REMOVAL OF HEAVY METAL IONS FROM

AQUEOUS SOLUTION BY ION EXCHANGE ON

SULFURIC ACID TREATED PEAT

by

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ABSTRACT

Removal of metal ions from aqueous solution by simple and inexpensive techniques is of considerable importance in the control of water pollution. The large-scale use of synthetic ion-exchange resins for this application is frequently considered impractical due to the high cost of resin. Peat, which is widely available, has a native cation exchange 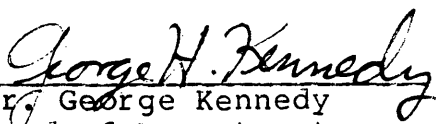capacity. However, as a result of its impermeability toward water and its propensity for leaching, peat is not suitable for use as an ion exchanger in the column mode. It has previously been shown that the product resulting from the treatment of peat with hot concentrated sulfuric acid has the following properties: (i) granular form suitable for column use, (ii) enhanced cation exchange capacity compared to the untreated peat, and (iii) resistance to leaching up to a pH of approximately 9. We have now evaluated the use of this treated peat for simultaneously removing a wide variety of heavy metal ions from aqueous solution. The variables investigated were total concentration of heavy metal ions, ionic strength, pH and flow rate. The species studied were: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and UO_2^{2+}. Treated peat was found to be very effective in removing all of the above species over a wide range of the parameters investigated.

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INTRODUCTION

In light of the increased interest in and controls
placed on the pollution of our environment, new technologi-
cal advances must be made to fulfill mankind's goals. One
such area of importance is that concerned with controlling
the problem of water pollution. This problem is so impor-
tant that a number of Government agencies have set concen-
tration guidelines and limits for heavy metals in domestic
water supplies (1). A list of these is given on Table I.
Simple and inexpensive techniques for the removal of heavy
metals from waters would appeal to environmentalists and
industrialists alike. One such technique has been sug-
gested by E.F. Smith, et. al. (2).

The basis of this method involves the chemical modifica-
tion of peat to form a cation exchanger which has effective
Na^+ capacities within 25 percent of those now commercially
available (Dowex, Amberlite, etc). The modification simply
involves the treatment of wet (or dry) peat with small
amounts of concentrated sulfuric acid, drying and then grind-
ing and sieving to a desired particle size.

Other investigations of the use of peats in environmen-
tal applications have been made. Non-treated peat has been

TABLE I: Limits for Heavy Metals In Domestic Water
        Supplies and Waste Discharge Streams (1)

Metal	Domestic Water Supply Limit	Discharge Limits*	
		One Day Maximum	30 Day Average
Cr	50 ppb	7.0 ppm	2.5 ppm
Ni	---	4.1 ppm	1.8 ppm
Cu	50 ppb	4.5 ppm	1.8 ppm
Zn	200 ppb	4.2 ppm	1.8 ppm
Cd	10 ppb	1.2 ppm	0.5 ppm
Pb	50 ppb	0.6 ppm	0.3 ppm

*   Discharge limits are the limits set for the indus-
    trial discharge of contaminated water into streams,
    lakes, etc.

shown to successfully remove organic compounds (3), heavy metal ions (4), pollutants from dye house effluents using the Hussong-Couplan process (5), and proteins (6) from industrial wastewaters. Dewatered peat has been shown to remove heavy metal ions from wastewater (7). Peat has also been used as a filter in water purification systems where metals have previously been precipitated (8). Sulfuric acid treated peat has been used to remove metal ions (9, 10, 11) and organic compounds from water (12) and ammonia and amine compounds from air (13).

The work of Smith, et. al. (2), dealt primarily with optimizing the physical characteristics of the modified peat by varying the modification processes. One of the main problems associated with the use of raw peat was that of leaching, or the passing into solution of soluble organic compounds contained in the material. They found that leaching problems could be minimized by the use of 4 ml concentrated sulfuric acid per 10 g of wet peat (1.2 g dry) at a reaction temperature of 150°C for two hours. Higher capacities were obtained using more drastic reaction conditions but these caused leaching, swelling and general particle breakdown of the exchanger. The increased capacity of the treated peat with respect to the non-treated peat seems to be due to the

sulfonation of some of the available aromatic sites and the oxidation of aliphatic constituents to carboxyl groups. Preliminary recovery efficiency testing or the ability of the exchanger in the column mode to efficiently remove metal ions from solutions, was also carried out which showed that the presence of competing ions has a lowering effect and that the flow rate is the most significant variable. The developmental work of Smith, et. al. (2) was used as the starting point for this research. The research reported here differs significantly from their work in that the simultaneous removal of many metal ions from solution was studied in detail while varying pH, concentration, ionic strength and flow rate.

Commercial ion exchangers could be used for removing heavy metal ions from industrial wastewaters but the large scale use of these resins is frequently prohibitive on a commercial scale. The raw material for many of the commercial ion exchange resins (polystyrene based) is a by-product of the petroleum industry and its price has escalated in recent years. Accordingly, the primary reason for focusing on treated peat as an ion exchanger in this work is economic. Peat is widely available in many areas of the U.S.A. and throughout the world, and the treatment process discussed here is simple and relatively inexpensive.

OBJECTIVES

The purpose of this study was to evaluate the feasibility of using sulfuric acid treated peat (from hereon referred to as S.A.T.P.) as a cation exchanger for the purification of waters containing trace levels of heavy metal ions. The species studied in this investigation were Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and UO_2^{2+}. These particular species were chosen because of the harmful effects they can have on the biosphere (14) and because of their common appearance in municipal and industrial wastewater (15). Initially, Cr^{3+} was included in the study but was abandoned because Cr^{3+} proved to be very difficult to elute from the S.A.T.P. columns and therefore proved difficult to quantitivley determine by the methods used for the other elements studied. Of course, the strong binding of Cr^{3+} to S.A.T.P. is useful information in itself indicating that this ion would be effectively removed from solution by the S.A.T.P. The research involved the following aspects:

(1) Preparing the S.A.T.P.; quantitatively determining its cation exchange capacities for Na^+, Ba^{2+} and La^{3+}; confirming its stability over a range of pH values when in contact with an aqueous solution; and determining its moisture holding ability (for gravimetric mass balance considerations).

(2) Evaluation of methods to quantitatively determine the amount of each metal removed from solution by S.A.T.P.

(3) Evaluating the S.A.T.P.'s ability to simultaneously remove the metals of interest from aqueous solution, and studying the effect of pH, flow rate, concentration, and ionic strength on the removal.

EXPERIMENTAL

Description of Peat Used in Study

The raw peat used in this study was obtained from the
Irish Peatlands Experimental Station, Glenamoy, County Mayo,
Ireland. It was dug at a depth of approximately 3.5 feet
and was of a well decomposed sphagnum type. The peat was
dark brown in color and contained very few noticeable plant
remains. Percent moisture, percent ash, and percent organic
matter for this peat were determined by the method outlined
by the American Society of Testing Materials (17). This
peat was used in this work because it has been extensively
studied by others working in this series of experiments and
accordingly it was appropriate to concentrate on the Irish
peat.

A porcelain evaporating dish was brought to constant
weight by heating in a muffle furnace at $550^{\circ}C$ for three
hours, allowed to cool in a desiccator over anhydrous $CaCl_2$,
and weighed. An amount of as-received (raw) peat was added
to the dish, the dish plus raw peat weighed and placed in a
$110^{\circ}C$ oven for sixteen hours to determine percent moisture.
After cooling in a desiccator and weighing, the dish plus
dry peat were placed under infra-red heating lamps to begin

the charring step. After one hour, the dish was transferred
to a muffle furnace (550°C) and left for one hour. The dish
plus ash was then removed, cooled in a desiccator, and
weighed. The ashing step was repeated to check for constant
weight. The data and equations used are given in Table II.
From this experiment it was found that the Irish peat has
the following characteristics:

$$\text{Percent Moisture} = 90.4\%$$

$$\text{Percent Ash (as Received)} = 0.386\%$$

$$\text{Percent Ash (Dry)} = 4.01\%$$

$$\text{Percent Organic Matter} = 9.26\% \text{ (by difference)}$$

Peat in its natural form is impervious to water and also
readily leaches organic matter into solution which makes it
undesirable for water treatment in a continuous flow or col-
umn type system. These problems can be greatly minimimzed
by treating the peat with concentrated sulfuric acid accord-
ing to the method devised by Smith, et. al. (3).

Preparation of the Treated Peat

The S.A.T.P. was prepared by drying the as-received peat
in a 110°C oven for 24 hours, cooling in a desiccator, and
then weighing. The peat was then transferred to a large

TABLE II: Data and Equations Used In A.S.T.M.
          Charactization of Irish Peat (17)

Item	Weight
Evaporating Dish	102.0787g
Dish + Raw Peat	159.0787
Dish + Dry Peat	107.6276
Dish + Ash (1)	102.3012
Dish + Ash (2)	102.3009

$$\% \text{ Moisture} = \frac{g(\text{as rec'd peat}) - g(\text{dried peat})}{g(\text{as rec'd peat})} (100\%)$$

$$\% \text{ Ash (as rec'd)} = \frac{g(\text{ash})}{g(\text{as rec'd peat})} (100\%)$$

$$\% \text{ Ash (dry)} = \frac{g(\text{ash})}{g(\text{dry peat})} (100\%)$$

$$\% \text{ Organic Matter} = 100\% - (\% \text{ Ash (as rec'd)} + \% \text{ Moisture})$$

Pyrex beaker and concentrated sulfuric acid added in the ratio of 4.0 ml to 1.2 g dried peat. The mixture was then slowly heated to 150°C on a hot plate in a fume hood and allowed to react (with stirring) for two hours. The mixture was allowed to cool whereupon it was washed with successive aliquots of deionized water with constant stirring until the pH of the wash water was approximately that of the deionized water. The exchanger was then dried in a 110°C oven for 24 hours, ground with a mortar and pestle, and sieved to a particle size less than 500 microns and greater than 354 microns. This particle size is appropriate for industrial applications (17) and homogenization of particle size is necessary to increase the precision of the data from metal ion removal experiments as different particle sizes tend to have slightly different capacities (2) and characteristics for solutions flowing through them.

Description of the Apparatus

All of the ion exchange experiments were carried out using the column mode instead of the batch mode. The principal reason for the use of the column mode was that the metal solution continually came in contact with "fresh" exchanger in the H$^+$ form, thus effecting a more efficient separation

of the metal ions from the solution.   It is also a more eco-nomical method for use industrially as it is a continuous process.

The apparatus used consisted of a one-liter separatory funnel (used as a delivery reservoir) connected to a 30 cm length of 6 mm I.D. Pyrex glass tubing (which served as the column).   A piece of porous polyethylene sheet (available from Sargent-Welsh) was inserted at the end of the column to retain the exchanger, and a teflon stopcock assembly was connected to the lower end of the column to regulate the flow of solutions through the apparatus.   All connections were made with Tygon tubing.   A diagram of the apparatus appears on Figure 1.

The stopcock at the base of the column was used to regulate the very slow flow rates required during the protonation, rinse, and elution cycles.   High flow rates (≥ 5 ml/min) needed for passing metal ion solutions through the column were obtained by using a peristaltic pump.   The pump was connected between the separatory funnel and the column by Tygon tubing.

Effect of pH on the Physical Nature of S.A.T.P.

These experiments were performed to confirm the pH stability range of the S.A.T.P. found by Smith, et. al. (2). A 0.200 g sample of S.A.T.P. was added to a clean 250 ml Erlenmeyer flask. One hundred ml of pH buffer (18, 19) was added and the flask stoppered. The flask was allowed to equilibrate (with periodic shaking) for one week at which time it was inspected visually for leaching. This procedure was followed for the alkaline pH's of 7.0 through and including 12.0.

These experiments did confirm the results of the previous workers. The flask at pH 7.0 had a very slight yellow color, indicating very slight leaching. The pH 8.0 test showed a little darker color and pH 9.0 through 12.0 showed pronounced leaching.

Effect of Moisture on S.A.T.P.

From the previous A.S.T.M. experiments, it was seen that raw peat will hold considerable moisture. This gave rise to interest in the moisture holding capacity of the S.A.T.P. An experiment was designed to compare the relative affinities for moisture of dried S.A.T.P., dried peat and anhydrous $CaCl_2$. Approximately 1.0 g of each compound was dried

FIGURE 1: Apparatus Used for Ion Exchange Experiments

Separatory Funnel
(Reservoir)

Tygon Tubing

30 cm Length of 6 mm
I.D. Pyrex Glass Tubing

Exchanger

Porous Polyethylene Disc

Teflon
Stopcock
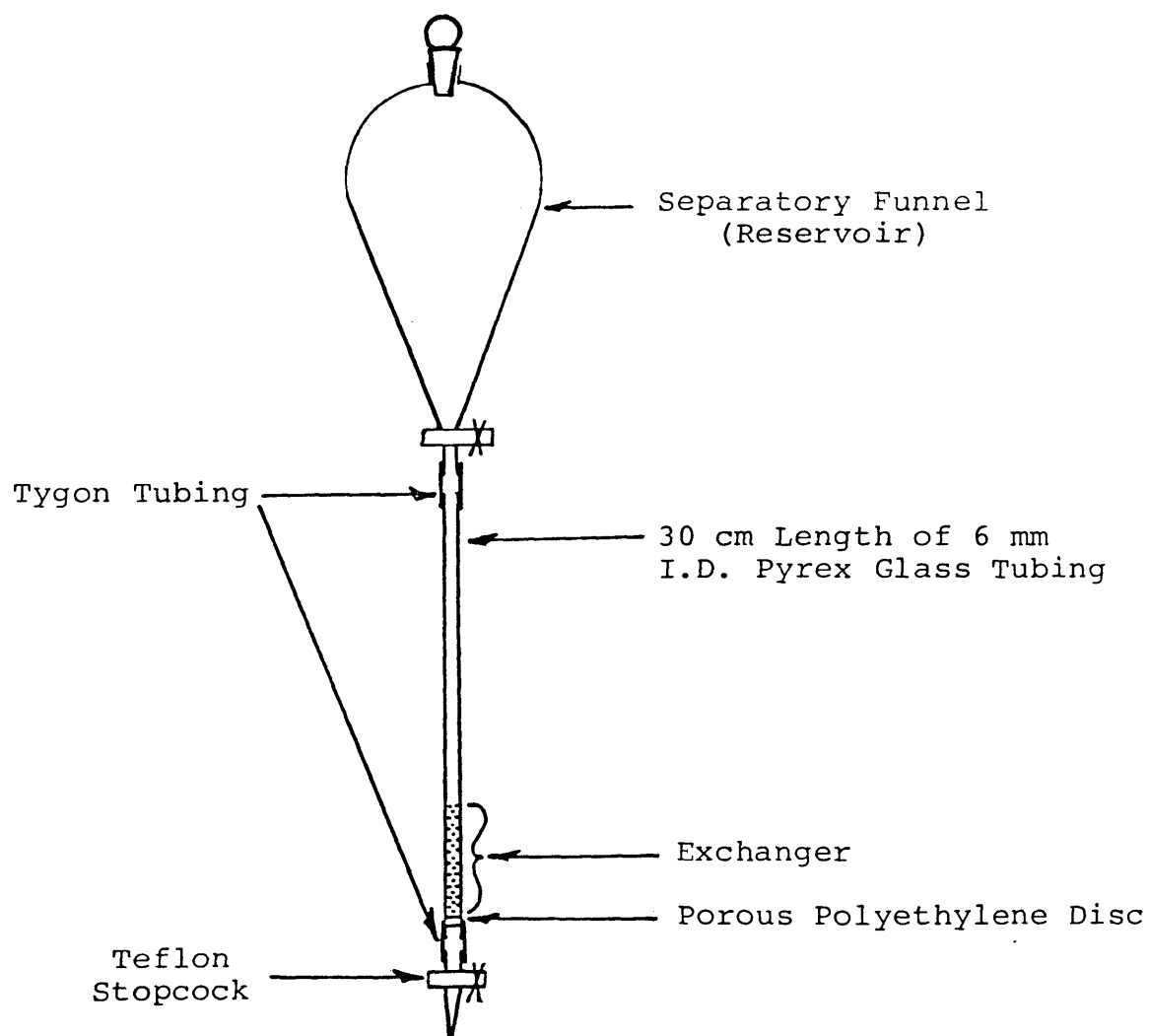
in a 110°C oven for 24 hours, transferred to tared small
beakers which were placed in a clean dry desiccator with
0.500 ml (approx. 0.500 g) deionized water contained on a
watch glass. The apparatus was monitored until no "free"
water droplets were visible (approximately three days). The
three beakers containing the compounds were removed and re-
weighed. The increase due to moisture gain was calculated
to be 32.0%, 10.3%, and 4.88% for anydrous $CaCl_2$, dried
S.A.T.P., and dried peat, respectively. It is interesting
to note that the treatment process increased the peat's
water absorption capacity by a factor of two and allowed it
to compete successfully for one-third of the moisture that
the anhydrous $CaCl_2$ absorbs. From this experiment it can
be seen that for gravimetric considerations, peat and
S.A.T.P. should both be dried before using but not stored
over $CaCl_2$ in a desiccator when complete dryness is desired.
The data for this experiment are shown on Table III.

Determination of Ion Exchange Capacities

Ion exchange capacity determinations were carried out as
described by Vogel (20) in the column mode. Samples of
1.0000 g of S.A.T.P. were made into slurries by first wet-
ting with small amounts of methanol, and then with deionized

water. The slurries were then loaded into the columns. Fifty ml of 3 $\underline{N}$ HCl was then passed through each column at a flow rate of 1 ml/min to protonate the exchange sites. Deionized water ($\geq$300 ml) was then passed through each column until the pH of the effluent was the same as pure deionized water. This removed the excess acid left over from the protonation step.

The effective capacities for Na^+ and Ba^{2+} were determined by passing 100 ml of 0.1 $\underline{M}$ solutions of their chloride salts through the 1.0000 g S.A.T.P. columns in the H^+ form at a flow rate of 1 ml/min. The columns were then rinsed with 20 ml (approx. 20 bed volumes) of deionized water and the total column effluents were collected and titrated with 0.01 $\underline{N}$ NaOH to a phenolphthalein end point. Each capacity determination was performed in triplicate and the average and range were computed.

The effective capacity for La^{3+} was determined by passing 100 ml of 0.1 $\underline{N}$ La(NO$_3$)$_3$ through a 1.0000 g S.A.T.P. column in the H^+ form at a flow rate of 1 ml/min, rinsing the column with 20 ml of deionized water, and collecting the total effluent. A potentiometric titration of the effluent with 0.0995 $\underline{N}$ NaOH was employed because La^{3+} acts as a Lewis acid and complexes OH^- leading to precipitation of La(OH)$_3$.

TABLE III: Data From Anhydrous $CaCl_2$, Dried S.A.T.P.
and Dried Peat Desiccator Experiments

	WEIGHT	
ITEM	INITIAL	AFTER 3 DAYS
$CaCl_2$ + Beaker 1	64.2262g	64.5589g
Beaker 1	63.1871	63.1871
$CaCl_2$	1.0391	1.3718
% Increase	---	32.0181%
S.A.T.P. + Beaker 2	50.0291	50.1302
Beaker 2	49.0474	49.0474
S.A.T.P.	0.9817	1.0828
% Increase	---	10.2985%
Peat + Beaker 3	50.4504	50.4994
Beaker 3	49.4470	49.4470
Peat	1.0034	1.0524
% Increase	---	4.8834%

In other words, the reaction of La^{3+} with OH^- and eventual precipitation, continually removes OH^- and therefore suppresses pH increase in the solution until all of the La^{3+} has been reacted. This would give a phenolphthalein end point which would indicate the complete titration of H^+ and La^{3+}, not H^+ alone.

The effective capacities of Na^+, Ba^{2+}, and La^{3+} and the titration curve for the La^{3+} effluent with 0.0995 $\underline{N}$ NaOH are shown on Table IV and Figure 2, respectively.

Procedure For Evaluating The Simultaneous Removal of Cationic Metal Species From Aqueous Solution Using S.A.T.P.

The major portion of this study was directed at the simultaneous removal of many metal ions, at trace level concentrations, from aqueous solution by ion exchange on S.A.T.P. using the column mode. All previous studies using S.A.T.P. involved only a single metal ion at a time and did not evaluate the influence of pH, ionic strength, and flow rate in great detail. The cationic metal species investigated were: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and UO_2^{2+}. These experiments were designed to test S.A.T.P.'s ability to simultaneously remove these metal cations from aqueous solution over a range of flow rates, pH's, concentrations, and ionic strengths.

TABLE IV: Effective Capacities for Na^+, Ba^{2+} and La^{3+}

Ion	Effective Capacity	Range
Na^+	0.71 meq.	0.028 meq.
Ba^{2+}	1.12	0.080
La^{3+}	1.22	---

Figure 2: Titration Curves for La^{3+} Effluent and 100 ml
0.1 $\underline{N}$ La$(NO_3)_3$ with 0.0995 $\underline{N}$ NaOH

ml 0.0995 $\underline{N}$ NaOH
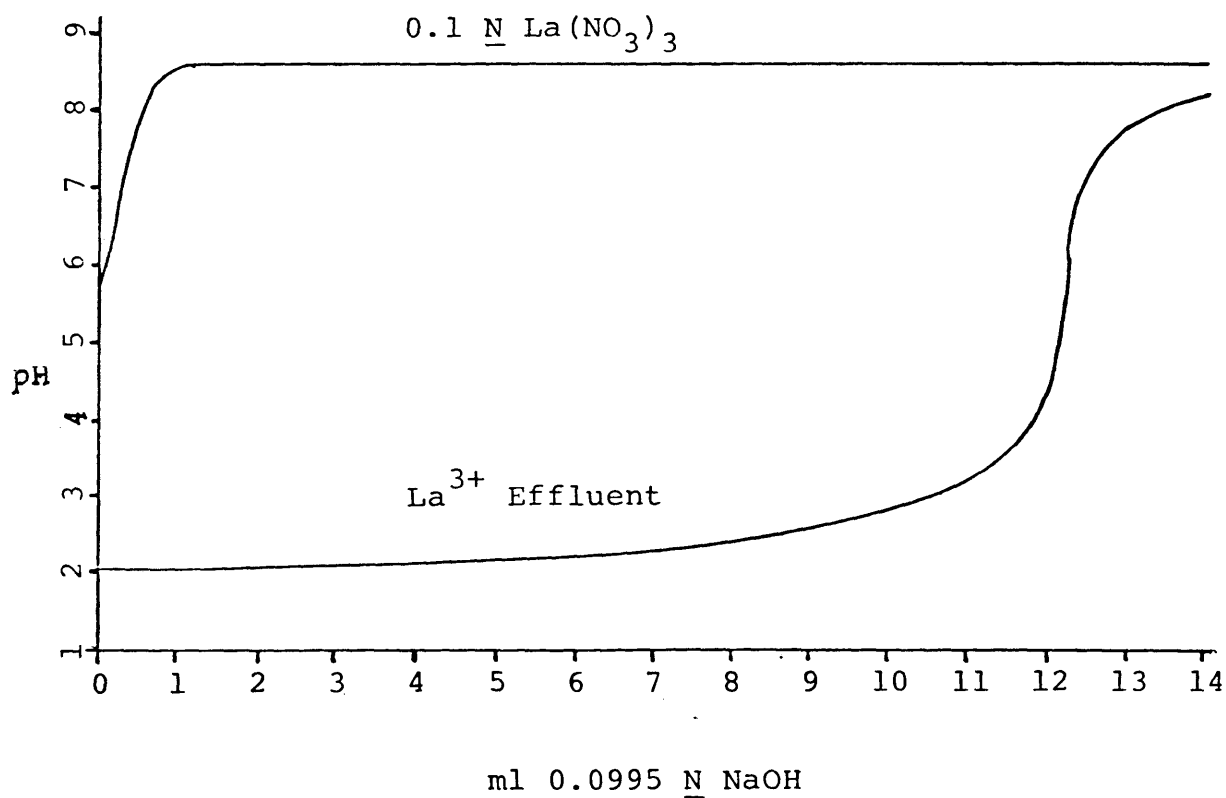
The general procedure followed was:

(1) A known volume of metal ion solution was quantitatively transferred to a delivery reservoir connected to a column loaded with 1.0000 g S.A.T.P. in H^+ form (see Figure I).

(2) Solution flow was started through the column at the desired flow rate.

(3) At the moment the delivery reservoir became empty, it was rinsed quickly with deionized water (approx. 20 ml) to assure that all the metal ion solution had passed through the column.

(4) Solution flow was stopped when the last of the deionized water wash had reached the top of the exchanger in the column.

(5) The metal ions were eluted from the column with 90 ml 3 N HCl (discussed later in "Elution of Metal Ions From S.A.T.P. Columns").

(6) The eluate was collected in a 100 ml volumetric flask and was brought to volume with 3 N HCl.

(7) The metal ion concentration in the eluate was measured by Atomic Absorption Spectrophotometry (A.A.S.).

Preparation of Standard Aqueous Metal Ion Solutions

Standard aqueous solutions of each metal ion of interest were prepared by weighing out appropriate amounts of each metal's nitrate salt, dissolving it in deionized water and diluting to 1.000 liter with same to obtain concentrations of 1.0×10^{-2} M. These solutions are referred to as the stock standard metal ion solutions.

Standardization of Aqueous Metal Ion Solutions

The stock standard metal ion solutions were standardized by means of ion exchange on Amberlite IR-120 cation exchange resin. Approximately three grams of the synthetic resin was washed repeatedly with aliquots of deionized water to remove fines and was then transferred as a slurry to the column apparatus. One hundred ml of 3 N HCl was passed through the column at 1 ml/min to ensure that the resin was in the H^+ form. The column was then rinsed free of residual acid by passing one liter of deionized water through it at 1 ml/min. 25.00 ml of stock standard metal ion solution was passed through the column at 1 ml/min, followed by 25 ml deionized water to ensure that all the metal ion solution had contacted the resin and that all the displaced acid was washed from the column. The effluent and washing were collected in

a beaker and titrated to a phenolphthalein end point with standard NaOH (9.661×10^{-3} $\underline{N}$). This procedure was carried out twice for each stock standard metal ion solution. The data from these experiments is shown on Table V.

Preparation of Trace Metal Ion Solutions

1.000×10^{-3} $\underline{M}$ stokc metal ion solutions were prepared from the 10^{-2} $\underline{M}$ stock standard metal ion solutions by dilution into volumetric flasks with deionized water. These solutions were then used to prepare trace metal ion solutions. For convenience, throughout this thesis the term "10^{-n} $\underline{M}$ M_i^{2+}" refers to a multi-metal ion solution which was 10^{-n} $\underline{M}$ in each of the following ions: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and UO_2^{2+}; in other words, these solutions were 8×10^{-n} $\underline{M}$ in total heavy metal ions. In order to keep the relationship of total metal to S.A.T.P. fixed at 1.6×10^{-4} equivalents M_i^{2+} per 1.0000 gram S.A.T.P. (approx. 1 eq. Mi^{2+} to 6.25 eq. S.A.T.P.) the total number of metal ion equivalents in each sample solution which was passed through the column was maintained constant. These trace metal ion solutions were prepared by pipetting 10.0 ml of each stock 10^{-3} $\underline{M}$ metal ion solution into a calibrated beaker and bringing to the appropriate volume with deionized water to obtain the

TABLE V: Data From Standardization
of Metal Ion Solutions

MOLAR CONCENTRATION x 10^2

Metal Ion	Trial A	Trial B	Avg	RSD(%)
Cr^{3+}	0.9903	0.9862	0.9882	0.29
Mn^{2+}	1.578	1.581	1.579	0.11
Co^{2+}	1.017	1.033	1.025	1.09
Ni^{2+}	1.004	1.022	1.013	1.24
Cu^{2+}	1.027	1.038	1.033	0.76
Zn^{2+}	1.042	1.048	1.045	0.42
Cd^{2+}	1.046	1.044	1.045	0.14
Pb^{2+}	1.007	1.003	1.005	0.28
UO_2^{2+}	1.019	1.006	1.013	0.91

concentration desired. For example, to obtain a 1.000×10^{-5} $\underline{M}$ multimetal ion solution, 10.0 ml of $\underline{each}$ 10^{-3} $\underline{M}$ stock solution was pipetted into a calibrated beaker and diluted to one liter with deionized water. $\underline{All}$ of this solution was then passed through a column at the flow rate desired. For this type of operation it was not necessary to carry out the dilution in a volumetric flask as $\underline{all}$ of the diluted solution was used in the experiment. The important point here is that one has knowledge of the $\underline{total\ equivalents}$ of metal ion passed through the column.

Appropriate pH adjustments of the solutions were made by adding 0.1 $\underline{N}$ NaOH or HNO_3 to obtain the desired pH's just prior to obtaining desired volumes. Adjustments of ionic strength were made by adding appropriate volumes of 1.0 $\underline{M}$ KNO_3 solution prior to dilution.

Regulation of Flow Rate

As mentioned earlier, regulation of the flow rate through the column was made by the use of a peristaltic pump when the desired flow rate was greater than 5 ml/min. The peristaltic pump used in this study was a Masterflex Peristaltic Pump model number WZ10R57 with head numbers 7014 and 7015. The pump apparatus included a Solid State Masterflex Con-

troller which regulated the revolutions per minute of the
pump motor. The pump was calibrated by connecting it to the
column apparatus (loaded with 1.000 g S.A.T.P.) and measur-
ing the flow rate with a stopwatch and a graduated cylinder
to correlate the volume delivered per time period to the
Controller setting. This was carried out with both pump
heads to a maximum flow rate of 103 ml/min. A peristaltic
pump was used because of its ease of adaptability to this
system and because it also avoided contact of the trace
metal ion solutions with any extraneous metal surfaces.

Elution of Metal Ions from S.A.T.P. Columns

Initially, it was intended that the metal ions exchanged
on the S.A.T.P. would be measured using Energy Dispersive
X-Ray Flourescence Spectrometry (E.D.X.R.F.) which is a
rapid and direct method. However, after extensive research
with the technique, it was found that interelement effects
due to unpredictable metal dispersion in the sample could
not be compensated for. For example, the effect of Co on
Ni could not be determined because their relative amounts in
each sample (or in each particle per sample) could not be
known prior to analysis. Therefore, appropriate standards
could not be established. This type of problem with the

E.D.X.R.F. technique favored the use of another technique:
elution of the metal ions from the S.A.T.P. columns with a
strong acid followed by Atomic Absorption Spectrophotometric
(A.A.S.) analysis.

Difficulties with this technique were also encountered
in terms of efficiently removing the bound metal ions from
the columns of S.A.T.P. It was found that these problems
were of a kinetic nature in that the elution step needed a
"four day pause." When eluting the metal ions from the
S.A.T.P. column with 90 ml of 3 $\underline{N}$ HCl, approximately 45 ml
of the 3 $\underline{N}$ HCl were allowed to flow through the column at
$\leq$0.5 ml/min, the elution step was stopped for four days (the
"four day pause") and then the remaining 45 ml of the 3 $\underline{N}$
HCl was passed through the column at $\leq$0.5 ml/min and the
whole eluate collected in a 100 ml volumetric flask which
was then brought to volume with 3 $\underline{N}$ HCl.

This seemingly magical "four day pause" technique was
stumbled upon during preliminary elution experiments.
Initially a continuous elution of 80 ml 3 $\underline{N}$ HCl was attemp-
ted and was found $\underline{not}$ to elute 100% of all metal ions. This
was attempted after two successive 40 ml elutions of 3 $\underline{N}$ HCl,
four days apart, showed a 100% combined elution of all metal
ions. Another continuous elution attempt was made with 80

ml of 6 $\underline{N}$ HCl hoping that the increase in concentration would aid in the elution. It did not and again less than 100% of the metal ions were eluted. Postulating that the four day pause between the two 40 ml 3 $\underline{N}$ HCl elutions was the cause for the 100% elution of the metal ions, another attempt was made. This time a total of 90 ml of 3 $\underline{N}$ HCl was transferred to the delivery reservoir. First 45 ml was allowed to pass through the column at 0.5 ml/min. The elution was stopped and the apparatus was left to sit for four days then the remaining 45 ml of 3 $\underline{N}$ HCl was allowed to pass through the column at 0.5 ml/min. The combined eluate was diluted to 100 ml and the metal ion content measured by A.A.S. These results again showed that 100% of the metal ions were eluted by the "four day pause" technique.

The main objective of this work was the removal of heavy metal ions from aqueous solution by ion exchange on S.A.T.P. In the present context, the main reason for removing the bound metals from the exchanger was for the purpose of their measurement by A.A.S. However, one might add, parenthetically, that the difficulty experienced in removing the bound metal ions from the S.A.T.P. columns provides further testimony to the effectiveness of retention of these metal ions by the S.A.T.P.

Measurement of Metal Ions Exchanged on S.A.T.P. Columns

The measurement of the metal ions (with the exception of UO_2^{2+}) exchanged on the S.A.T.P. columns was carried out with Atomic Absorption Spectrophotometry (A.A.S.). Each eluate solution (brought to 100 ml volume) was analyzed by A.A.S. on an Instrumentation Laboratory Model IL-951 A.A.S. The band width and absorbance line used for each element were taken directly from the users manual for the instrument (22). The lamps used were Perkin-Elmer Hollow Cathode lamps. The standard conditions used in A.A.S. analysis for each metal ion are given in Table VI.

Standards for the analysis were multielement aqueous solutions prepared from mixtures of the 1.000×10^{-3} $\underline{M}$ stock solutions in a 3 $\underline{N}$ HCl matrix. The instrument had an integrated microprocessor which automatically determined standard curves from the analysis of standards introduced to the A.A.S. The calibration curves were inspected visually through the use of the display on a cathode ray tube connected to the microprocessor.

"Scaled-Up" Experiment

This experiment was designed to test the S.A.T.P.'s ability to remove the metal ions of interest from aqueous solu-

TABLE VI: Standard Conditions Used
in A.A.S. Analysis (22)

Element	Absorbance Line (nm)	Band Width (nm)	Lamp Amperage (ma)
Cr_1	357.9	1.0	15
Mn	279.5	0.5	15
Co	240.7	0.3	8
Ni	232.0	0.15	25
Cu	324.7	1.0	12
Zn_2	213.9	1.0	14
Pb	217.0	1.0	8
Cd_2	228.8	1.0	8

1 N_2O was used instead of air for oxidant in the case of
Cr; acetylene was used for fuel in all analysis.

2 D_2 background correction employed

tion on a larger scale than had been previously attempted in this work. 50.0 g of Irish S.A.T.P. was loaded into a 22 mm I.D. Pyrex glass column (approximately 50 cm in height) and protonated by passing 2,500 ml 3 $\underline{N}$ HCl through the column at a flow rate of 0.5 ml/min. The column was rinsed with 50 liters of deionized water at a flow rate of 0.5 ml/min at which time the effluent had obtained a pH of 4.6, indicating that effectively all excess acid had been rinsed from the column.

A 15.0 liter solution which was 1.000×10^{-5} $\underline{M}$ in each of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and UO_2^{2+} was prepared by diluting standard stock metal ion solutions with deionized water in a clean five-gallon bottle. No adjustment of the ambient pH or ionic strength was made. The solution was constantly stirred by means of a large teflon coated stirring bar and a magnetic stirer. The solution was then pumped through the column, using the previously described peristaltic pump system, at a flow rate of 49 ml/min.

The metal ions were then eluted from the column by five successive elutions of 900 ml 3 $\underline{N}$ HCl each. Each eluate was collected in a clean one-liter volumetric flask, brought to volume with 3 $\underline{N}$ HCl, analyzed for all metals of interest (except UO_2^{2+}) by A.A.S., and all five values were added to

obtain total recovery. As previously mentioned in the ac-

knowledgements, all UO_2^{2+} analysis were graciously carried

out by Geolabs using a fluorometric technique.

RESULTS AND DISCUSSION

Peat and S.A.T.P. Used in Study

The Irish peat used in this study was identical to that
used in the developmental work of Smith, et. al. (3) and in
the removal of pesticides from aqueous solution using
S.A.T.P. by Djebbar (13). The sulfuric acid treatment pro-
cess was also the same. The S.A.T.P. prepared had similar
leaching and exchange capacity characteristics compared to
that prepared by Smith and Djebbar.

Standardization of Aqueous Metal Ion Solutions

The technique for the standardization of aqeous metal
ion solutions used in this study proved to be very accurate
and precise. The data from the standardizations are shown
in Table V. Initially, all standard metal ion solutions
(except for Mn^{2+} which was purchased as a solution) were
prepared gravimetrically from their hydrated nitrate salts
to be 1.000×10^{-2} $\underline{M}$. Some deviation from gravimetrically
determined concentrations was expected due to the frequent
variability of hydration of nitrate salts. The standar-
dization results are all within ±5% of the expected gravi-
metrically produced concentrations. The precision of the
technique proved to be excellent as all duplicates have less

than 1.24% relative standard deviation (RSD), with five elements less than 0.50% RSD.

This standardization technique was not found in the literature but showed itself to be both accurate and precise and well suited for this study.

Efficiency of Simultaneous Metal Ion Removal by S.A.T.P.

The main portion of this study was dedicated to determining the recovery efficiency for removing of a number of metal cations from solution by ion exchange on the S.A.T.P. Recovery efficiency is defined as:

$$R.E. = \frac{M_e}{M_t} \ (100\%)$$

Where M_e is the amount of a metal bound to the exchanger, and M_t is the total amount of that same metal contained in the initial solution which was passed through the column.

The parameters varied in these experiments were:

(1) pH from 2.0 through 8.0

(2) Flow Rate 11.1, 19.6 and 46 ml/min

(3) Concentration 10^{-5} M and 10^{-4} M in each metal ion

(4) Ionic Strength 2.4×10^{-4}, 2.4×10^{-3}, and 1.0×10^{-2}

Effect of pH

The pH parameter was varied along with all other para-
meters. In other words, experiments were carried out at
pH's of 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 at differing
flow rates, ionic strengths, and concentrations. The raw
data and the graphed average data (simple averaging of raw
data duplicates) are shown in Tables VII through X and on
Figures 3 through 18, respectively. For clarity in the
figures, the data points have been omitted on all but
Figures 3 and 4, but can be found in Tables VII through X.
In general, the recovery efficiency was poorest at low pH's
(2.0 and 3.0) for all metal ions. It rose rapidly to pH 4.0
where it remained fairly constant through pH 8.0. A slight
decrease in recovery efficiency was noted for some metal
ions at pH 7.0 through 8.0, most noticeably for Cu^{2+}, Pb^{2+},
and UO_2^{2+}.

The lower recovery noticed at low pH's is due to the
competition of H^+ with the metal ions for the exchange
sites. The slight decrease in recovery at higher pH's is
probably due to metal complexation and/or precipitation with
OH^-. The magnitude of this effect varies from element to
element depending on each metal ion's tendency to complex
strongly and/or precipitate with OH^- (22).

TABLE VII: Recovery Efficiency Data (%) (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) for Samples #101 through #317, 1 Liter 10^{-5} $\underline{M}$ M_i^{2+} at an Ionic Strength of 2.4×10^{-4}, pH's $\underline{2.0}$ through 8.0 and Flow Rates of 11.1, 19.6 and 46.0 ml/min

Sample No.	pH	Flow Rate	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
101	4.0	11.1 ml/min	101.00	90.70	95.86	99.50
102	5.0	"	101.77	91.21	97.70	98.08
103	6.0	"	98.93	88.94	95.76	96.00
104	7.0	"	102.09	89.99	98.82	95.03
105	8.0	"	103.51	92.30	97.80	95.06
111	4.0	"	97.76	94.44	98.04	100.98
112	5.0	"	95.83	93.35	99.20	100.25
113	6.0	"	98.16	98.07	103.56	100.06
114	7.0	"	97.98	97.32	101.86	95.88
115	8.0	"	97.21	96.40	103.94	92.35
201	4.0	19.6 ml/min	93.57	93.42	97.09	96.16
202	5.0	"	92.26	93.86	95.93	95.31
203	6.0	"	96.63	95.45	97.67	96.16
204	7.0	"	96.20	94.16	95.66	91.06
205	8.0	"	96.05	95.28	99.81	92.38
206	2.0	"	34.04	35.60	39.29	61.16
207	3.0	"	78.72	77.06	81.07	88.20
211	4.0	"	89.68	89.41	90.41	92.95
212	5.0	"	90.62	91.62	96.34	94.33
213	6.0	"	93.21	88.94	97.53	93.36
214	7.0	"	93.06	88.80	96.47	88.98
215	8.0	"	92.63	88.77	97.15	86.59
216	2.0	"	29.42	28.54	33.67	56.12
217	3.0	"	75.62	69.12	80.56	90.81
301	4.0	46.0 ml/min	76.10	74.58	77.66	82.59
302	5.0	"	82.29	77.13	84.51	88.51
303	6.0	"	82.83	77.54	84.75	89.80
304	7.0	"	84.29	76.25	86.52	84.83
305	8.0	"	83.56	76.25	85.06	79.10
306	2.0	"	28.87	27.25	31.15	48.47
307	3.0	"	66.01	62.84	69.11	76.58
311	4.0	"	77.48	76.69	80.08	83.88
312	5.0	"	81.08	79.98	83.32	86.24
313	6.0	"	82.58	79.88	84.58	88.73
314	7.0	"	83.38	78.45	86.52	85.30
315	8.0	"	83.20	76.18	87.27	85.58
316	2.0	"	28.69	26.74	31.76	47.75
317	3.0	"	65.61	61.38	67.81	74.85

TABLE VIII: Recovery Efficiency Data (%) (Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}) for Samples #101 through #317, 1 Liter 10^{-5} $\underline{M}$ M_i^{2+} at an Ionic Strength of 2.4 x 10^{-4}, pH's $\overline{2}.0$ through 8.0 and Flow Rates of 11.1, 19.6 and 46.0 ml/min

Sample No.	pH	Flow Rate	Zn^{2+}	Cd^{2+}	Pb^{2+}	UO_2^{2+}
101	4.0	11.1 ml/min	92.23	95.01	98.35	92.41
102	5.0	"	92.08	93.76	97.87	92.41
103	6.0	"	89.17	93.59	94.88	96.61
104	7.0	"	89.02	95.19	89.47	92.41
105	8.0	"	83.25	97.06	87.54	88.21
111	4.0	"	92.69	94.83	97.68	96.61
112	5.0	"	92.38	94.48	97.68	96.61
113	6.0	"	93.15	94.65	95.17	96.61
114	7.0	"	93.30	96.08	89.18	88.21
115	8.0	"	89.78	95.19	86.48	96.61
201	4.0	19.6 ml/min	86.72	92.79	95.36	92.41
202	5.0	"	87.64	93.14	94.59	96.61
203	6.0	"	89.78	96.70	94.98	92.41
204	7.0	"	85.96	93.23	89.96	84.01
205	8.0	"	83.66	95.81	87.45	88.21
206	2.0	"	37.01	40.65	81.85	46.20
207	3.0	"	78.62	84.25	92.27	84.01
211	4.0	"	81.52	92.61	94.98	96.61
212	5.0	"	84.43	91.10	95.17	96.61
213	6.0	"	82.59	90.56	95.56	92.41
214	7.0	"	83.21	90.74	90.54	88.21
215	8.0	"	81.06	92.96	90.44	84.01
216	2.0	"	31.20	34.69	76.93	42.00
217	3.0	"	75.25	83.00	89.86	79.81
301	4.0	46.0 ml/min	73.42	76.15	87.67	71.40
302	5.0	"	75.71	81.49	90.34	79.81
303	6.0	"	75.86	82.91	90.73	84.01
304	7.0	"	75.71	82.56	82.91	75.60
305	8.0	"	75.10	80.60	77.02	75.60
306	2.0	"	30.59	33.80	69.21	33.60
307	3.0	"	63.93	70.55	85.03	63.00
311	4.0	"	69.59	76.68	88.03	75.60
312	5.0	"	74.49	80.33	89.96	84.01
313	6.0	"	76.32	81.79	91.31	84.01
314	7.0	"	75.25	80.86	86.10	75.60
315	8.0	"	74.95	81.13	86.19	92.41
316	2.0	"	30.74	33.89	67.66	33.60
317	3.0	"	63.93	70.72	84.07	71.40

FIGURE 3: Mn^{2+} Graphed Averaged Data,
pH, vs. Recovery Efficiency,
for 10^{-5} $\underline{M}$ M_i^{2+} Solutions at
Flow Rates of 11.0, 19.6, and
46.0 ml/min

A: 11.0 ml/min
B: 19.6 ml/min
C: 46.0 ml/min

Figure 4: Co^{2+} Graphed Averaged Data,
pH vs. Recovery Efficiency,
for 10^{-5} $\underline{M}$ M_i^{2+} Solutions at
Flow Rates of 11.0, 19.6, and
46.0 ml/min

A: 11.0 ml/min
B: 19.6 ml/min
C: 46.0 ml/min

FIGURE 5: Ni^{2+} Graphed Averaged Data,
pH vs. Recovery Efficiency,
for 10^{-5} $\underline{M}$ M_i^{2+} Solutions at
Flow Rates of 11.0, 19.6, and
46.0 ml/min

A: 11.0 ml/min
B: 19.6 ml/min
C: 46.0 ml/min

FIGURE 6: Cu^{2+} Graphed Averaged Data,
          pH vs. Recovery Efficiency, for
          10^{-5} M M_i^{2+} Solutions at Flow
          Rates of 11.0, 19.6, and 46.0
          ml/min

A: 11.0 ml/min
B: 19.6 ml/min
C: 46.0 ml/min

FIGURE 7: Zn^{2+} Graphed Averaged Data, pH vs. Recovery Efficiency, for 10^{-5} $\underline{M}$ M_i^{2+} Solutions at Flow Rates of 11.0, 19.6 and 46.0 ml/min

A: 11.0 ml/min

B: 19.6 ml/min
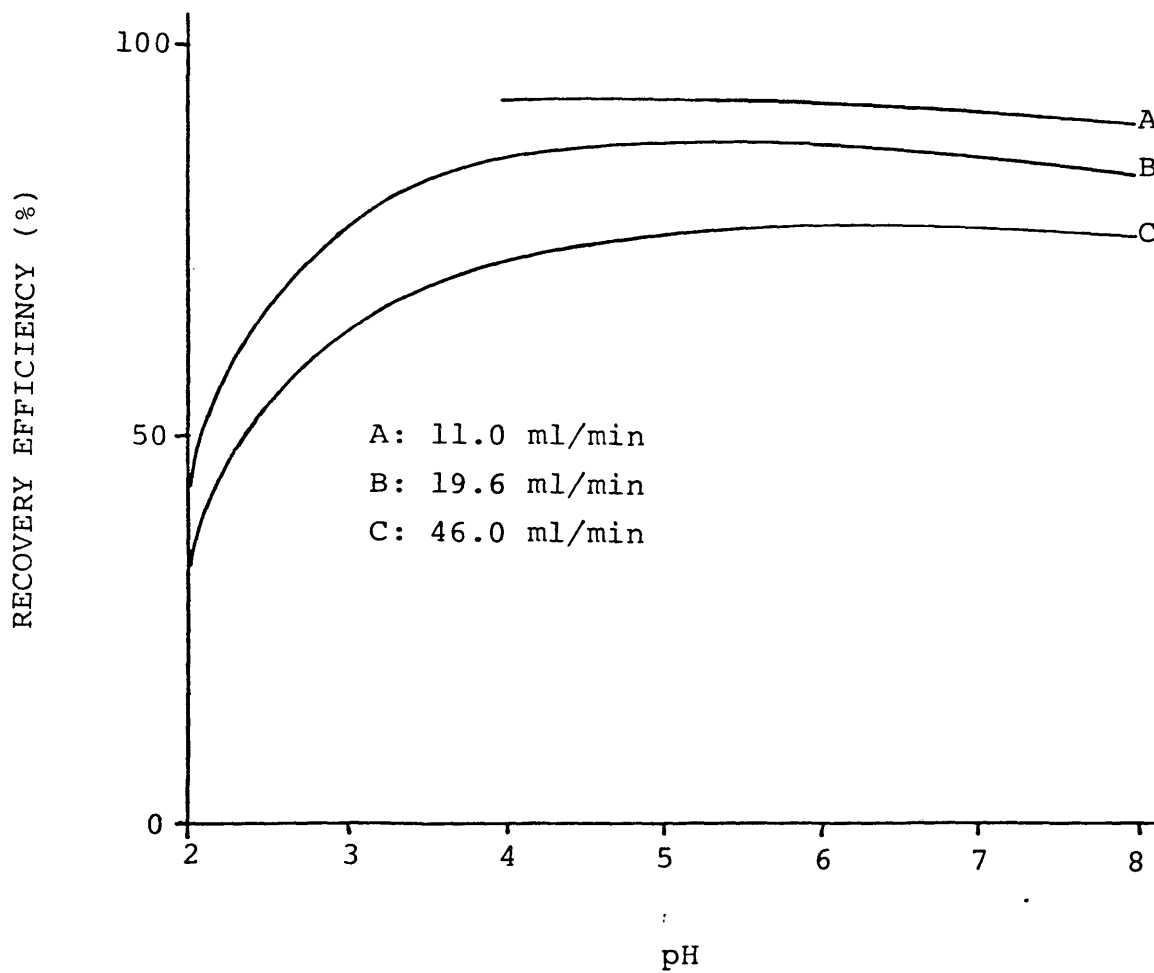
C: 46.0 ml/min

FIGURE 8: Cd^{2+} Graphed Averaged Data,
pH vs. Recovery Efficiency,
for 10^{-5} $\underline{M}$ $M_i{}^{2+}$ Solutions at
Flow Rates of 11.0, 19.6 and
46.0 ml/min

A: 11.0 ml/min
B: 19.6 ml/min
C: 46.0 ml/min
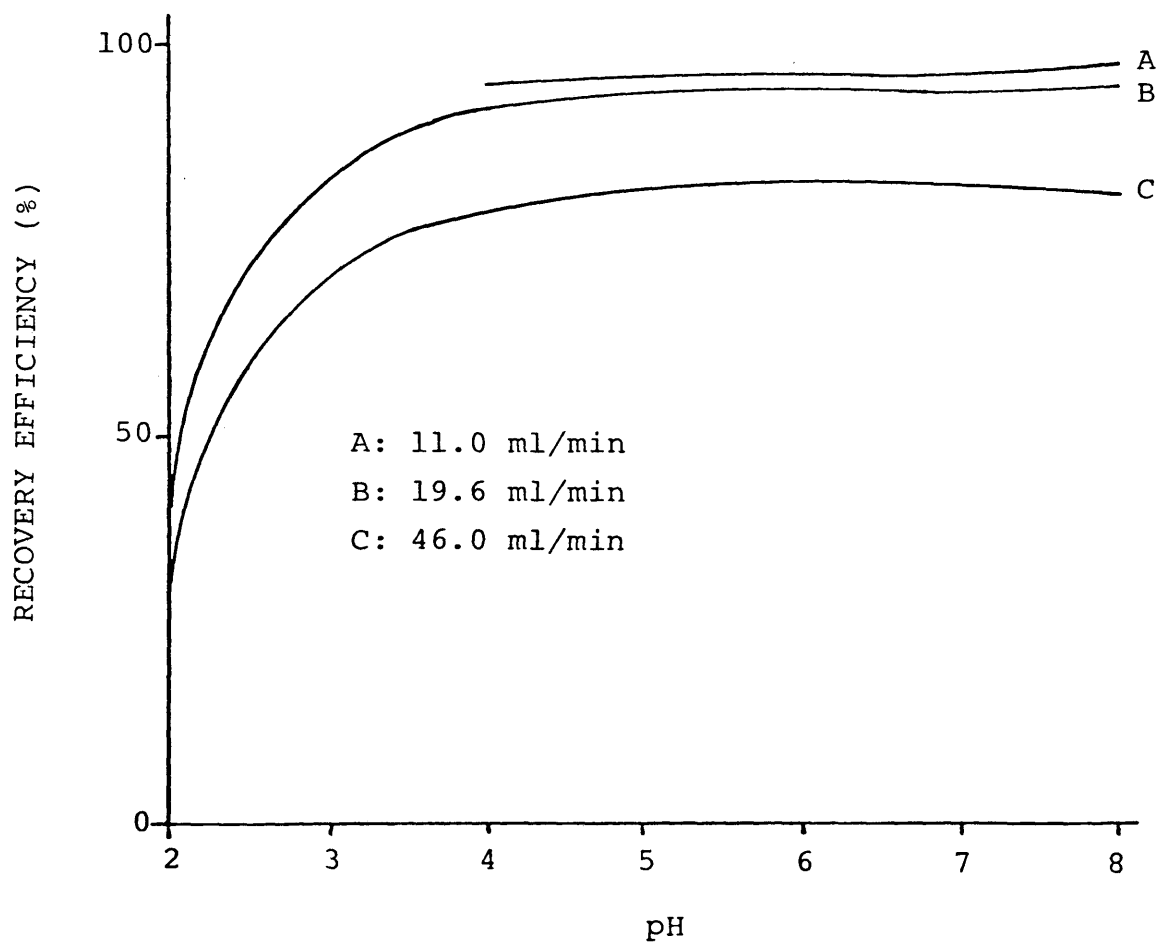
FIGURE 9: Pb^{2+} Graphed Averaged Data, pH vs. Recovery Efficiency, for 10^{-5} $\underline{M}$ M_i^{2+} Solutions at Flow Rates of 11.0, 19.6 and 46.0 ml/min

A: 11.0 ml/min
B: 19.6 ml/min
C: 46.0 ml/min
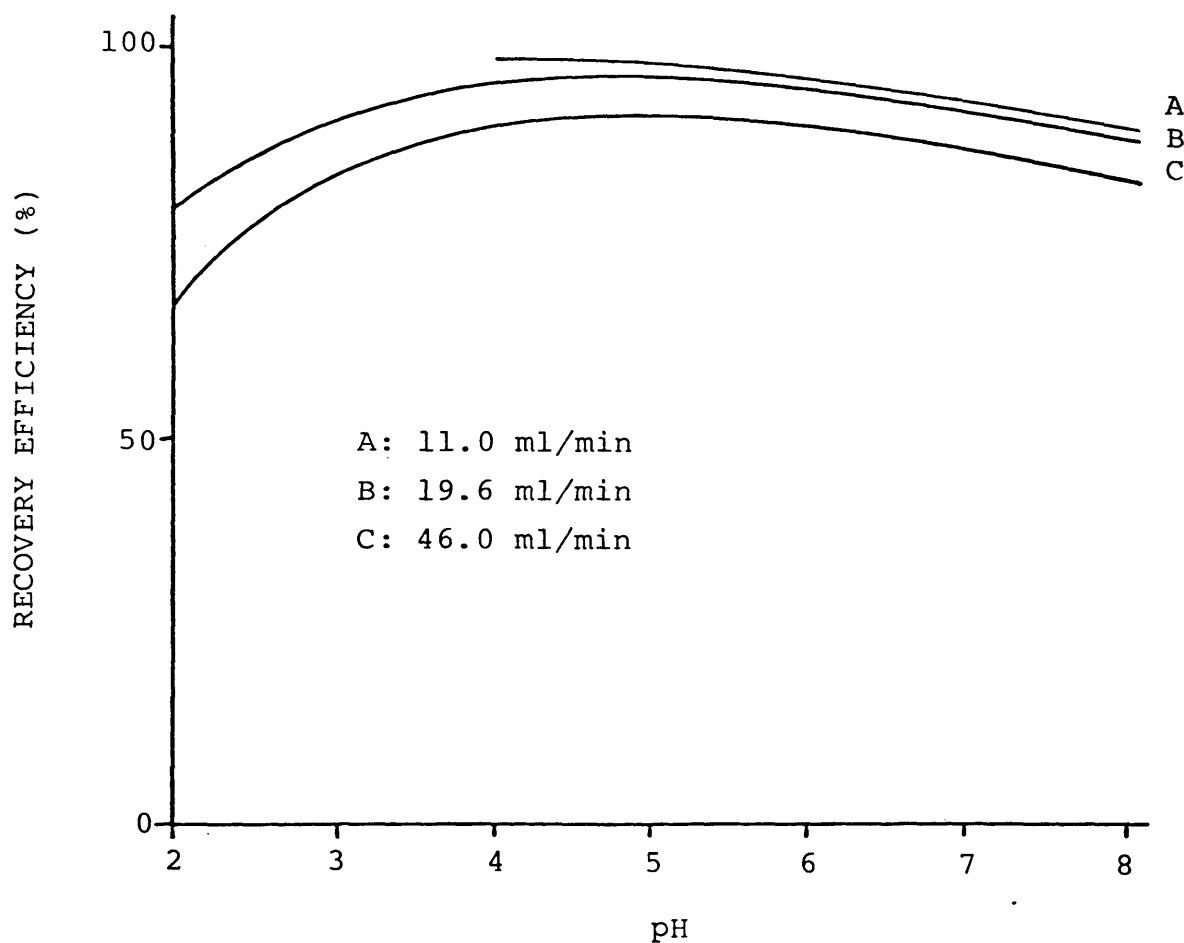
FIGURE 10: UO_2^{2+} Graphed Averaged Data
pH vs. Recovery Efficiency,
for 10^{-5} $\underline{M}$ M_i^{2+} Solutions at
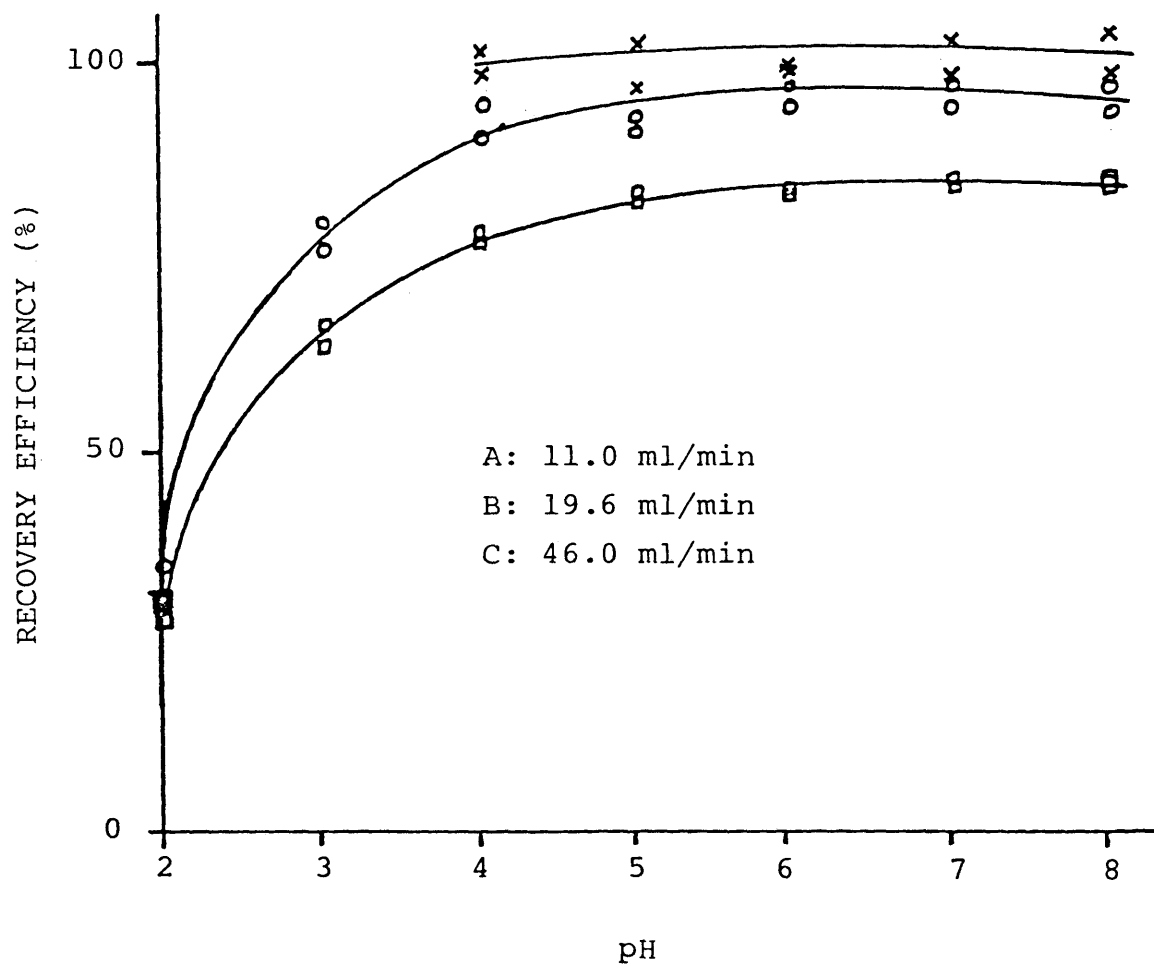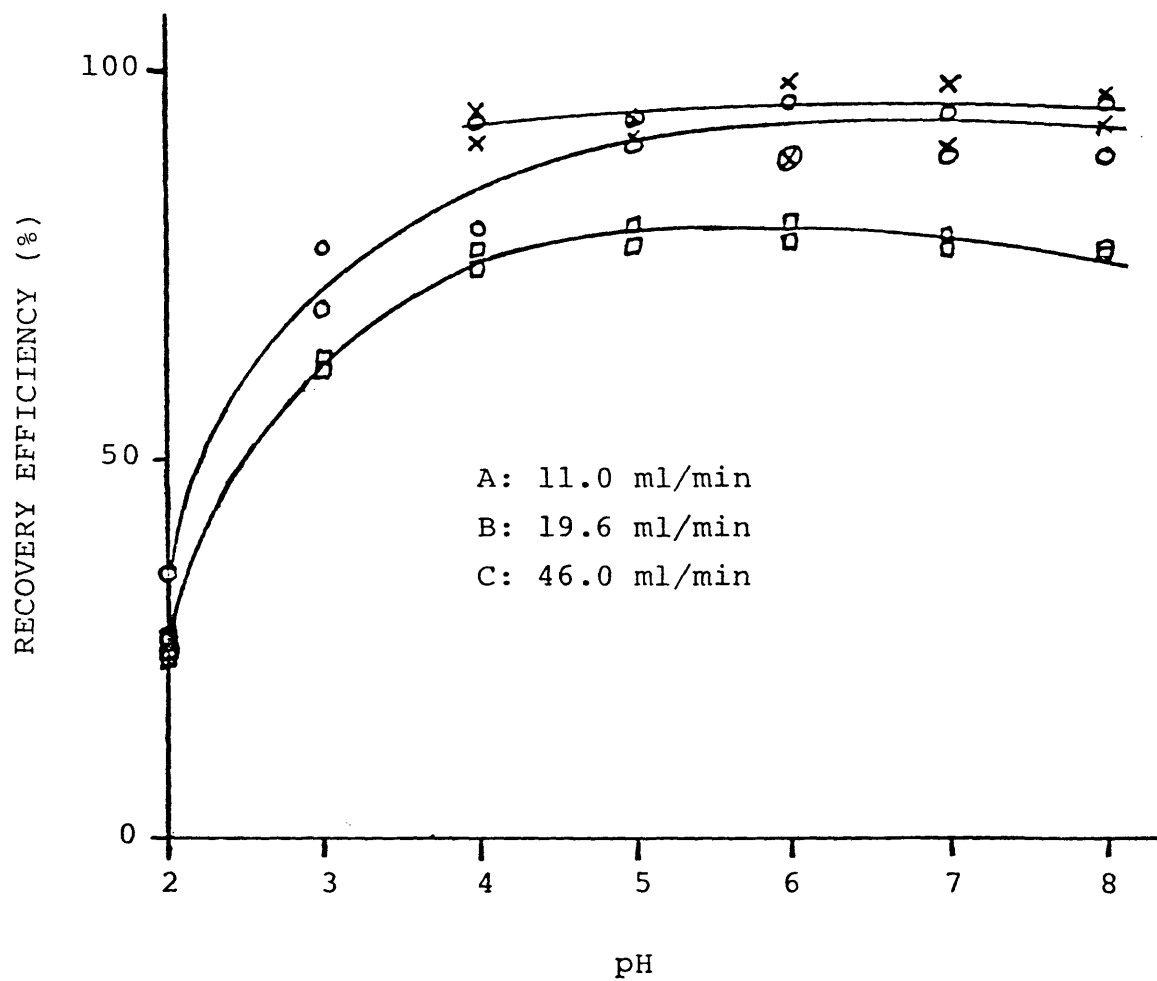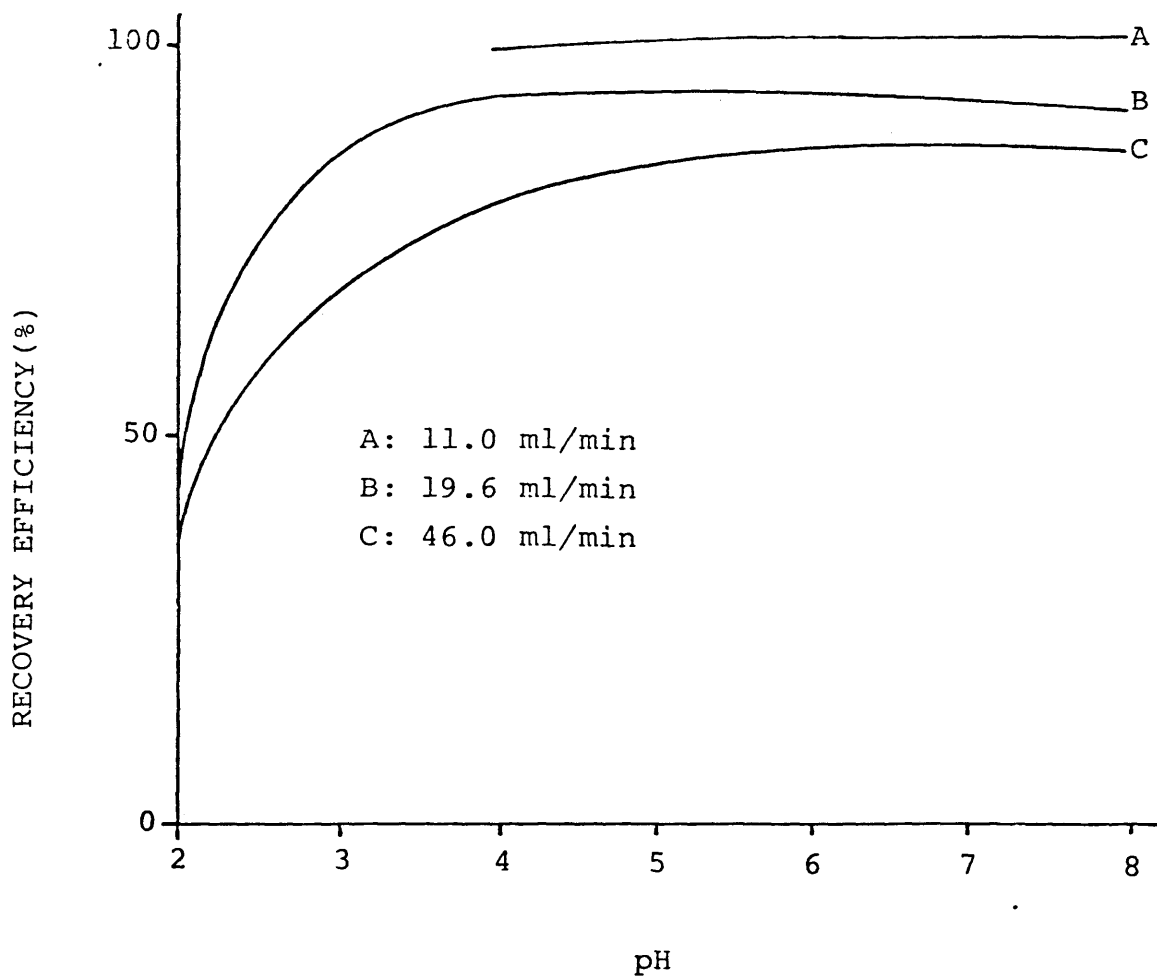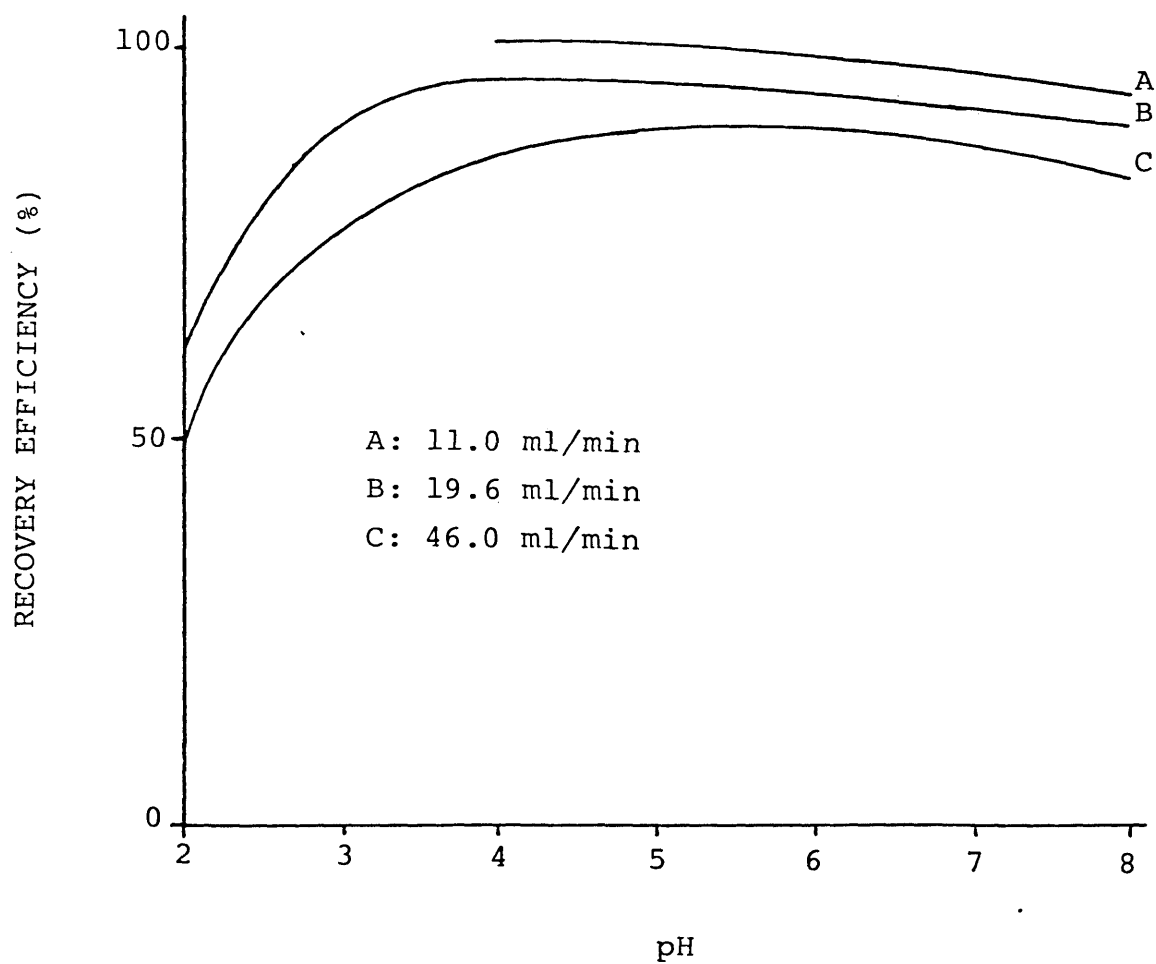Flow Rates of 11.0, 19.6 and
46.0 ml/min

A: 11.0 ml/min
B: 19.6 ml/min
C: 46.0 ml/min

TABLE IX: Recovery Efficiency Data (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) For Samples #501 through #607, pH's 2.0 through 8.0, a Flow Rate of 46.0 ml/min, and Various Ionic Strengths and Concentrations of Mi^{2+}

Recovery Efficiency (%)

Sample No.	pH	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
501[1]	4.0	65.03	62.81	68.63	74.57
502	5.0	68.45	63.45	71.05	75.04
503	6.0	70.53	67.02	74.39	78.85
504	7.0	73.58	67.56	76.78	70.60
505	8.0	69.58	64.07	75.35	74.19
506	2.0	30.22	24.91	35.00	47.21
507	3.0	55.56	49.13	62.16	67.36
511	4.0	67.47	64.34	68.50	75.76
512	5.0	68.09	65.08	68.77	76.90
513	6.0	69.98	65.86	70.71	78.16
514	7.0	75.15	70.24	76.57	71.23
515	8.0	75.41	68.24	77.83	74.00
516	2.0	29.49	25.72	34.96	49.48
517	3.0	55.93	51.00	59.60	70.95
601[2]	4.0	39.14	41.67	47.71	69.18
602	5.0	44.75	41.19	50.64	71.01
603	6.0	47.48	48.32	52.79	72.65
604	7.0	45.66	46.86	53.94	63.58
605	8.0	48.86	54.50	58.20	68.05
606	2.0	11.40	14.18	19.15	36.67
607	3.0	27.49	33.59	38.98	60.57

[1] Sample Nos. 501 through 517: 100 ml 10^{-4} M Mi^{2+}, $I = 2.4 \times 10^{-3}$

[2] Sample Nos. 601 through 607: 1 Liter 10^{-5} M Mi^{2+}, $I = 1.0 \times 10^{-2}$

TABLE X: Recovery Efficiency Data (Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+})
For Samples #501 through #607, pH's 2.0 through
8.0, a Flow Rate of 46.0 ml/min, and Various Ionic
Strengths and Concentrations

Recovery Efficiency (%)

Sample No.	pH	Zn^{2+}	Cd^{2+}	Pb^{2+}	UO_2^{2+}
501[1]	4.0	62.25	71.88	85.71	67.20
502	5.0	67.91	73.30	85.42	71.40
503	6.0	70.82	77.84	88.03	71.40
504	7.0	71.89	81.84	77.41	58.80
505	8.0	66.38	78.55	83.97	67.20
506	2.0	34.57	38.61	67.37	33.60
507	3.0	48.79	64.85	81.37	58.80
511	4.0	67.45	68.14	86.87	67.20
512	5.0	66.53	66.19	86.39	67.20
513	6.0	67.76	70.99	87.06	67.20
514	7.0	72.81	77.04	64.48	54.60
515	8.0	71.58	77.75	76.44	58.80
516	2.0	33.80	37.54	65.34	33.60
517	3.0	56.29	63.34	77.02	58.80
601[2]	4.0	41.76	47.06	80.50	63.00
602	5.0	45.26	51.51	81.95	67.20
603	6.0	48.79	54.35	81.95	71.40
604	7.0	46.65	51.60	69.11	54.60
605	8.0	51.54	57.74	74.32	58.80
606	2.0	13.46	14.95	52.80	29.40
607	3.0	30.13	35.32	74.03	50.40

[1] Sample Nos. 501 through 517: 100 ml 10^{-4} M M_i^{2+},
$I = 2.4 \times 10^{-3}$

[2] Sample Nos. 601 through 607: 1 Liter 10^{-5} M M_i^{2+},
$I = 1.0 \times 10^{-2}$

FIGURE 11: Mn^{2+} Graphed Averaged Data,

      pH vs. Recovery Efficiency,

      for Selected Concentrations of M_i^{2+}

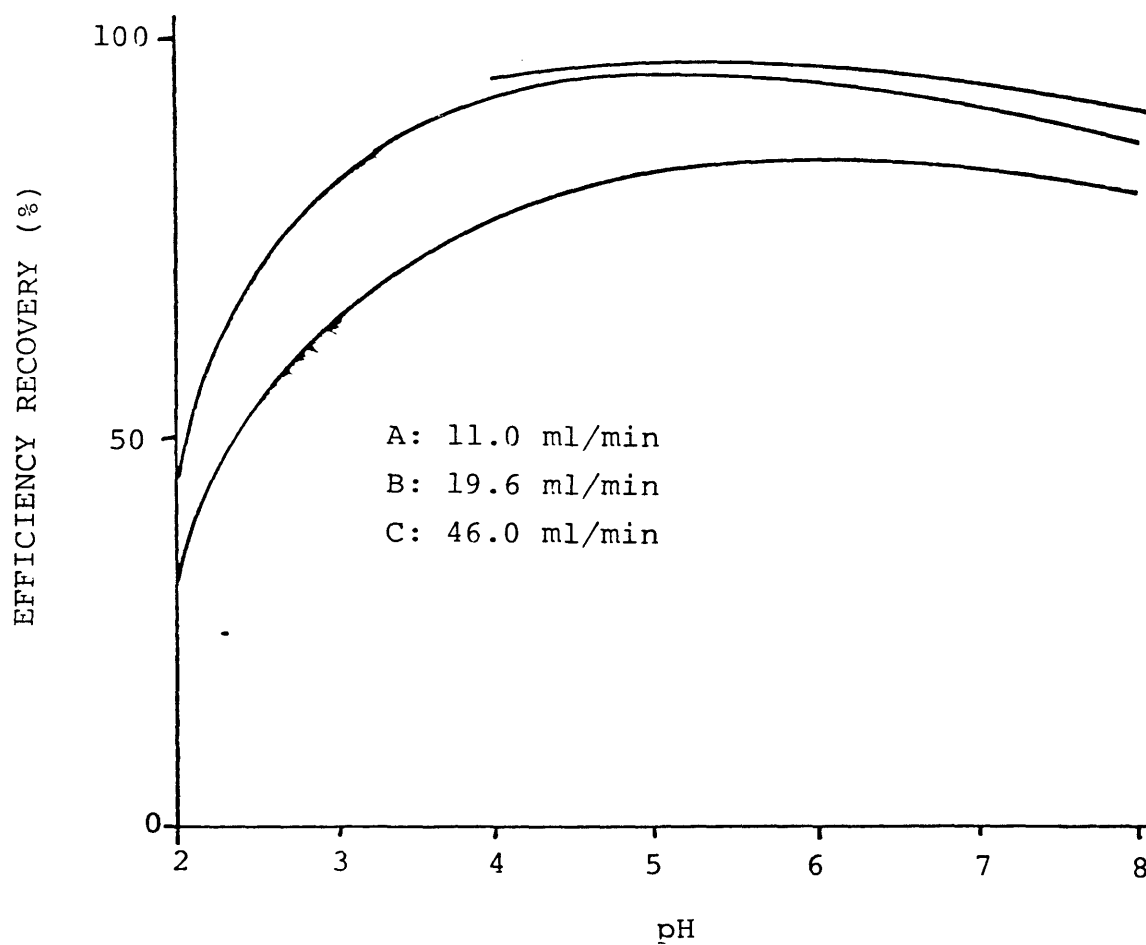   and Ionic Strengths at a Flow

      Rate of 46 ml/min

A: 10^{-5} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-4}

B: 10^{-4} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-3}

C: 10^{-5} $\underline{M}$ M_i^{2+}, I = 1.0 x 10^{-2}

FIGURE 12: Co^{2+} Graphed Averaged Data,
pH vs. Recovery Efficiency,
for Selected Concentrations of M_i^{2+}
and Ionic Strengths at a Flow
Rate of 46 ml/min

A: 10^{-5} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-4}
B: 10^{-4} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-3}
C: 10^{-5} $\underline{M}$ M_i^{2+}, I = 1.0 x 10^{-2}

FIGURE 13: Ni^{2+} Graphed Averaged Data,
pH vs. Recovery Efficiency,
for Selected Concentrations of M_i^{2+}
and Ionic Strengths at a Flow
Rate of 46 ml/min

A: 10^{-5} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-4}
B: 10^{-4} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-3}
C: 10^{-5} $\underline{M}$ M_i^{2+}, I = 1.0 x 10^{-2}

FIGURE 14: Cu^{2+} Graphed Averaged Data,
pH vs. Recovery Efficiency,
for Selected Concentrations of M_i^{2+}
and Ionic Strengths at a Flow
Rate of 46 ml/min

A: 10^{-5} $\underline{M}$ M_i^{2+}, I - 2.4×10^{-4}
B: 10^{-4} $\underline{M}$ M_i^{2+}, I = 2.4×10^{-3}
C: 10^{-5} $\underline{M}$ M_i^{2+}, I = 1.0×10^{-2}

FIGURE 15: Zn^{2+} Graphed Averaged Data,
          pH vs. Recovery Efficiency,
          for Selected Concentrations of M_i^{2+}
          and Ionic Strengths at a Flow
          Rate of 46 ml/min

A: 10^{-5} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-4}
B: 10^{-4} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-3}
C: 10^{-5} $\underline{M}$ M_i^{2+}, I = 1.0 x 10^{-2}

FIGURE 16: Cd^{2+} Graphed Averaged Data,
pH vs. Recovery Efficiency,
for Selected Concentrations of M_i^{2+}
and Ionic Strengths at a Flow
Rate of 46 ml/min

A: 10^{-5} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-4}
B: 10^{-4} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-3}
C: 10^{-5} $\underline{M}$ M_i^{2+}, I = 1.0 x 10^{-2}

FIGURE 17: Pb^{2+} Graphed Averaged Data,
pH vs. Recovery Efficiency,
for Selected Concentrations of M_i^{2+}
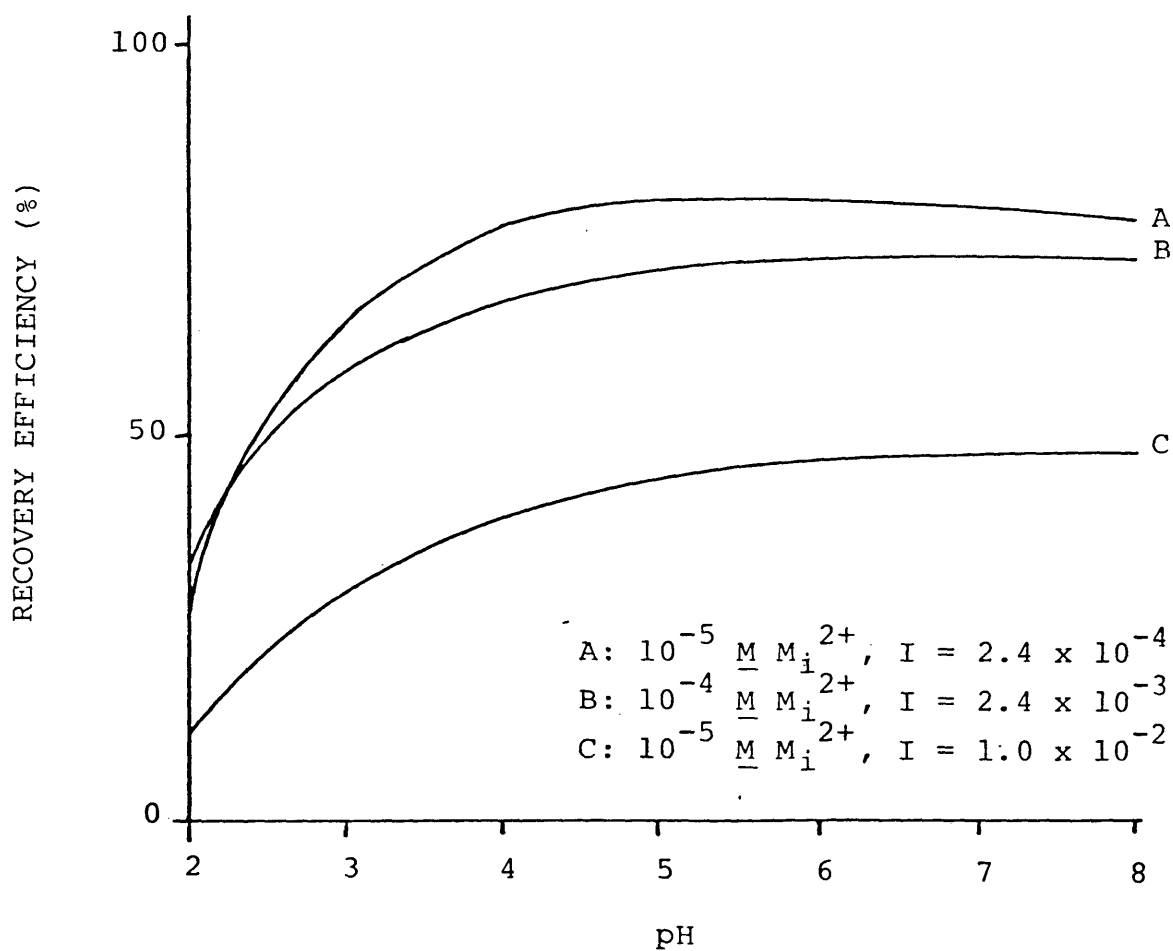and Ionic Strengths at a Flow
Rate of 46 ml/min

A: 10^{-5} $\underline{M}$ M_i^{2+}, $I = 2.4 \times 10^{-4}$
B: 10^{-4} $\underline{M}$ M_i^{2+}, $I = 2.4 \times 10^{-3}$
C: 10^{-5} $\underline{M}$ M_i^{2+}, $I = 1.0 \times 10^{-2}$
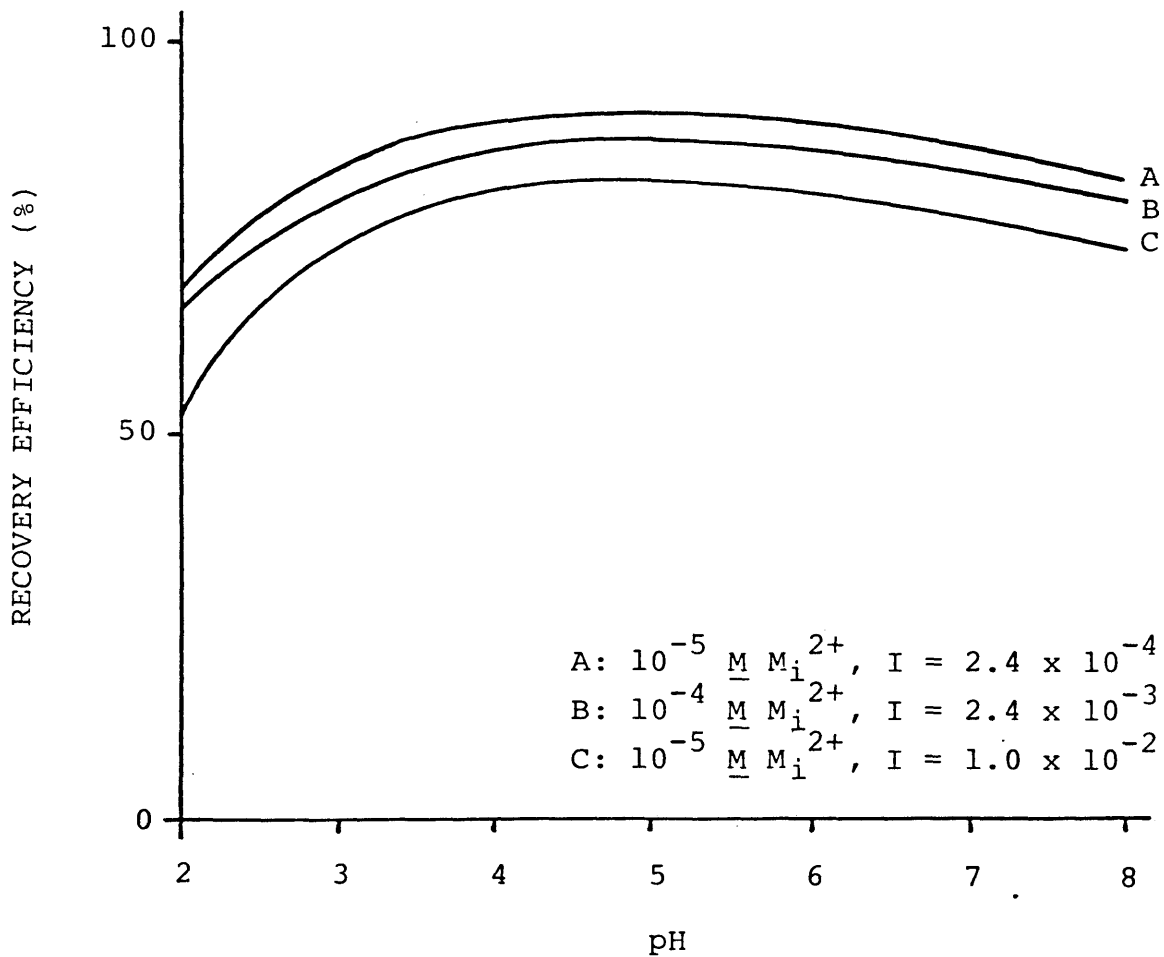
FIGURE 18: UO_2^{2+} Graphed Averaged Data,
         pH vs. Recovery Efficiency,
         for Selected Concentrations of M_i^{2+}
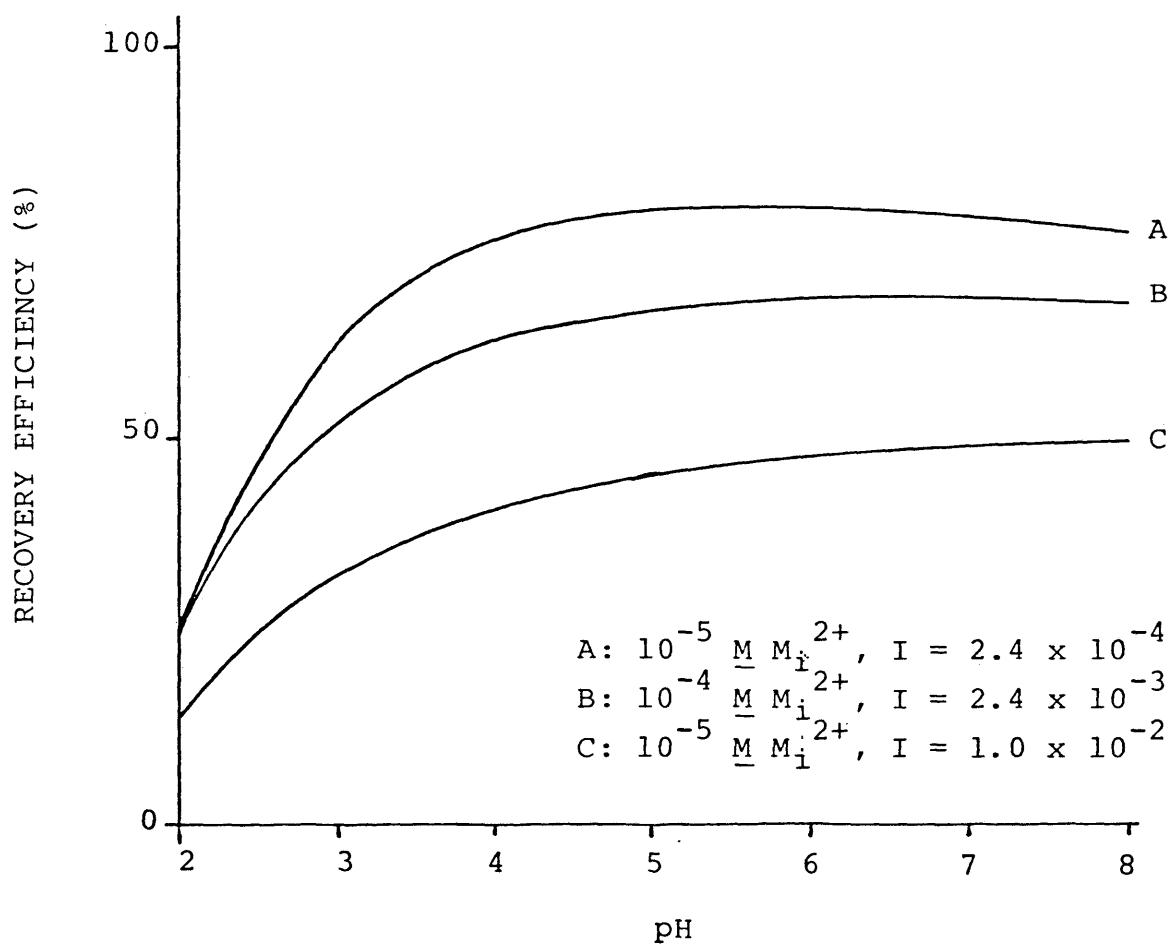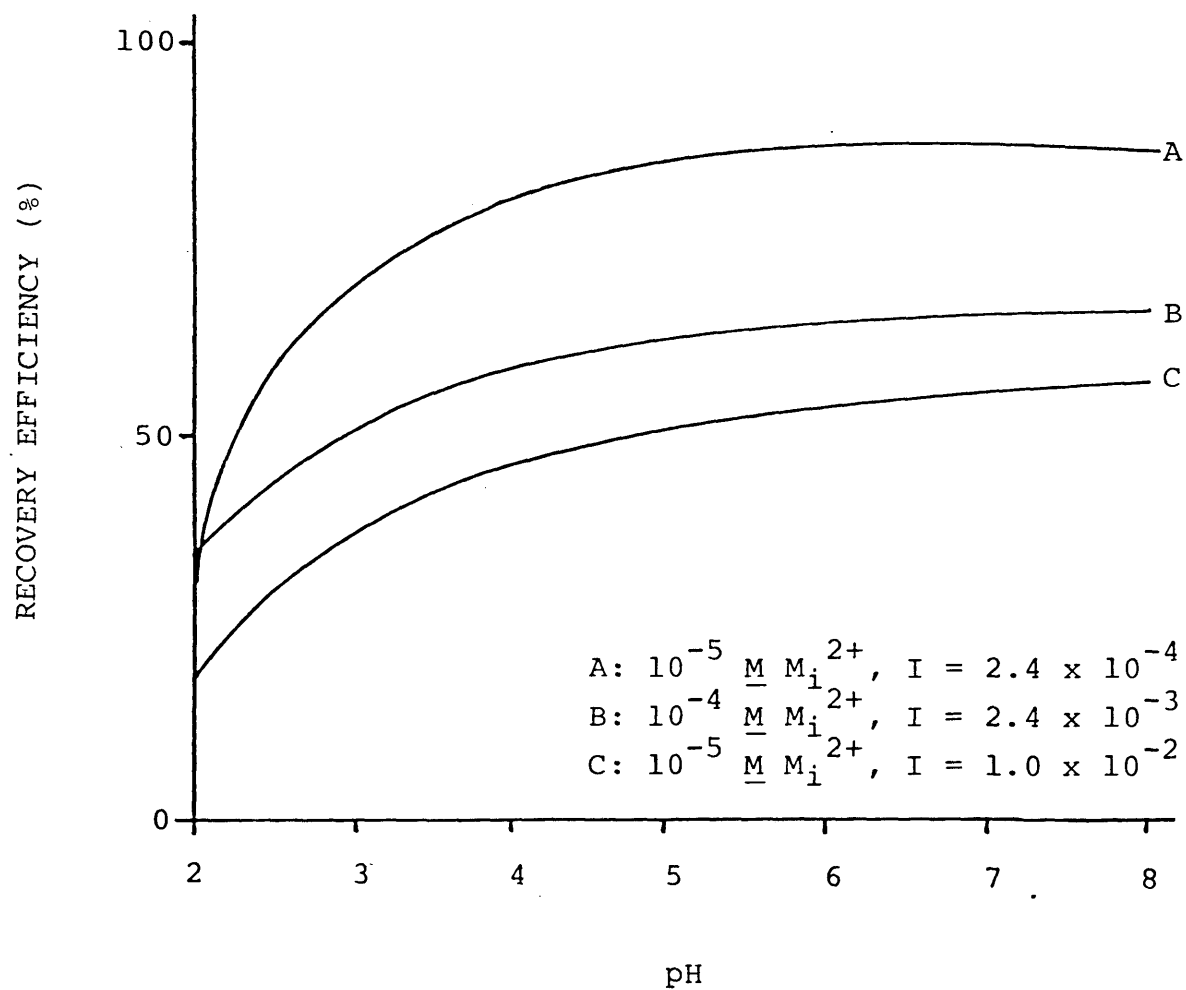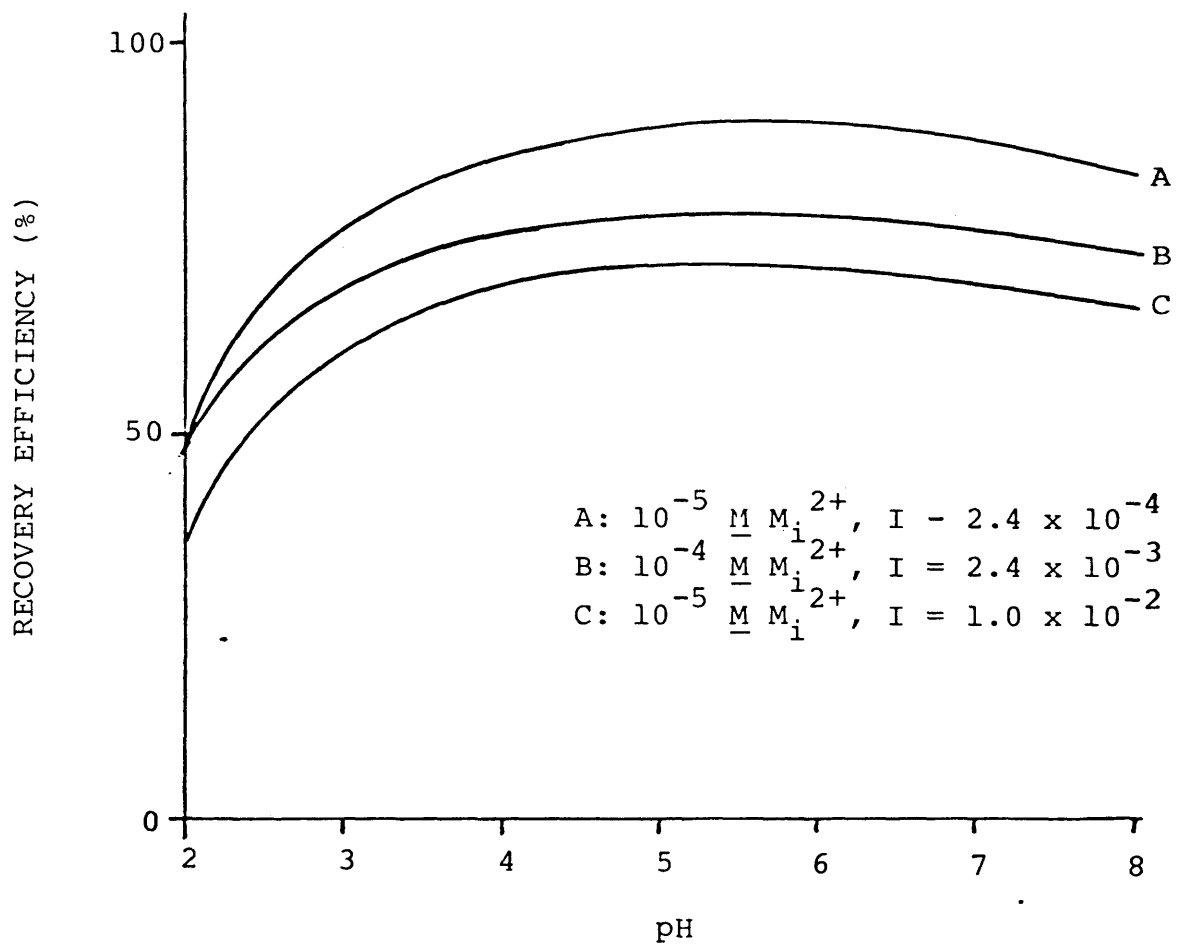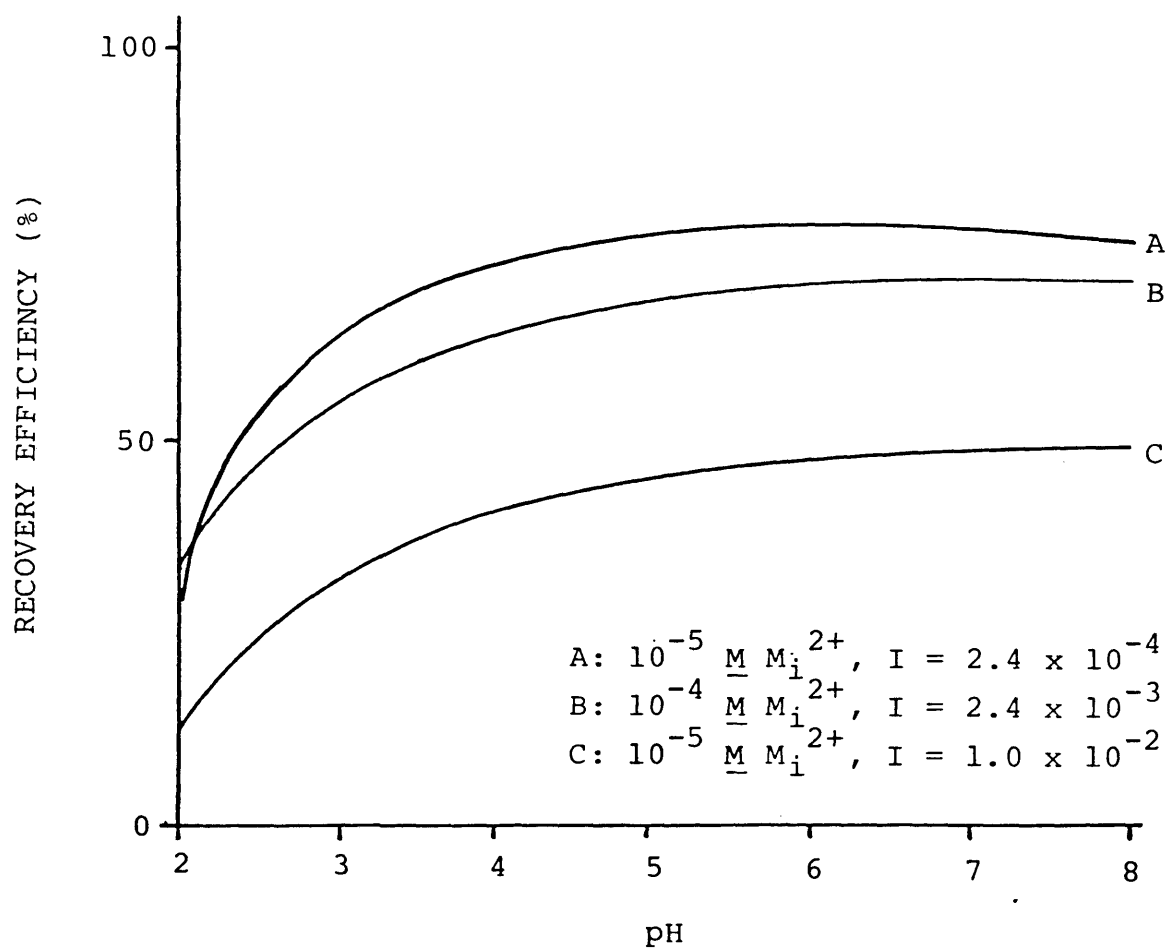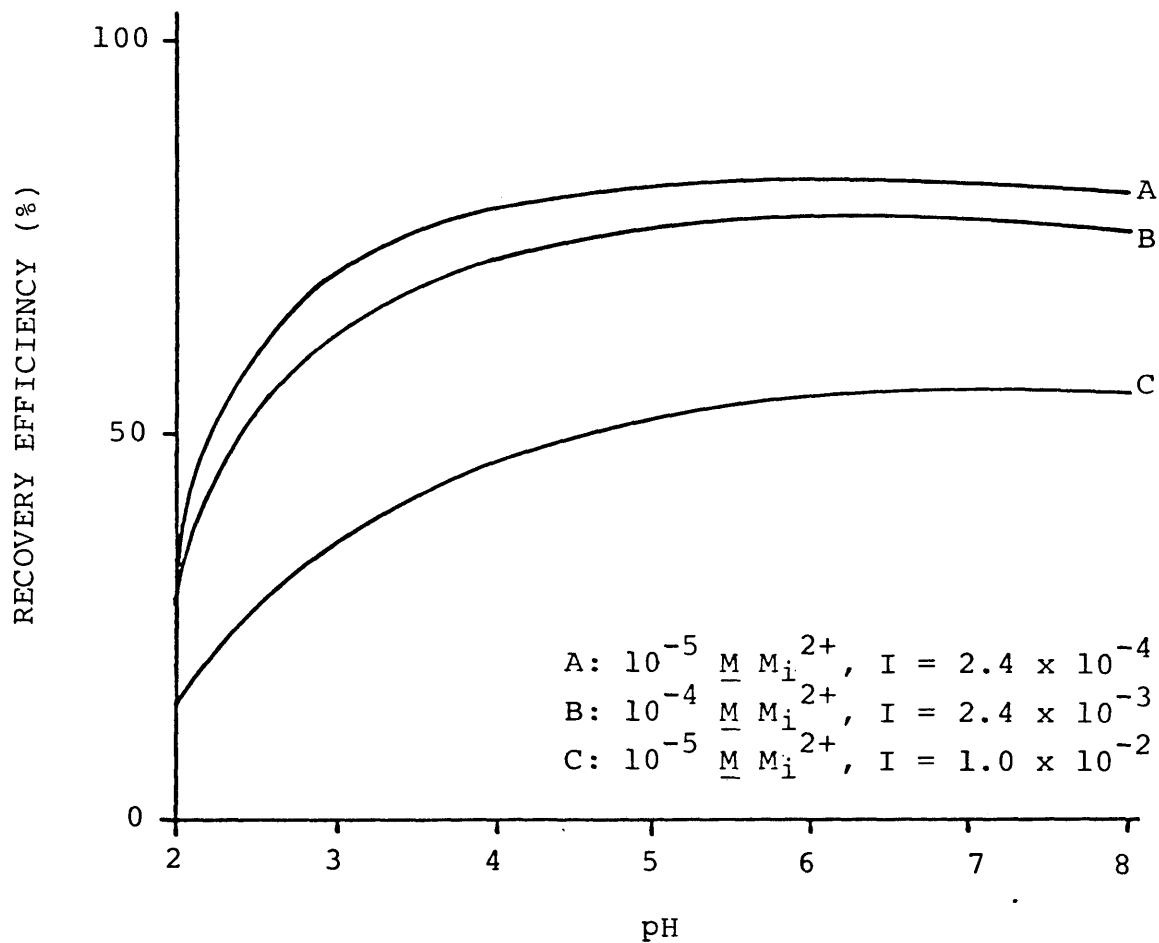   and Ionic Strengths at a Flow
         Rate of 46 ml/min

A: 10^{-5} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-4}
B: 10^{-4} $\underline{M}$ M_i^{2+}, I = 2.4 x 10^{-3}
C: 10^{-5} $\underline{M}$ M_i^{2+}, I = 1.0 x 10^{-2}
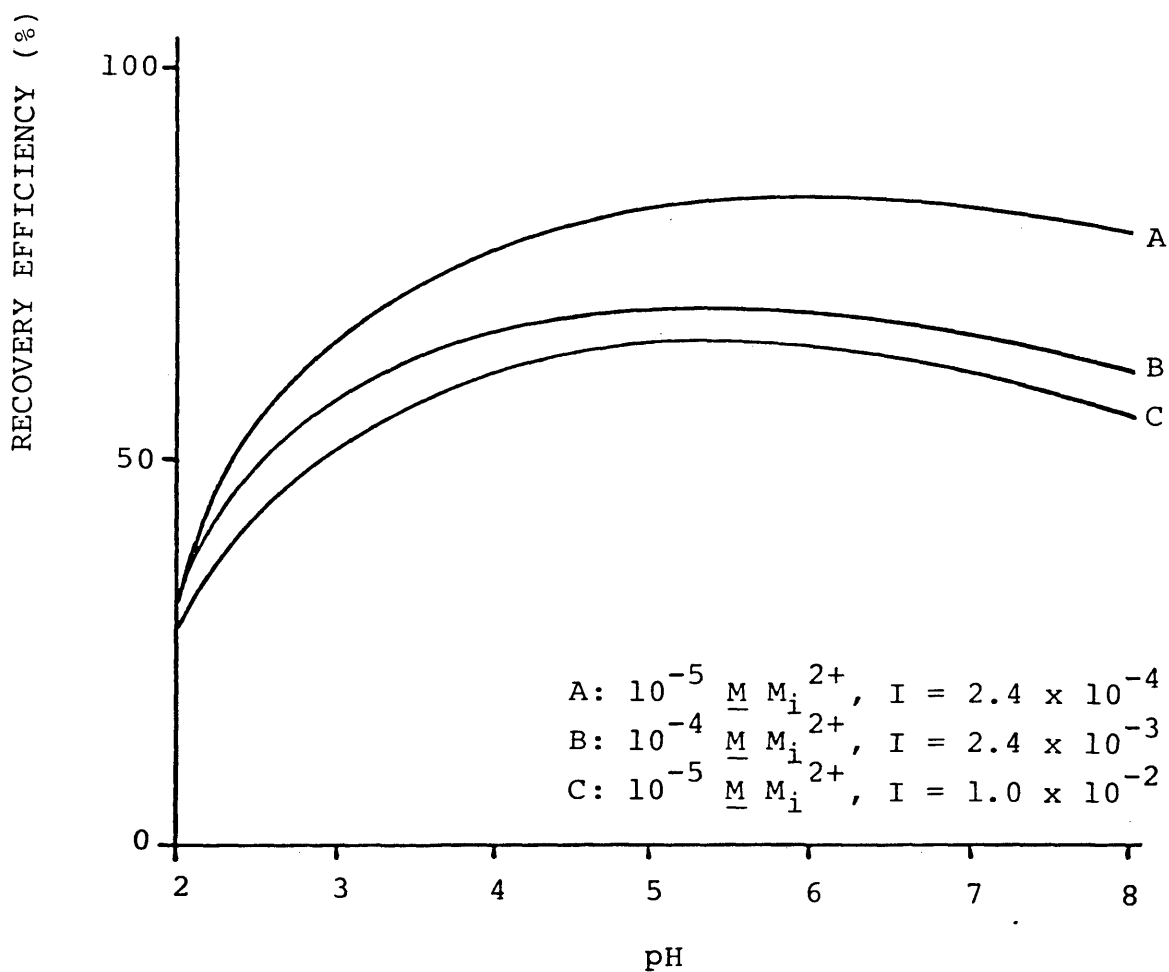
Effect of Flow Rate

The flow rates investigated in this study were 11.1, 19.6, and 46.0 ml/min which correspond to 9.63, 17.0, and 39.9 gallons per minute per square foot of exchanger. These flow rates are similar to those used in water purification systems (24). One liter of 1.000×10^{-5} $\underline{M}$ in each metal ion was passed through 1.000 g columns of S.A.T.P. in duplicate at each pH and flow rate. The raw data and the graphed averaged data are shown in Tables VII and VIII and Figures 3 through 10, respectively.

In general, an increase in flow rate caused a noticeable decrease in the recovery efficiency of all metal ions. The smallest decrease in R.E. due to an increase in flow rate was seen in the Pb^{2+} data and the largest was seen in the Mn^{2+} data. The S.A.T.P. proved to be very effective, over the range of flow rates investigated, in removing all metal ions studied. At the highest flow rate used, greater than 72% R.E. was found for all metal ions at pH's ≥ 4.0. Again, it should be mentioned that only a slight excess of exchanger was used and that in industrial applications where a larger excess would be used, these effects would most probably be greatly reduced.

The general trend of decreasing R.E. with increasing
flow rate is probably a kinetic effect whereby shorter con-
tact times of the metal ions with the S.A.T.P. reduce the
occurrence of exchange reactions. The magnitude of this ef-
fect on each element would depend on each element's reaction
rate with the exchange sites and diffusion rate into the ex-
changer. For example, in the case of Pb^{2+}, it appears that
shorter reaction times are required for exchange to occur
than for those of Mn^{2+}. Another possible factor causing
lower recovery efficiencies at higher flow rates is that the
height equivalent of a theoretical plate decreases with in-
creased flow rate and consequently results in lower metal
ion removal from solution.

Effect of Total Metal Ion Concentration

The concentrations investigated were 1.000×10^{-5} M and
1.000×10^{-4} M in each metal ion. These concentrations are
between one and four orders of magnitude higher than those
of the E.P.A. limits set for drinking water (1, 2). The ex-
periments in this portion of the study were carried out at
pH's of 2.0 through 8.0 and at a flow rate of 46.0 ml/min.
As mentioned previously, the experiments carried out at the
higher concentration were accompanied by a corresponding de-

crease in volume of solution passed through the 1.000 g col-

umns of S.A.T.P. This was necessary in order to maintain

the total exchanger equivalents to total metal ion equiva-

lents ratio constant at 6.25. The raw data and average

graphed data are shown on Tables VII through X and Figures

11 through 18, respectively. When graphically comparing the

data, it is seen that an increase in concentration causes a

decrease in R.E. for all metals studied. The smallest ef-

fect is seen in the Pb^{2+} data and the largest is seen in the

Ni^{2+} data.

This effect is again probably due to the shorter contact

time of the metal ions with the S.A.T.P. because the de-

creased volume of the higher concentration solution would,

at the same flow rate, cause a shorter contact time with the

S.A.T.P. than the contact time for the solution of lower con-

centration. The S.A.T.P. proved to be effective in removing

all metal ions from solution and the data resulted in R.E.

values greater than 60% (pH 4.0 through 8.0) at a concentra-

tion of 1.000×10^{-4} $\underline{M}$ in each metal ion. Again, it is

important to keep in mind the relatively small excess of

exchanger used compared to total metal in terms of what

would be employed in a commercial process.

Effect of Ionic Strength

The experiments to determine the effect of ionic strength (I) on the recovery efficiency of the metal ions studied, were carried out at pH's 2.0 through 8.0, a flow rate of 46.0 ml/min, and ionic strength values of 2.4×10^{-4}, 2.4×10^{-3}, and 1.0×10^{-2}. The lower I values (2.4×10^{-4} and 2.4×10^{-3}) were due only to the concentrations of the heavy metal ions alone in the particular solutions, and were not adjusted by the addition of any extra salt. The solutions at an ionic strength of 1.0×10^{-2} were 1.000×10^{-5} $\underline{M}$ in each of the metal ions of interest, with 1.0 $\underline{M}$ KNO_3 added to bring the ionic strength up to 1.0×10^{-2}. The raw data and graphed averaged data are shown on Tables VII through X and Figures 11 through 18, respectively. The results from this portion of the study show a decrease in recovery efficiencies for all metal ions with an increase in ionic strength. The smallest effect was seen with Pb^{2+} and the largest with Mn^{2+}, Co^{2+}, and Ni^{2+}. At the highest I (1.0×10^{-2}), greater than 40% R.E. was found for Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}, and greater than 60% R.E. was found for Cu^{2+}, Pb^{2+}, and UO_2^{2+} (pH $\underline{\geq}4.0$).

In general, the decrease of recovery efficiency with increasing ionic strength can be explained parallel to that of

decreasing pH. There are simply more ions in solution to compete for a limited number of sites at higher ionic strengths than at lower ionic strengths. On an individual ion basis, Pb^{2+}, Cu^{2+}, and UO_2^{2+} again tend to show the most favorable competition for exchanger binding sites at all ionic strengths owing to their relatively higher apparent affinities for the S.A.T.P. compared to Mn^{2+}, for example. Pb^{2+} again proves to have the most favorable exchange characteristics when compared to all other ions studied.

A further contributing factor to this observed trend may be the decrease in activity of the heavy metal ions of interest with the increase in ionic strength of the solution. For example, typically the activity coefficients of these ions at a concentration of 10^{-5} $\underline{M}$ and I equal to 2.4 x 10^{-4} are generally taken to be 1.0. However, at 10^{-4} $\underline{M}$ M_i^{2+} and I equal to 10^{-3}, the activity coefficient decreases to 0.87. At a concentration of 10^{-5} $\underline{M}$ and an I of 1.0 x 10^{-2} the activity coefficient is 0.67 (25). Therefore, one might assume at higher ionic strengths of the solutions and correspondingly lower activity coefficients of the heavy metal ions, the effectiveness at which each ion participates in the exchange equilibrium decreases. In other words, at higher ionic strengths, the number of metal ions available

for exchange is effectively less than the actual concentration of the metal ions and thereby the recovery efficiency is decreased. It is assumed here that I has a more pronounced effect on the solution species than on the bound species.

"Scaled-Up" Experiment

This experiment was designed to determine what effect a larger excess of exchanger would have on the recovery efficiency. The ratio of meq. exchanger to meq. metal ion was 20.8 instead of the 6.25 as in other experiments, however, the column height to diameter ratio was kept constant to retain similar column characteristics to the other experiments in this work. The results showed that essentially 100% recovery efficiency was found for all metal ions of interest. The data from the five sequential 900 ml 3 $\underline{N}$ HCl elutions are given on Table XI. It is interesting to note that essentially all metal ions exchanged were eluted during the first 900 ml elution negating the need of the "four day pause" elution technique. This effect was observed late in this research and may warrant further investigation.

Analysis of Error In Recovery Efficiencies

Almost all experiments were performed in duplicate. The

TABLE XI: Data from "Scaled-Up" Experiment
          Sequential 900 ml 3 $\underline{N}$ HCl Elutions

Recovery Efficiency (%) By Elution

Metal Ion	1st	2nd	3rd	4th	5th	Total
Mn^{2+}	98.06	0.28	--	--	--	98.34
Co^{2+}	103.62	--	--	--	--	103.62
Ni^{2+}	102.61	--	--	--	--	102.61
Cu^{2+}	102.73	1.36	--	--	--	104.09
Zn^{2+}	97.35	0.65	0.15	0.14	--	98.29
Cd^{2+}	100.36	0.60	0.12	--	--	101.08
Pb^{2+}	101.67	--	--	--	--	101.67
UO_2^{2+}	--	--	--	--	--	(1)

1   UO_2^{2+} Recovery Efficiency was not measured as all
    solutions to be analyzed were sent to Geolabs prior
    to this experiment.

only experiments which were not duplicated were the ionic
strength experiments carried out at I = 1.0 x 10^{-2} and the
scaled-up experiment. From the duplicate analysis an aver-
age relative standard deviation (RSD) was calculated from
all of the recovery efficiency data to determine the average
precision of the study. This overall RSD was found to be
2.87% with a standard deviation (s) of 1.18. The precision
of the A.A.S. analysis was also calculated from the data
taken from the IL-951 A.A. Spectrophotometer. The instru-
ment was programmed to test each sample ten times (with no
delay) for one second each and then display the average con-
centration and its RSD value. From these data, an average
overall value (RSD) of the precision of the A.A.S. analysis
for all metals combined (with the exception of UO_2^{2+}) was
found to be 1.60% with an s of 0.70. Therefore, approxima-
tely 56% of the scatter in the data was due to the spectro-
meter. This leaves 44% of the scatter in the data due to
laboratory technique (pH adjustment, flow rate adjustment,
volumetric transfers, etc.) and the nonhomogeneity of the
S.A.T.P. In general, the results are very precise. When
analyzing the data on an element-by-element approach, 78% of
the scatter in the Pb^{2+} data appears to be of the non-
determinate type (24) and 100% of the scatter of Co^{2+} ap-
pears to be of the determinate instrument type. An element-

by-element breakdown of the anlysis of error is shown on
Table XII.

TABLE XII: Element-By-Element Analysis of Error
             In Recovery Efficiency

Element	A-Tot. Scatter from Duplicates $\overline{RSD}_A$	s	B-A.A.S. Scatter $\overline{RSD}_B$	s	Non-Determinate Scatter $\overline{RSD}_A - \overline{RSD}_B$
Mn^{2+}	2.20%	2.20	1.09%	0.34	1.11%
Co^{2+}	2.01	2.39	2.19	1.10	-0.18
Ni^{2+}	3.49	3.06	2.89	1.88	0.60
Cu^{2+}	1.98	1.55	0.94	0.26	1.04
Zn^{2+}	2.25	2.46	1.57	0.96	0.68
Cd^{2+}	2.20	2.65	1.33	0.52	0.87
Pb^{2+}	5.36	16.7	1.20	0.39	4.16
UO_2^{2+}	3.47	3.53	--	--	--
Average	2.87%	(s=1.18)	1.60%	(s=0.70)	1.18% (s=1.38)

CHEMICALS AND EQUIPMENT USED

All chemicals used were of reagent grade quality. Deionized water was prepared by passing water through Coolbaugh Hall's central deionizing system and then through a series of three Barnstead Hose Nipple Cartridges. The first cartridge was an Organic Removal #D8904, the second a High Capacity (standard) #D8901, and the last was an Ultrapure (mixed-bed) #D8902. This water was then stored in a 50 liter polypropylene bottle until used. All glassware was cleaned according to E.P.A. specifications (26). Equipment used included the apparatus and IL-951 A.A. Spectrometer previously described, a Sargent-Welsh Model IP pH meter, and general laboratory glassware.

SUMMARY AND CONCLUSIONS

Previous workers (2) have shown that sulfuric acid treated peat (S.A.T.P.) has the ability to remove (singly) Na^+, Ba^{2+}, Cu^{2+}, and Pb^{2+} from aqueous solutions and that the presence of counter ions and increases in flow rate tend to decrease the recovery efficiency of the metal ions.

The purpose of this study was to quantitatively evaluate the feasibility of using S.A.T.P. as a cation exchanger (in the column mode) to simultaneously remove Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and UO_2^{2+} from aqueous solution over a wide range of chemical and physical parameters.

The results of these experiments proved that the S.A.T.P. was very effective in simultaneously removing all of the investigated metal ions from aqueous solution over a wide range of pH, flow rate, metal ion concentration, and ionic strength at a small excess (6.25 meq. exchanger per meq. total heavy metal) of exchanger. A number of trends associated with the parameters varied were observed:

(i) Recovery efficiency at low pH ranges for all metal ions decreased with a decrease in the solution pH (4.0 to 2.0).

(ii) Recovery efficiency at high pH ranges for some

metal ions (most noticeably Cu^{2+}, Pb^{2+} and UO_2^{2+}) decreased slightly with increas-ing solution pH (7.0 to 8.0).

(iii) Recovery efficiency decreased for all metal ions with an increase in flow rate (least noticeably for Cu^{2+}, Pb^{2+} and UO_2^{2+}).

(iv) Recovery efficiency decreased for all metal ions with increasing concentration.

(v) Recovery efficiency decreased for all metal ions with increasing ionic strength of solution (least noticeably for Cu^{2+}, Pb^{2+} and UO_2^{2+}).

These general trends can be explained by a few chemical principles. The decrease in the activities of all ions associated with increasing ionic strengths (higher concentrations, low pH, high concentration of counter ions) would effectively minimize their participation in exchange reactions thereby lowering the recovery efficiency. Complexation of all metal ions with OH^- would increase with pH increases in solution and would also cause a decrease in recovery efficiency. Increasing the flow rate shortens the contact time of the solution with the exchanger which in turn reduces the chance of an exchange reaction occurring. In other words the exchange reaction:

$$R\text{-}H^+ + M_i{}^{2+} \longrightarrow R\text{-}M_i{}^{2+} + H^+$$

is time dependant and at higher flow rates, does not go to completion (or reach quilibrium).

The relative recovery efficiencies between individual metal ions depend on a number of chemical properties of the metal ions themselves and of the S.A.T.P. For example, each metal ion has its own specific aqueous equilibria (speciation/complexation with OH^-, etc.) which would affect its participation in exchange reactions. The heterogeneity of available exchange sites in the S.A.T.P. also has an effect on the relative affinities of each metal ion for the S.A.T.P. Thus an in-depth theoretical treatment of these trends would seem to be an insurmountable task, well out of the scope of this work. In fact, the primary objective of this work was to establish the suitability of the S.A.T.P. for potential industrial applications, not a refined study of the actual mechanisms per se. Nevertheless, the relative trend of higher recovery efficiencies for Pb^{2+} and $UO_2{}^{2+}$ can be generally explained by their relatively smaller hydrated radii when compared to the other ions studied. When ionic charges are equal, the element which has the smaller hydrated radius tends to have a higher affinity (or selectivity) for the ex-

changer (26). It should be noted, however, that the experiments in this study are of a dynamic nature and do not represent equilibrium situations. That is due to the fact that the experiments were carried out in a continuous manner in a column mode rather than in an equilibrium batch operation.

As previously mentioned, the general trends in recovery efficiency with respect to the parameters varied, were found using a small (6.25) excess of exchanger. The "scaled-up" experiment was conducted at an exchanger excess of 20.8 in terms of equivalents and in this case 100% recovery efficiency was found for all metal ions investigated. One would expect to use an even greater excess of exchanger to metal in industrial applications and therefore expect much greater recovery efficiencies than reported here using a small excess of exchanger.

In conclusion, sulfuric acid treated peat is very effective in simultaneously removing many metal ions from solution over a broad range of solution parameters and flow rates, and may be a potential viable alternative or adjunct to conventional water treatment processes. In-depth experimental studies of pilot plant scale related to specific needs in water treatment would vastly enhance the attractiveness of this technique to industry.

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