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FATE OF METAL IONS DURING DOMESTIC TREATMENT OF WATER CONTAINING ORGANICS

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ABSTRACT

Preliminary to water treatment experiments we tested several filter media to determine Cd^{2+} loses during filtration at pH 8. The initial concentrations of Cd^{2+} were 4.5 and 45 ppb. Various filtering materials sorb different amounts of Cd^{2+} from solution as a function of their surface area and the speed of filtration. Polycarbonate filter membranes in combination with a polycarbonate support apparatus gave the lowest Cd^{2+} losses when the filtrate is collected directly in a volumetric flask.

The effectiveness of Cu^{2+}, Cd^{2+}, and Zn^{2+} removal from solution by alum coagulation was measured with fulvic acid present and absent. A factorial experimental design and analysis of variance were used to determine the effect on metal ion removal of the individual variables pH, metal ion concentration, alum concentration, and fulvic acid concentration and their combinations. The variable levels model water treatment plant conditions. Maximum metal ion losses of 96% for Cu^{2+}, 59% for Cd^{2+}, and 82% for Zn^{2+} were measured in the presence of fulvic acid. In its absence the maximum metal ion losses observed were 93% for Cu^{2+}, 14% for Cd^{2+} and 53% for Zn^{2+}. Fulvic acid enhances metal ion removal under most experimental conditions. The practical implications of the results is that strong complexes between natural water organic matter and metal ions enhance their removal by the alum coagulation process.

INTRODUCTION

There are many problems associated with the presence of trace metal ions in drinking water (Craun and McCabe, 1975). Those such as Cd^{2+}, Pb^{2+}, and Hg^{2+} are serious health hazards, while Zn^{2+} and Cu^{2+} are associated with taste and staining problems. Due to pollution and/or natural causes, many water sources exceed metal level standards set by the United States Environmental Protection Agency. More serious than their presence in drinking water sources, metal concentrations exceeding health standards are sometimes found in treated water (McCabe, 1974).

Coagulants are used in typical water treatment processes, but procedures specifically designed to remove trace metals are not common. Coagulants are generally aimed at the removal of suspended matter, dissolved organic matter, and inorganic species contributing to water hardness. Coagulants are, however, also responsible for some removal of trace metals from waste water (Linstedt, et al., 1971; Nilsson, 1971; Oliver and Cosgrove, 1974; Maruyama et al., 1975; Leentvaar et al., 1978) and drinking water supplies (Logsdon and Symons, 1973; O'Connor, 1974; Naylor and Dague, 1975).

In this study we determined the extent of Cd^{2+}, Cu^{2+}, and Zn^{2+} losses as a function of metal ion concentration, coagulant (alum) concentration, pH, and natural organic matter (soil fulvic acid) concentration. Our study differs from previous work in several respects. First, alum concentrations and pH were chosen to resemble treatment plant parameters, and organic matter concentrations were set at typical levels for lake and river waters (Reuter and Perdue, 1977). Thus, our results will offer guidelines to actual drinking water treatment processes. Second, we specifically considered the effect of organic

matter on metal ion removal by alum coagulation. Finally, we based our study upon a statistical experimental design, and deduced metal ion removal mechanisms with the aid of analysis of variance (ANOVA).

Before doing water treatment experiments we learned how to avoid trace metal ion losses while using Cd^{2+} as an example. Quantitative analysis of Cd^{2+} at the ppb level may be done by various techniques but the analysis is often complicated by difficulties in maintaining the integrity of the sample during preanalysis manipulations. Typically, losses of metal ions from solution due to sorption of the ions onto the different materials encountered during storage, dilution, filtration, etc. are minimized by lowering the pH of the sample (Zief and Mitchell, 1976; King et al., 1974). In some cases the sample must be non-acidic during filtration (Hiraide et al., 1976), especially in environmental systems (Lund and Onshus, 1976; Florence, 1972; Benes̆ et al., 1976; Kunkel and Manahan, 1973). In this filtration study which is preliminary to water treatment experiments, we learned that losses of Cd^{2+} during filtration vary depending on the filter materials used and the rapidity of the filtration.

EXPERIMENTAL

Filtration Experiment

The filter media tested were (1) Whatman #2 paper (42.5 mm) with a polyethylene Büchner funnel and a glass filter flask; (2) fritted glass filters of fine (4-5.5 μm), medium (10-15 μm), or coarse (70-100 μm) porosity with a glass filter flask; (3) cellulose acetate membranes (0.45 μm porosity, Millipore Corp.) on a thick coarse fritted glass support (Millipore Corp.) or a polycarbonate support; and (4) polycarbonate membranes (0.4 μm, Nuclepore Corp.) on the polycarbonate filter apparatus (47 mm, Nuclepore Corp., Swin-Lok Holder).

The glass filter flasks were soaked for two hr (minimum in 2 M HNO_3, and then rinsed with distilled, deionized water. The glass filters were

cleaned by the filtering of about 100 mL of 1 M HNO_3, followed by washing with distilled, deionized water until the pH of the filtrate was the same as that of unfiltered water. The polycarbonate apparatus was cleaned by passing 200 mL of 1 M HNO_3 through it followed by at least 300 mL of distilled, deionized water. Preliminary experiments determined that no cadmium (<1 ppb) could be leached from any of the other filter materials by filtering 100 mL of 0.01 M HNO_3, so no pretreatment of the paper or polymeric membranes was necessary.

A new 10 ppm standard Cd^{2+} solution was prepared from Fisher 1000 ppm Atomic Absorption standard cadmium solution for each experiment. The 100 ppm Cd^{2+} standards were prepared at least every two days. For the cellulose acetate membrane on a glass support, glass filter, and paper filter experiments the procedure involved adding an aliquot of 100 ppm Cd^{2+} standard solution to each of two sample bottles of distilled, deionized water. After raising the pH of both solutions to 8 with NaOH, both were diluted to 50 mL. Then one solution was filtered while the other as a control was poured directly into a filter flask. All filtrations were followed by approximately 40 mL rinses of distilled, deionized water of the same pH as the analytical solution. Both filtered and unfiltered solutions were then transferred to 100 mL polyethylene volumetric flasks and acidified to pH 3 with HNO_3 before diluting to the mark. The Cd^{2+} levels of both solutions were determined by differential pulse anodic stripping voltammetry (DPASV) during the day of preparation.

In the tests of the polymeric membranes, with the exception of the cellulose acetate membrane-glass support combination already described, a different procedure was used. Several experiments demonstrated that the unfiltered sample gave small but consistent Cd^{2+} losses, so control experiments were not necessary. A filtration apparatus which allowed collection of the filtrate directly in a volumetric flask was constructed, thereby eliminating the need for a filter flask. A Nuclepore 47 mm polycarbonate filter support

with a 100 mL funnel and Nuclepore 0.4 μm polycarbonate filter membrane was used in the apparatus. The entire apparatus consists of a 25 cm tall wide mouth jar capped with a two-hole #14 rubber stopper. Through one of the stopper holes is a 10 cm polyethylene tube that is connected to the filter support assembly with Tygon tubing at one end, and which empties into a collection flask with another piece of Tygon tubing at the other end. The other hole of the rubber stopper contains an L-shaped glass tube, through which the jar is evacuated by aspiration.

In the experiments, an aliquot of standard Cd^{2+} solution is added to 30 mL of distilled, deionized water; the pH is raised to 8.0 with NaOH; and then the sample is diluted to 40 mL. The sample is filtered and followed through the filter with ∿40 mL of pH 8.0 distilled, deionized water. All the filtrate is collected in a 100 mL volumetric flask, acidified to pH 3.0 with HNO_3, and then diluted to 100 mL.

Cd^{2+} analyses using DPASV were made with a Princeton Applied Research Corp. Model 174 Polarographic Analyzer and Model 315 Electroanalysis Controller with a hanging mercury drop working electrode. In the analyses the plating was done for 1 or 2 min at -0.870 v and the stripping from -0.870 to - 0.350 v at 5 mv/sec using a 50 mv pulse. Each of at least two samples was analyzed at pH 3.0 in a 0.1 M KNO_3 medium, and all analyses involved at least triple replication for each cell solution. Regular baseline measurements of electrolyte were taken from -0.900 v to -0.300 v.

Materials and Equipment for the Water Treatment Experiment

Standard metal ion solutions were prepared by diluting new Fisher AAS 1000 ppm standard solutions. The solid soil fulvic acid (SFA) was isolated as previously detailed (Weber and Wilson, 1975). Deionized, distilled water

was used throughout. All solutions were prepared in polypropylene volumetric flasks (Nalgene Corp.). An Orion 701 digital pH meter with a 5 mm o.d. Vanlab combination electrode (#34106-79) was used to measure pH. Metal ion determinations were made by flame AAS using a Techtron AA5 spectrometer and a Heath model EU-205-11 strip chart recorder. SFA was detected at 260 nm with a Cary 14 spectrophotometer using 2 cm quartz cells.

Procedures for Water Treatment Experiment

To prepare solutions using the experimental parameters given in Table 1, the appropriate amounts of SFA, metal ion, and alum were added to approximately 47 mL of water in a 50 mL volumetric flask. The pH was adjusted with *ca*. 0.01 *M* KOH, then the solution was diluted to 50 mL. The solution was stirred and shaken for 5 min, and then was allowed to stand quiescent for 30 min. At the end of this coagulation period the solution was filtered using the apparatus already described. About 25 mL CO_2-free (pH 7) water was used to rinse the volumetric flask and filter aparatus. The filtrate and rinsings were collected in a 100 mL volumetric flask and diluted to the mark with 1.0 mL reagent HNO_3, 1.0 mL 1.00 *M* KNO_3, and water. Metal ion concentrations were determined by AAS, and UV absorption at 260 nm was used to determine SFA concentrations by comparison to a calibration curve.

Between filtrations the filter apparatus was cleaned by discarding the used membrane, rinsing with 250 mL *ca*. 0.1 *M* KOH, with 250 mL *ca*. 0.1 *M* HNO_3, and finally with 50 mL water. Blank studies demonstrated that no Cu^{2+}, Cd^{2+}, Zn^{2+}, or SFA remained after this treatment.

All volumetric flasks were cleaned prior to each experiment by rinsing with water, soaking in 0.1 *M* KOH, rinsing with water, soaking in 2 *M* HNO_3, and finally rinsing with water.

Data were collected from blank experiments (no alum present) to determine background losses of metal and SFA, and from a 2^4 factorial experiment in which we used the design in Table 1. Percent metal ion losses from the factorial experiment were analyzed by ANOVA.

The number of equivalents of carboxyl groups per gram SFA was determined by potentiometric titration. SFA (0.02380 g) was dissolved in 25 mL 0.1 M $NaClO_4$ and two 10 ml aliquots were withdrawn. Each was diluted to 15 mL with 0.1 M $NaClO_4$ and titrated with standardized 0.1 M NaOH after the solution was purged with N_2. A sample of water-derived fulvic acid (WFA) was studied similarly. The SFA and WAF have carboxyl group concentrations of 6.7 and 5.9 meq/g, respectively. Subtraction of these values from total acidity values gives phenol values for SFA (6.7 meq/g) and WFA (4.7 meq/g) (Weber and Wilson, 1975).

RESULTS AND DISCUSSION: FILTRATION EXPERIMENT

Observations

Preliminary experiments for the different filter media and supports demonstrate that Cd^{2+} contamination from the materials is insignificant. The filter supports and filter flasks do have a noticeable influence on Cd^{2+} losses in the paper filter, glass filter, and cellulose acetate membrane-glass support experiments so control experiments were used to calculate the percentage loss of metal ion from solution due to filtration. A 5% loss of Cd^{2+} due to the polycarbonate filter support alone, with no membrane, was observed when 124 ppb of Cd^{2+} were passed through the support at pH 8.0.

Since the testing of these various filtering methods was done as a preliminary study to the water treatment investigation, the paper and

glass filter data are averages of fewer experiments than the membrane data. Data for the polycarbonate membrane tests, given in Table 2, show reproducible measurements from replicate experiments. For the other materials tested, the percent Cd^{2+} losses reported are $\pm$ 6% at the 100 ppb level and $\pm$ 10% at the 5-10 ppb level.

Table 3 comprises the combined Cd^{2+} losses for the various materials tested and their filter support assemblies. The Whatman #2 paper was analyzed using 10 ppb to 124 ppb Cd^{2+} (at filtration). Approximately 75% of the Cd^{2+} was lost from solution at low metal concentrations and 29% lost from the 45 ppb initial level.

As reported by King et al. (1974), glass has an affinity for Cd^{2+} in solution. In agreement with these results, the borosilicate glass filters caused relatively high losses of Cd^{2+} in our experiments with the notable exception of the coarse porosity filter. Its performance is attributed to the low surface area of glass coming in contact with solution during filtration and the short time required for the solution to pass through the fritted filter. The coarse porosity filter required 1 or 2 sec to filter 50 mL of solution, while the medium and fine filters needed 10-15 sec. These large losses of cadmium to glass filters precludes their use in trace metal analysis at pH 8.

Another example of the influence of glass in the filter system is the relative losses of Cd^{2+} found using a cellulose acetate membrane on a thick coarse porosity glass support and on a polycarbonate support. The loss of Cd^{2+} from the glass-supported filter was double that of the plastic-supported filter. Cellulose acetate membranes produced Cd^{2+} losses comparable to the filter paper tested.

Of the polymeric materials, the lowest losses occurred when using a polycarbonate membrane and filter apparatus. Data from Table 3 show that

about 9-20% of the Cd^{2+} is lost during filtration when a 124 ppb solution is filtered and 33-60% when a 12 ppb solution is filtered. The filter assembly alone without a membrane caused a loss of 5% of the cadmium in the 124 ppb Cd^{2+} experiment.

Conclusions

At pH 8 various filtering materials sorb different amounts of Cd^{2+} from solution as a function of the number of sorption sites and the speed of filtration. Polycarbonate filter membranes in conjunction with a polycarbonate support apparatus give the lowest losses of Cd^{2+} when the filtrate is directly collected in a volumetric flask. Although we studied only Cd^{2+} solutions, similar results should occur for other trace metal solutions in the absence of extensive hydrolysis. Thus, we found a filtration technique that considerably decreased metal ion loss, and we used this approach in the water treatment experiments discussed below.

FACTORIAL EXPERIMENTAL DESIGN AND ANOVA

Factorial design of experiments enables us to simultaneously investigate the effects of all independent variables on metal ion losses. When there are n variables to be considered, 2^n experiments are necessary to measure the effect of all combinations of variables when each variable is tested at a high and low level. Center point experiments, where variable levels are the average of high and low levels, may be added to the design to detect any nonlinearity in the experimental response between the extreme levels. The results of all the experiments are statistically analyzed by analysis of variance (ANOVA).

The first requirement in establishing a factorial experimental design is to decide what variables are to be tested. In this study, in which we are interested in metal ion removal during a water treatment process with humic materials present, the effects of varying metal ion concentration, pH, alum concentration, and soil fulvic acid concentration are determined. Next a high and low level are assigned to each variable. These variable settings should be chosen to adequately cover a range normally encountered for the variables. In our study the variable levels cover a range of values normally seen by water treatment plants, except for metal ion concentrations which were chosen to be within the detection limit of flame atomic absorption spectroscopy (AAS). Once variable levels are established, the high level, center point, and low level are designated at +, 0, and -, respectively. A $2^3 + 2$ (2^3 experiments involving the high and low variable levels plus 2 center point experiments) experimental design is shown in Table 4. This table shows the variables chosen and the experiments needed to run $2^3 + 2$ experiments in duplicate (20 experiments), and in random order. Duplication provides the experimental random error term needed for analysis of variance. Randomization of the experimental order is needed to avoid systematic errors such as aging of stock solutions. A cube can be used to graphically display this experimental design. The vertices of the cube represent the 2^3 experiments when each axis is one of the 3 variables.

When the experiments have been completed, the effect of each variable and variable interaction on the metal losses can be calculated with ANOVA. The result of these calculations, a measure of the extent of influence each variable had in the measured metal ion losses compared to random error, is termed the F statistic (or variance ratio). More complete descriptions of factorial design and ANOVA are available (Natrella, 1963: Youden, 1951), and should be consulted for necessary details.

RESULTS AND DISCUSSION: WATER TREATMENT EXPERIMENT

Background Losses

In our study of Cu^{2+}, Cd^{2+}, and Zn^{2+} removal by treatment with alum, we first considered the extent to which these metals are removed from solution by processes other than alum coagulation. Since all three of the metal ions in this study may be lost by adsorption on vessel walls (Tölg, 1972; Struempler, 1973; Beneš and Kopička, 1974; King *et al.*, 1974; Batley and Gardner, 1977), we determined losses during filtration with the polycarbonate and polypropylene filter apparatus. A second background effect on dissolved metal ion concentrations is the formation of insoluble metal hydroxides or metal ion-fulvic acid complexes. Finally, metal ion contaminations are possible. Because of the common occurrence of Zn^{2+} in laboratory materials and reagents, this metal ion is most susceptable to contamination problems (Robertson, 1968). In the determination of background metal ion losses all effects just mentioned are combined.

Background Cu^{2+}, Cd^{2+}, and Zn^{2+} losses from a series of water treatment experiments performed without alum are given in Table 5. Losses are small with one exception. The experiment involving 1 ppm Cu^{2+} and 0 ppm SFA, and at pH 7 resulted in a loss of 24%. This Cu^{2+} loss, which is due to the formation of $Cu(OH)_2$, is predictable from the solubility product constant of this species. There are no other observed differences in losses of Cu^{2+} and Cd^{2+} in the absence and presence of SFA, but Zn^{2+} losses increase slightly when SFA is present. The latter phenomenon is not due to SFA interference in the measurement of Zn^{2+} by AAS. An experiment in which 1000 ppb, 750 ppb, and 500 ppb Zn^{2+} solutions without SFA and with 20 ppm SFA were compared revealed no differences in Zn^{2+} detection.

The background experimental results cannot be applied to the four-variable experimental results (alum present) as a correction factor. The benefit of making such a background correction to the measured metal ion losses is that metal ions lost by mechanisms not involving alum, such as adsorption to vessel walls, could be distinguished from metal losses that result from alum treatment. In this case the use of such a correction factor would be improper because the strong interaction of SFA with alum is not accounted for by the background experiments. This interaction will be discussed with the other ANOVA results. The behavior of the three metal ions are quite different in the presence of alum (see below).

General ANOVA Results

We calculated percent metal ion losses (Table 6) from the AAS metal ion concentration determinations. The greatest losses of metal ion generally occurred in solutions with the high level of alum (50 ppm) and high pH (7). The metal ion removal ranged from 6 to 96% for Cu^{2+}, from -6 to 59% for Cd^{2+} (negative loss is a contamination), and from -7 to 82% for Zn^{2+}. Cu^{2+} is far more effectively removed from solution than the other two ions under the same conditions.

Table 7 has the ANOVA results for two factorial experiments with Cd^{2+}, Cu^{2+}, and Zn^{2+}. The first set includes SFA and the second set excludes it. The ANOVA results are expressed as the F statistic for each variable effect and interaction. The underlined values identify those F values for which there is at least 99% confidence that the measured effect of the variable or variable interaction is not due to random error. A variable's significance is interpreted to mean that there is a relatively large difference in metal ion losses between a variable's low level and high level. In other words, a variable is important if metal ion losses show a strong dependence on the variable level.

ANOVA reveals that for most experiments, in the presence and absence of SFA the most significant experimental variables are pH (C) and alum concentration (B). F statistics of variables B and C are the largest for five of the six experiments shown in Table 7. The variable combinations most significantly affecting metal ion losses are interactions between pH and alum concentration (BC), pH and SFA concentration (CD), and SFA and alum concentrations (BD). F statistics for metal ion concentrations (A) are very small in all experiments: 3 and 2 for the Cu^{2+} experiments, 1 and 7 for Cd^{2+}, and 3 and 0.2 for Zn^{2+}. These low values demonstrate that variation of metal ion concentrations from 1000 to 500 ppb has little effect on the percent metal ion removal. All interactions with this variable are also insignificant.

There are exceptions to these generalized results. Alum concentration (B) is unimportant in the Cd^{2+} experiment with no SFA present. In the SFA experiments, BDC interactions are significant for Zn^{2+} and Cd^{2+}, but not for Cu^{2+}. Finally, the BC interaction is only significant for Zn^{2+} in the experiments without SFA.

There are three reasons for these exceptions. First, the different behavior of the three metal ions towards hydrolysis and SFA complexation accounts for some of the variation. The BC interaction for Zn^{2+}, as an example, appears much more important than for the other two metal ions. Second, the different AAS metal ion sensitivities introduce a varying experimental error for the metal ions. In particular, the poorer signal to noise ratio in the Zn^{2+} measurements results in a greater experimental error for Zn^{2+} than for Cu^{2+} or Cd^{2+}. Finally, the sensitivity of ANOVA is different for each of the three metal ions. Because there is an adequate spread between the high and low variable levels chosen, there is a sufficient range of Zn^{2+} and Cu^{2+} losses in the experiments to produce a robust analysis of variance. The Cd^{2+} losses, however, are relatively small and the effects of the variables at their high

and low levels are not as clearly distinguishable. As a result, nearly all the variables and interactions in the Cd^{2+} ANOVA appear significant at the 95% confidence level. However, the 99% confidence level (underlined values) is used to evaluate the significance of all effects of the six metal ion ANOVA summaries in Table 7, and all following discussion refers to that confidence level.

Effects of pH on Metal Ion Removal

The importance of pH (C) in the experimental processes is predictable since Al^{3+} hydrolysis is very pH dependent. In aluminum sulfate solutions more concentrated than 21 ppm the insoluble $Al(OH)_3$ species predominates from pH 5 to 7 (Hayden and Rubin, 1974). The alum concentration - pH interaction (BC) in the ANOVA reflects the increased aluminum ion hydrolysis when alum concentration and pH are increased. Since background experiments show that metal ion removal involves the coagulation of hydrolyzed aluminum ion, the significance of pH, alum concentration, and their combination is expected.

In contrast, the pH range (C) has little interaction with the metal ion concentration range (A) as seen by the 99% confidence level insignificance of the AC interaction. The formation of insoluble $M(OH)_2$ with Cd^{2+}, Zn^{2+}, and Cu^{2+} with one expection, is not theoretically expected at the experimental concentrations (1 to 0.5 ppm). The exceptional case of $Cu(OH)_2$ formation (pH 7, 1 ppm Cu^{2+}, and SFA absent) is observed in background experiments. At 1 ppm metal ion concentration with no SFA present in the pH 5 to 7 range, the predominant metal ion species are Cd^{2+} (100 to 81%) and $Cd(OH)^+$ (0 to 19%); Zn^{2+} (100%); and Cu^{2+} (100 to 60%), $Cu(OH)^+$ (0 to 30%), and $Cu_2(OH)_2^{2+}$ (0 to 10%) (Beneš and Kopička, 1974; Patterson, et al., 1977; Sylva, 1976).

Several groups have shown that metal ion SFA stability constants are strongly pH dependent (Bresnahan, et al., 1978; Saar and Weber, 1979; Cheam and Gamble, 1974). Approximately a four-fold increase in stability constants and a three-fold increase in the number of binding sites accompanies a pH change from 4 to 6 in the Cu^{2+}-SFA system (Bresnahan, et al., 1978). This pH influence is important because the SFA complexation reaction dominates the speciation of Cu^{2+}, and has an important role in Cd^{2+} and Zn^{2+} speciation. Measurements of SFA bound to Cu^{2+} versus free Cu^{2+} (Cu^{2+} and SFA are both 2×10^{-4} M, pH is 6, and ionic strength is 0.1 M) reveal 96% of Cu^{2+} is SFA bound (Bresnahan, 1977). Under the same conditions 53% of available Cd^{2+} is bound to SFA (Saar and Weber, 1979). The lesser role of SFA in Cd^{2+} speciation reflects the approximately 10^2 smaller conditional stability constant for Cd^{2+}-SFA. Zn^{2+}-fulvic acid complexes are also weaker than the Cu^{2+} analogs (Mantoura et al., 1978).

Effects of Alum Concentration on Metal Ion Removal

The significance of alum concentration (B) in the ANOVA results is related to metal ion removal indirectly through SFA removal. Alum coagulation is an established, efficient procedure for removing organic matter (color) such as humic materials from solution (Hall and Packham, 1965; Gauntlett and Packham, 1973; Leentvaar et al., 1977; Narkis and Rebhun, 1975, 1977). SFA losses in our water treatment experiment show that when we used 30 ppm or more alum, 91-98% of the SFA was removed by the alum coagulation process (Table 8). The ANOVA results also suggest that metal ion removal by alum coagulation proceeds by an alum-SFA interaction. Both alum concentration (B) and the alum concentration-SFA concentration (BD) combination are significant at the 99% confidence level for all three metal ions. The significance of the BD interaction indicates that metal ion removal can be linked to SFA losses.

Effects of Alum-SFA Interactions on Metal Ion Removal

The alum-SFA interaction causes a reversal in the metal ion loss trends when alum concentrations are 10 ppm or lower. When alum is present, the trend of metal ion loss with SFA present is opposite to the trend with SFA absent (Table 6). When alum is used in all experiments, a comparison of cases with and without SFA reveals two opposing trends. In pairs or experiments with 50 ppm alum (numbers 1 and 2, 3 and 4, 9 and 10, and 11 and 12) metal ion losses increased when SFA was present. In contrast, for the pairs of experiments with only 10 ppm alum (numbers 5 and 6, 7 and 8, 13 and 14, and 15 and 16) metal ion losses usually decreased when SFA was present. Apparently, when the alum present is insufficient to totally adsorb SFA, the soluble SFA portion desorbs metal ions from the alum floc. In contrast when the alum totally adsorbs SFA, it scavanges metal ions from solution. Thus, the largest metal ion losses occur for high alum and high SFA concentrations at the high pH level (Table 6, numbers 1 and 9).

Narkis and Rebhun (1977) show that at low humic substance concentrations (up to 10 ppm) the optimum alum dosage for humic substance removal occurs when the milliequivalents of alum and humic substance anionic charge are equal. The major charged aluminum species is $Al_8(OH)_{20}^{4+}$. The charge on typical humic materials including our SFA is caused by dissociation of carboxylic and phenolic functional groups. We can assume that carboxylic (pK_a 3 to 5), but not phenolic (pK_a ca. 10) groups contribute to the anionic character of SFA in the pH 5 to 7 range. A calculation based on a 6.7 meq/g concentration of carboxylic groups in our SFA sample shows that 89 ppm of alum (F.W. 666) should be required to completely remove 20 ppm SFA. Since the experimental alum dosages were 10 to 50 ppm, 40 to 90% of the total SFA is expected in the filtered solutions. Soluble SFA was not seen when 30 ppm and 50 ppm alum dosages were used. Instead, a sharp change in

SFA removal occurred between the 10 ppm and 30 ppm dosages (Table 8). It is apparent that our SFA in the 10 to 50 ppm range is more readily removed from solution than expected from the Narkis-Rebhun model.

Summary of ANOVA Results

In summary, three important observations can be made from the metal ion and SFA loss results. First, pH and alum concentration are the most influential variables for metal ion removal in the range of pH and alum concentration used in typical water treatment processes. Second, the influence of these two variables is greater when SFA is present in the 10 to 20 ppm range. This observation is interesting because humic materials in this concentration range are often present in untreated water (Reuter and Perdue, 1977). Third, SFA itself causes insignificant metal ion removal except when interacting with the alum coagulation process.

Modes of Metal Ion Removal

Some deductions concerning the chief mechanism of metal removal and the most important metal species involved in the mechanism can be made by combining the ANOVA results and the background experiment results. The possible metal removal modes are: (1) precipitation of a metal ion species independent of alum flocculation, (2) coprecipitation of an insoluble metal ion species with the alum floc, and (3) adsorption of a soluble metal ion species to the alum floc. Possible soluble metal ion-containing species are metal ion-SFA complexes (M^{2+}-SFA), soluble metal ion-hydroxo complexes ($M(OH)^{+}$), and hydrated metal ions (M^{2+}).

First, we will comment on the species present during the experiments. In the absence of organic matter the predominant metal ion species, as already mentioned, are M^{2+} and $M(OH)^{+}$. In the presence of SFA under typical experi-

mental conditions, soluble Cu^{2+}-SFA predominates (96% of Cu^{2+}), but only 53% of Cd^{2+} is in the Cd^{2+}-SFA form (Saar and Weber, 1979). Thus in most cases mechanisms of metal ion removal involve removal of M^{2+}, $M(OH)^{+}$, and M^{2+}-SFA from solution. Minor exceptions appear to be the formation of a small amount of insoluble Zn^{2+}-SFA, and of insoluble $Cu(OH)_2$ as previously discussed.

The mode of metal ion removal may be deduced from the ANOVA interaction results and from the alum-free background experiments. Except for the two exceptions just mentioned we observe no precipitation of metal ion species independent of alum flocculation, and therefore discount this mode of metal ion removal. The absence of insoluble metal ion species also eliminates coprecipitation with the alum floc as a probable mechanism. The most likely mode is the adsorption of M^{2+}, $M(OH)^{+}$, and/or M^{2+}-SFA on the alum floc, which we remove by filtration. Other small metal ion losses observed during background experiments (Table 5) are due to manipulation of the solutions.

The principal mode of metal removal is a process involving M^{2+}-SFA and the coagulation of alum. The coagulating alum is effective in adsorbing dissolved SFA ions (Table 8), which in turn act as metal scavenging agents due to the formation of stable M^{2+}-SFA. Metal ion species such as M^{2+} and $M(OH)^{+}$ are less effectively removed from solution in the absence of SFA in most cases (Table 6). In addition, the effectiveness of the whole process is dependent on the extent of M^{2+}-SFA binding, which is a function of M^{2+}-SFA stability constants and pH. Thus, Cu^{2+} is removed more effectively than Cd^{2+} and Zn^{2+} because Cu^{2+} has a much higher M^{2+}-SFA stability constant. Since the fraction of M^{2+} bound as M^{2+}-SFA increases at higher pH, high pH levels also increase the extent of metal ion removal.

Conclusions

Factorial experimental design in which all variables are simultaneously changed and ANOVA of the results proved to be a powerful statistical tool for

the evaluation of important variables in metal ion removal during a water treatment process. The major advantages of this statistical design and ANOVA are the amount of information obtainable for a limited number of experiments, and the unique ability to reveal important variable interactions. In no other way could all variable interactions be seen. Experiments where one variable is varied at a time ignore variable interactions, and are therefore strictly invalid.

The experiments show that alum coagulation alone is effective to varying extents in the removal of trace heavy metal ions, but metal ion removal is greatly improved in the presence of fulvic acid. The mechanism of metal ion removal by alum coagulation and filtration appears to be the interactions between organic matter and metal ions. The removal efficiency of different metal ions is dependent on the metal ion-fulvic acid complex stability, which is much greater for Cu^{2+} than for Cd^{2+} and Zn^{2+}.

Our results have practical implications for water treatment plant operation. In the absence of natural organic matter metal ion removal is independent of the metal ion concentration (0.5 to 1 ppm level), but can be maximized by high alum concentration (30 to 50 ppm) and high pH (7). The presence of fulvic acid (10 to 20 ppm) at levels typical for humic materials in untreated water increases the extent of metal ion removal. Since our soil-derived and water-derived fulvic acid samples are so similar, SFA is a good model for natural water organic matter (Weber and Wilson, 1975; Wilson and Weber, 1977a; Wilson and Weber, 1977b; Bresnahan _et al_., 1978; Saar and Weber, 1979). Weakly complexed metal ions like the very toxic Cd^{2+} are not completely removed under any conditions in these experiments, but strongly complexed Pb^{2+} and Hg^{2+} should be effectively removed. Two mechanisms not incorporated in our experiments could modify their interpretation during coagulation processes under operating plant conditions. Adsorption of metal ions on particulate matter could improve metal ion removal, and excess humic materials might redissolve adsorbed metal species.

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Table 1. Water treatment experiment factor levels

Factor	Levels		
	High	Middle	Low
A = [Metal ion] ppb	1000	750	500
B = [Alum] ppm	50	30	10
C = pH	7	6	5
D = [SFA] ppm	20	10	0

Table 2. Polycarbonate membrane and apparatus test data

	Measured $[Cd^{2+}]$, (ppb)	
	45 ppb Level	4.5 ppb Level
Sample 1	36 40	2.2 2.6 2.9 1.8
Sample 2	36 40	2.4 2.2 3.0
Sample 3	41 37	
Average $[Cd^{2+}]$ ppb	38 (s=2.3)	2.5 (s=0.42)
Average Cd Loss	16%	44%

Table 3. Cadmium(II) losses due to filtration

Filter	Filtered Cadmium Conc. (ppb)	Percent Cadmium Lost
Whatman #2 Paper	20	73
	40	75
	124	29
Glass:		
Coarse Porosity	99	2
Medium Porosity	99	60
Fine Porosity	99	60
Cellulose Acetate:		
Glass supported	99	71
Polycarbonate supported	124	35
Polycarbonate	124	16
	12.4	44

Table 4. A $2^3 + 2$ factorial design

Factor	Level +	Level 0	Level -
A = $[Cu^{2+}]$, ppb	1000	750	500
B = [Alum], ppm	50	30	10
C = pH	7	6	5

Variables A	B	C	Order Repl. 1.	Repl. 2.
+	+	+	9	20
-	+	+	1	14
+	-	+	17	10
-	-	+	5	6
+	+	-	19	3
-	+	-	12	7
+	-	-	16	15
-	-	-	2	4
0	0	0	11	8
0	0	0	13	18

Table 5. Background metal ion losses in the absence of alum

Metal ion	Average % Loss			
	0 ppm SFA	10 ppm SFA	20 ppm SFA	S[a]
Cu^{2+}	3.8[b]	4.5	0	± 2.9
Cd^{2+}	1.6	2.5	2.2	± 3.3
Zn^{2+}	-1.0	9.1	9.4	± 7.2

[a]S = overall standard deviation estimate

[b]Does not include the loss for pH 7 and 1 ppm Cu^{2+} which was 24%

Table 6. Percent metal ion losses for the $2^4 + 6$ factorial experiment

	Level		
	+	0	-
A = [Metal ion] ppb	1000	750	500
B = [Alum] ppm	50	30	10
C = pH	7	6	5
D = [SFA] ppm	20	10	0

Experiments					Percent Losses[a]		
No.	A	B	C	D	Cu^{2+}	Cd^{2+}	Zn^{2+}
1	+	+	+	+	93	59	81
2	+	+	+	-	93	5	53
3	+	+	-	+	72	- 5	- 3
4	+	+	-	-	23	- 3	0
5	+	-	+	+	7	0	- 7
6	+	-	+	-	54	2	16
7	+	-	-	+	38	- 6	- 6
8	+	-	-	-	13	- 5	- 4
9	-	+	+	+	90	32	82
10	-	+	+	-	96	14	49
11	-	+	-	+	32	2	- 1
12	-	+	-	-	24	2	0
13	-	-	+	+	6	3	- 1
14	-	-	+	-	64	8	21
15	-	-	-	+	14	0	1
16	-	-	-	-	24	- 3	- 2
17	0	0	0	0	48	5	15
18	0	0	0	0	49	0	10
19	0	0	0	0	51	5	13
20	0	0	0	0	62	8	14
21	0	0	0	0	57	7	15
22	0	0	0	0	b	3	9

[a]A negative loss is an excess

[b]Not determined

Table 7. Water treatment experiment F statistics[a]

Factor[b]	SFA Present			SFA Absent		
	Cu^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Zn^{2+}
A	3	1	3	2	7	0.2
B	163	87	554	23	4	95
C	122	151	895	176	22	394
D	3	32	2			
AB	2	4	4	1	0.6	2
AC	7	6	0.1	0	1	0
AD	15	8	2			
BC	57	57	492	13	0	65
BD	35	43	96			
CD	60	32	3			
ABC	0.5	7	0.5	0	0	1
ABD	0	9	0			
ACD	6	15	0			
BCD	6	52	116			
ABCD	0.2	7	0.5			

[a]Underlined values indicate 99% confidence level significance. Literature F values for 99% confidence level are 21.20 for the Cu^{2+} and 16.26 for Cd^{2+} and Zn^{2+}.

[b]Factors A, B, C, and D are metal ion concentration, alum concentration, pH, and SFA concentration, respectively.

Table 8. Average SFA losses as a function of alum concentration[a]

Metal ion	Average % SFA loss		
	50 ppm alum	30 ppm alum	10 ppm alum
Cu^{2+}	95	98	0.3
Cd^{2+}	95	91	2
Zn^{2+}	94	91	3

[a]Averages of 10 and 20 ppm cases