0.10Pb, <.02Fe
----	----	0	0.06Fe, <0.1Pb
Cr(VI)	4.8	20	0.05Fe, 5.3Cr
"	4.8	50	0.05Fe, 05.3Cr
"	4.8	100	<0.02Fe, 5.2Cr
Fe(II)	4.8	50	0.04Fe
"	4.8	30	0.04Fe
"	4.8	10	0.03Fe
"	2.4	10	0.02Fe
"	2.4	20	0.03Fe
"	2.4	50	0.03Fe
"	2.4	0	0.11Fe
Cd(II)	2.4	0	0.12Cd
"	4.8	30	0.05Cd
"	4.8	50	0.04Cd
"	2.4	10	0.09Cd
"	2.4	50	0.03Cd
"	2.4	20	0.07Cd
Fe(III)	2.4	50	0.03Fe
"	2.4	100	0.01Fe
"	4.8	50	0.03Fe
"	4.8	100	0.02Fe

TABLE V

#	Ion		Found
201[*][2]	---	---	Fe .42 .02[6]
202[2]	---	---	Fe .41 .02[6]
203[5]	---	---	Fe .02
204[5]	---	---	Fe .05
206[5]	---	---	Fe .01
207[5]	All ions	5 ppm	1.1 Cd .35 Cu 2.8 Pb .04 Fe 1.2 Zn
208[3]	Cu	5	.02
209[4]	Cu	10	.03
210[3]	Cu	2	.07
211[4]	Cu	2	.07
212[3]	Zn	1.2	.11
213[3]	Zn	2.4	.14
214[3]	Zn	6.0	.07
215[3]	Pb	5.0	.05
216[3]	Pb	10	.05
217[4]	Pb	5	.05
218[4]	Pb	10	.05
219[3]	Cd	10	.03
220[3]	Cu	5	.06
221[4]	Cu	5	.03
222[3]	Cu	2.5	.01
223[4]	Cu	2.5	.01
224[3]	Zn	2.4	.03
225[3]	Zn	3.6	.14
226[3]	Zn	6.0	.20
227[3]	Pb	5	.11
228[4]	Pb	10	.05
229[3]	Cd	5	.03

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[*] 201, 203 - #1 well water
202,204,206 - #2 well water; otherwise river water

[2] 1.5 ppm FeO_4^{2-} added.

[3] 50 ppm FeO_4^{2-} added.

[4] 100 ppm FeO_4^{2-} added.

[5] 0 ppm FeO_4 added.

[6] After 1 day

with the oxidation of water to O_2. Of significant interest is the fact that oxygen exchange is second order in H^+ while the decomposition is only first order. This will allow future studies on oxygen transfer experiments in the neutral and basic region. A careful study of the rate of oxygen generation was made in several buffer media and the rate was found to be very dependent on the negative ion present in the buffer, i.e. OAC^-, much faster than PO_4^{3-}. Also it quickly became apparent that traces of $Fe(OH)_3$ precipitation caused a rapid catalysis of the solvent oxidation. The presence of excess PO_4^{3-} and its acid forms greatly decreased the iron hydroxide precipitation and gave reproducible rates of reaction. Of considerable interest is the report at the September meeting of the ACS in New York that the rate of reaction of FeO_4^{2-} with SO_3^{2-} was first order in each and gave $S_4O_6^{2-}$ as an intermediate. Upon communication with the other authors, it was found that they had incorrect data reduction and interpretation. The difference in buffer systems did not alter the rate equation. We are in correspondence with these authors and have some mutual interest in these related studies.

The various steps leading from FeO_4^{2-} - H_2O to a $Fe(OH)_3$ type precipitate are still completely unknown. It has been established that the reaction of Fe^{2+} with FeO_4^{2-} gives oxidation-reduction instantaneously whose product is very much lide (spectrally) the Fe^{3+}-Fe^{3+} dimer previously characterized. Stopped flow kinetics were used here and appeared to be too complicated for analysis in the present state of knowledge. Significantly the reaction of

FeO_4^{2-} with water gives only Fe(III) in dilute acid but subsequent reaction in the same media (in the presence of Fe^{3+}) gives much of the same dimer. It now has been shown that Fe(VI) reacts with Fe(III) to give an intermediate Fe(IV) which gives a slowly decomposing dimer by reaction with Fe(II). Considerable work needs to be done in this area.

The oxygen transfer studies were conclusive in showing that FeO_4^{2-} - H_2O_2 gave O_2 from the H_2O_2 only and that with SO_3^{2-}, 2/3 of one oxygen in SO_4^{2-} comes from the FeO_4^{2-}. A clear mechanism for these reactions was proposed.

Some results of the bacterial studies are given in Figures 1-7. These are the toxicity curves for FeO_4^{2-} and represent a minimum in the toxicity. This results because the FeO_4^{2-}, being a good oxidizing agent, reacts very quickly with the organic growth media and thus only a very small fraction of it is available for only a very short time for reaction with the Bacteria. In pure water more sensitivity is observed. I estimate that the average contact time with the bacteria at 29°C is about 1 second and that only 5-10% of the listed FeO_4^{2-} is actually present during that time. Therefore, the actual toxicity is considerably greater than shown in some of the graphs. It should be noted that for recombining pseudomonis, about 20 ppm is necessary to remove half of the colonies while with non-recombining pseudomonis about 2 ppm is necessary. $Fe(OH)_3$ product at these concentrations is completely ineffective in all cases. For river water, bacteria of many types, it is clear that 5 ppm is extremely effective but that a few survive even at 10 ppm. Again it should be pointed out that these values represent upper limits to the amounts of FeO_4^{2-} necessary to do the job since the removal of FeO_4^{2-} by the reaction with the nutrient broth is very rapid.

With E. Coli about 1 ppm FeO_4^{2-} is necessary for 1/2 kill and about 2-3 ppm for complete kill depending on the number of active cells present. When the cell population was decreased by a factor of about 20 the amount of FeO_4^{2-} needed was decreased. In essentially pure water the kill dose decreased dramatically with short (1-10 min) contact times and reached a maximum at about one hour. This is somewhat uncertain however since the FeO_4^{2-} is all decomposed long before one hour has passed. Thus the bacteria recover partially at low FeO_4^{2-} doses if put under favorable growing conditions after short contact periods.

The comparison of FeO_4^{2-} and Cl_2 on E. Coli show 1-3 ppm necessary for FeO_4^{2-} and .75-1 ppm for Cl_2. However taking into account the molecular weight Cl_2=71, K_2FeO_4=170 the valves per mole are .4-1.2 and .75-1.0 respectively for E. Coli. Thus on the mole basis they are about equally effective.

With the virus $P_{(22)}$ utilizing Salmon ela T (Q_1) and about 2 x 10^4 lysing units/ml. it took 0.6 ppm Cl_2 for 1/2 kill and 1 ppm for complete kill. Under comparable conditions it took 2.2 ppm for 1/2 kill and 7 ppm for complete kill with FeO_4^{2-}. Thus Cl_2 is more effective.

The curves for Cl_2 and FeO_4^{2-} on both virus and bacteria seem very simular suggesting similar mechanisms: probably nucleic acid oxidation.

A consideration of the potential usefulness of FeO_4^{2-} for purifying water suggests that it has its greatest potential application in the final treatment of water from rivers or wells meant for human consumption.

Treatment with 5 ppm or FeO_4^{2-} followed by sedimentation and/or filtration would make these changes or cause these effects:

1. The solution would become slightly more alkaline, thereby precipitating some trace metals.
2. Odors due to H_2S or S_8 or certain organic substances would be removed.
3. Iron complexed or in the Fe(II) state would be lowered to below .02 ppm.
4. Organic matter would be decreased or BOD would be decreased and a little oxygen would be put in the solution.
5. Colloidal material would be more easily removed.
6. Trace metals, i.e. Cd^{2+}, Zn^{2+}, Cu^{2+}, Hg^{2+} would be lowered.
7. Many bacteria would be eliminated.
8. Many viris would be inactivated.

These changes would be accomplished without high cost (crude estimate 1-5 cents per 1000 gallons depending on the purity of initial water and requirements of final water) and without contamination of the remaining water.

Considerable experimentation needs to be done. Since each of the above factors were tested independently, they may be interrelated and considerably more FeO_4^{2-} may be required to do all of the jobs listed. However, this work has established a potential usefulness for this substance and strongly suggests that considerably more research effort be applied.

A considerable saving could be achieved through the generation of Na_2FeO_4 at the water purification plant for direct use. This would negate the need for storage and transportation. The raw materials would be NaOH, scrap iron, and electricity. It could result in a considerable efficiency increase and more control over the process.

PUBLICATIONS, REPORTS AND TALKS PRESENTED

Publications - "Studies on the Mechanism of Isotopic Oxygen Exchange and Reduction of Ferrate (VI) Ion", Journal of the American Chemical Society, 93, 6058 (1971) with H. Goff enclosed.

"On the Use of FeO_4^{2-} for Purifying Natural Water", R. Kent Murmann, P. R. Robinson, Water Research, 8, 79 (1974) enclosed.

Talks - Summary Talk - University of Missouri Water Resources Research Center, Columbia, Missouri, May-June, 1972, 1973, 1974.

Colloquim - Chemistry Department, University of Missouri, Columbia, Misosuri, April 18, 1972, "A New Method of Purifying Natural Waters".

Invited Talks - Environmental Chemistry Conf., University of Missouri, 1973; University of Nebraska, November 1973; Amer. Water Works Conf., January 1974.

TRAINING ACCOMPLISHED

H. Goff took a Master's degree working partially on this work. He is now progressing on his Ph.D. at the University of Texas.

Paul R. Robinson has completed his Master's degree working partially on this subject. He is continuing in the environmental area at Scripps Institute, California, in his Ph.D. work.

Ronald Bateman is doing volunteer work on this project and may continue toward his Master's degree later on.

Bruce Monzyk is working now on his Master's degree, University of Missouri.

Ken Giese is now working on his Master's degree, University of Missouri.

APPENDIX

a. Copy of paper from Journal American Chemical Society.

b. Copy of paper from Water Research

c. Description of Biochemical Expts.

d. Product analysis on NH_3 Rx with $FeO_4^{2\ominus}$.

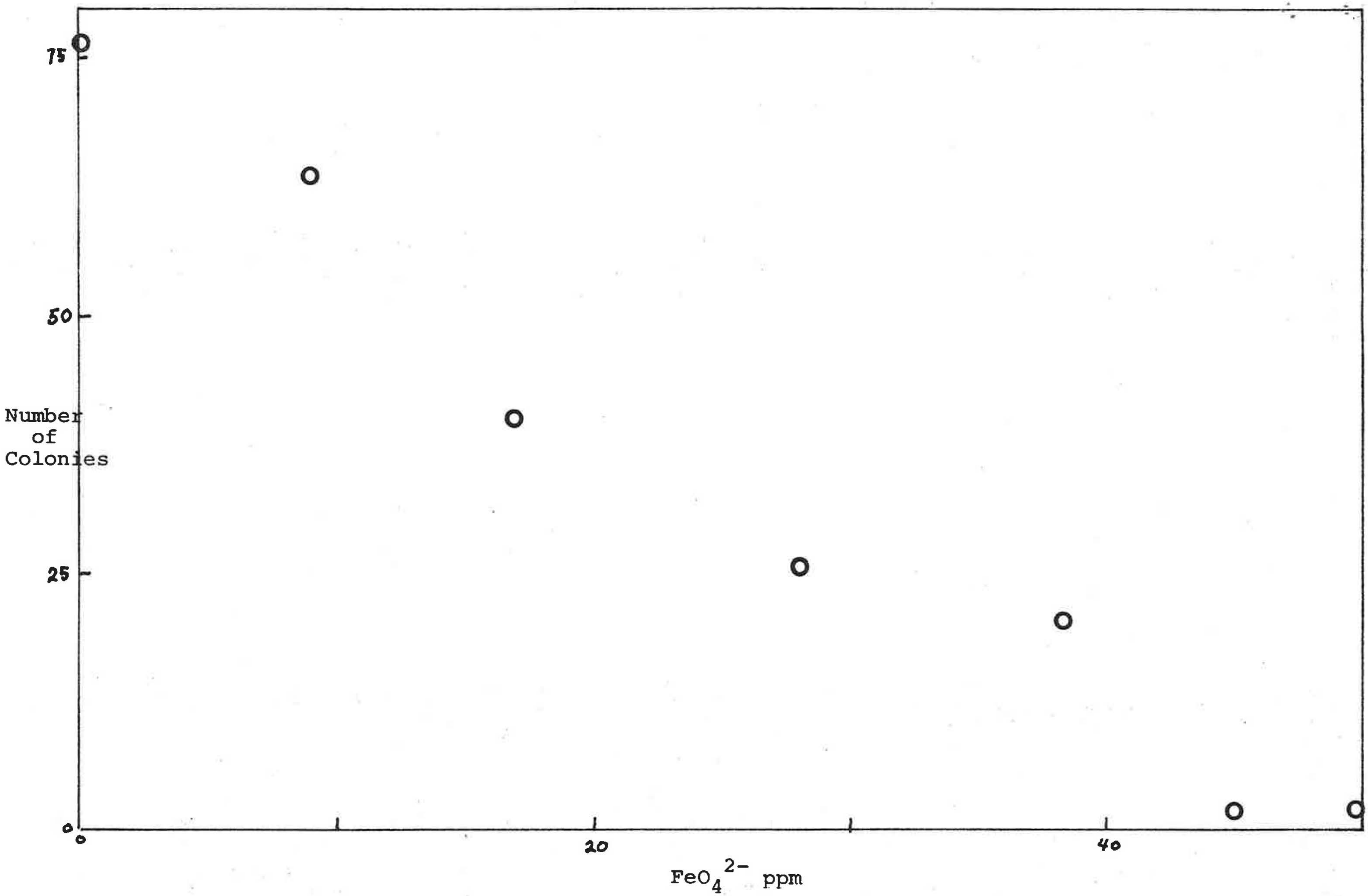
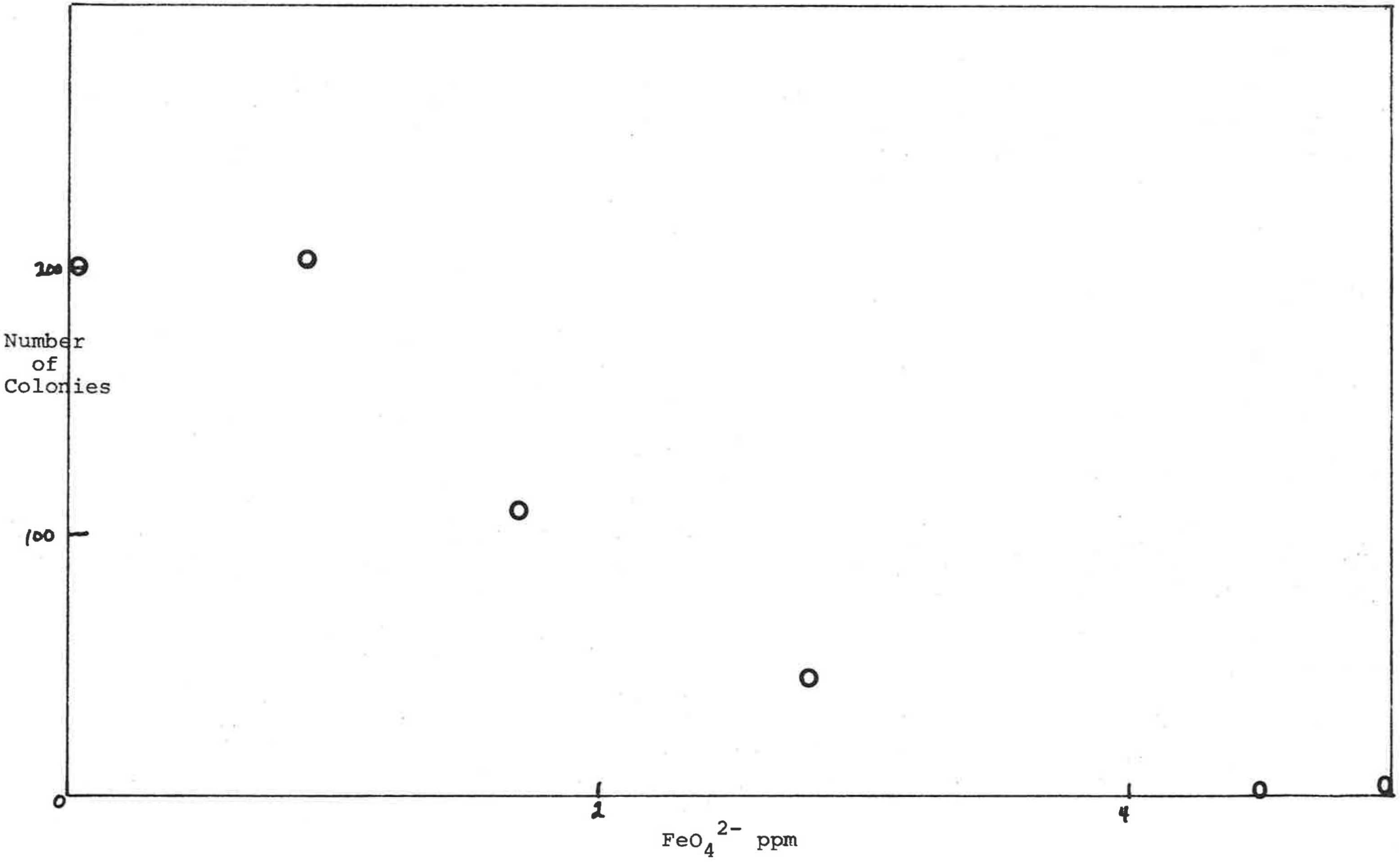


Figure 1 - Toxicity Curve for FeO_4^{2-} and Recombining Pseudomonas.

Figure 2 - Toxicity Curve for FeO_4^{2-} and Non-Recombining Pseudomonas



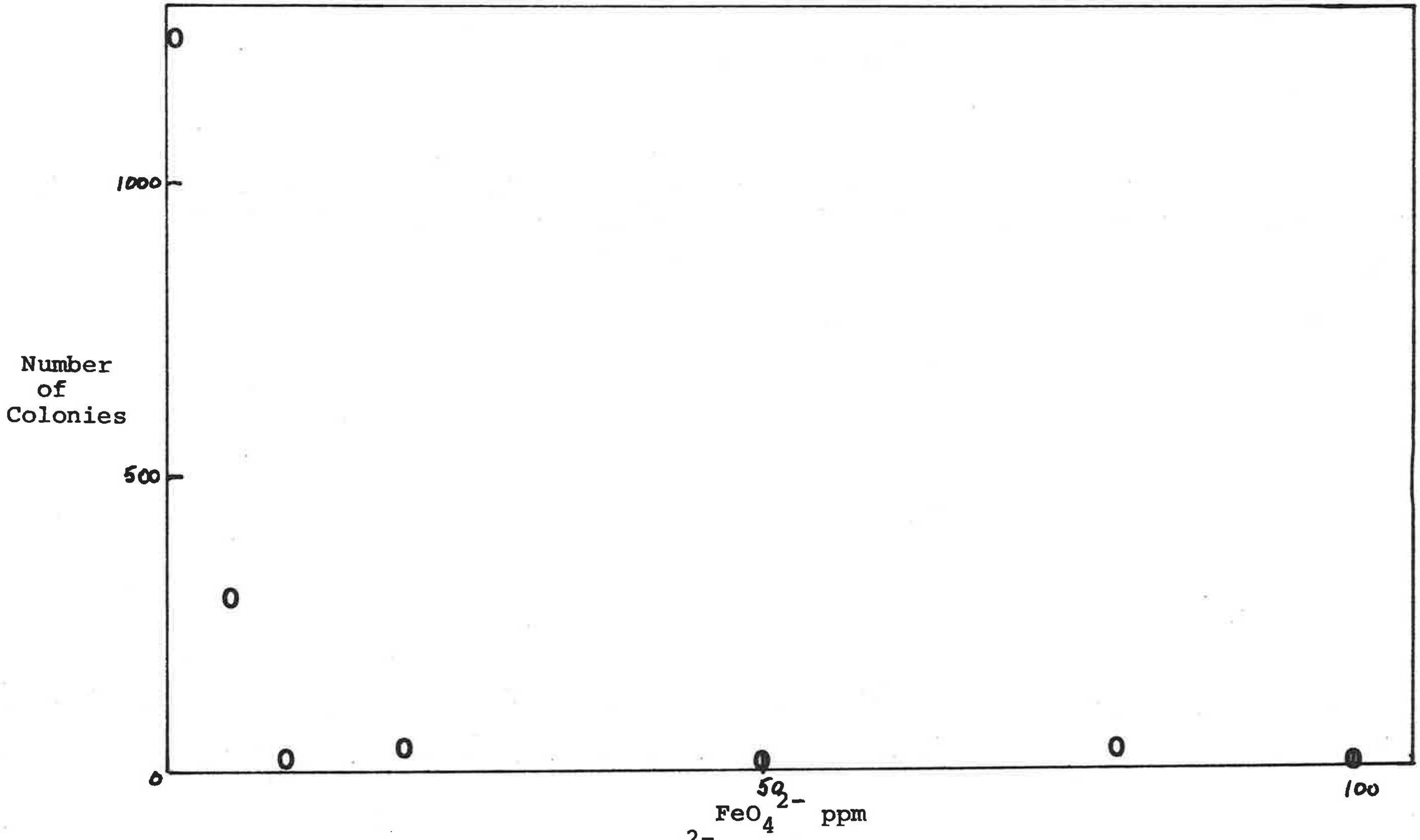
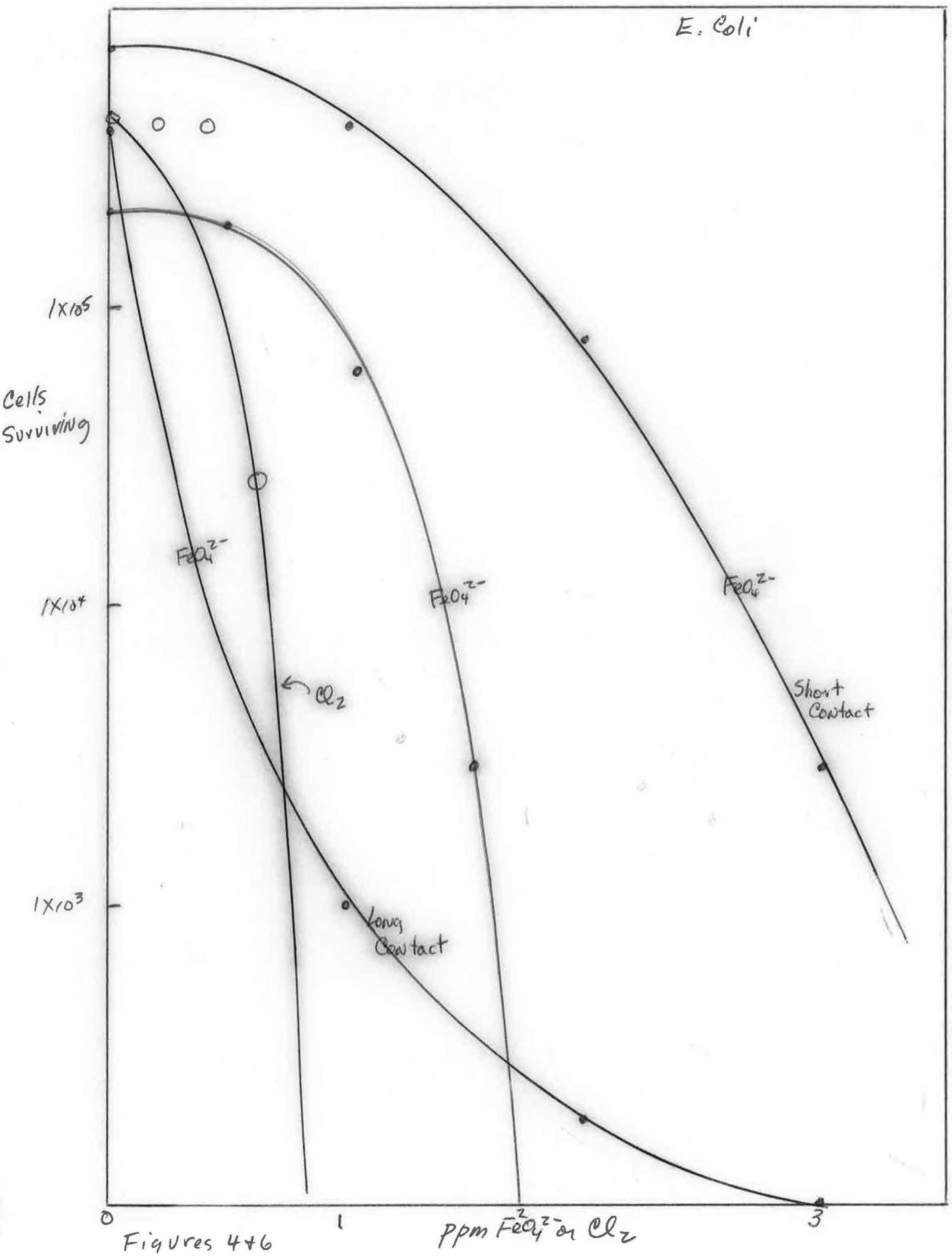


Figure 3 - Toxicity Curve for FeO_4^{2-} and River Water Bacteria


E. Coli
Cells Surviving
1X10⁵
1X10⁴
1X10³
FeO₄²⁻
FeO₄²⁻
FeO₄²⁻
Cl₂
Short Contact
Long Contact
0
1
2
3
ppm FeO₄²⁻ or Cl₂

Figures 4+6