THE ADSORPTION CHARACTERISTICS OF COPPER AND NICKEL ON GRANULAR ACTIVATED CARBON

By

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Poison is in everything, and no thing is without poison.

Only the dosage makes it either a poison or a remedy.

Paracelsus (1943-1541)

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But primarily I write these words for and to my sons. Truthfully, they have been the inspiration. I have tried to write in a clear and concise fashon, in some areas even deviating from the strict technical traditions to simplify a little, so that if by chance they pick these pages up a decade or more from now, they will understand them. I want them to understand the "why" of this and its science. Hopefully, they will be able to detect the enthusiasm for the method and the love of the search. It is not my purpose to pass to them a legacy of science . . . simply a desire to understand. It is not my thanks that I extend to them but a message and my clear wishes that they remain always above the game so that they may live the life long experience of learning with their own direction in mind and in a very intense and personal way.

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CAPTER I

INTRODUCTION

We survive in a biosphere of less than 100 kilometers in depth within a volume which comprises but a miniscule fraction of the total mass of the solar system. This biosphere is a balanced and self sustaining assembly of life forms interacting together and with the nonliving substances around them. This system has often been referred to as a delicate one. But if this characterization is at all accurate, it can be just as accurately described in its natural state as resilient and manifestly stable over the long term.

Our state of evolution and survival is living witness to the epochal endurance of the balance of life within the biosphere. Abundant evidence exists of massive glacial periods consuming whole continents, of significant fluctuations of solar radiation (1) and of an early age (Azoic) when the biosphere was almost totally anaerobic (2, 3). Through all of these environmental upheavals and planetary changes, life successfully evolved. But more importantly it developed the ability to adapt and survive. Just as lower life forms survive cataclysm through sheer fecundity, higher life forms, including man, survive primarily through utilization of complex actions and reactions to the environment summarily defined as intelligence.

For thousands of years this intelligence and survival through willful change caused man to alter his immediate environment and the balance of life by building shells around himself. More recently, a moment ago in geologic time, humanity developed the ability to cause significant planet wide environmental alterations. Ironically this was made possible by burning the decomposed remains of life forms from a complex energy soup of hydrocarbons called petroleum. This recent period during which we withdrew and used this power source was the industrial revolution, and it was an age responsible for the wholesale plundering of what appeared to be a planet of endless resources. We have taken full advantage of our newly found power and in less than one century, have flooded our environment with billions of kilograms of thousands of individual pollutants. Our elegant environmental system is being pushed to and sometimes beyond its limits and ability to respond.

There are at least two most simplified categories of this pollution: one that we can see, such as dirty air, dirty water, and a planetary abundance of trash. The other kind is that which we cannot see and often do not worry about. Within the latter category are air and water pollutants from the simply annoying to the deadly. Among the most dangerous of these unseen pollutants are the heavy metals.

Metals are not generally thought of in a role of blending with soil and water in their ionized and molecular forms. For many it is difficult to think of metals as a pollutant at all, but their presence and reality have proven exceedingly toxic and in many cases they are fatal to man.

Of the 106 elements represented on the Periodic Table, 80 are considered metals. A "heavy metal" is defined generally as one with a high atomic weight. From a human nutritional standpoint, these metals can also bear the title of "trace element" which is defined as an element normally injested by man at levels below 100 milligrams per day (4).

Of the 80 metals, 20 have been documented as potentially toxic to man at higher levels. However, there is a curious overlapping of the toxic effects of some metals at higher concentrations and their central metabolic role as an essential requirement for life at their "trace" concentrations. This metabolic contradiction is further complicated by attempting to pinpoint the actual causes of intracellular dysfunction (5).

Each heavy metal reacts somewhat differently within the cell and even reacts somewhat differently in various cell types, and if this complexity was not enough, the metals can enter the biological system and organism in different forms. They can form inorganic and organic compounds or they can complex with other macromollecular forms. Each of these individual species can further react differently and/or synergestically within the cell even though each may attach the same metal ion (4).

Within the cell there are abundant metal binding ligands in enzymes, substrates and structural components. These ligands can be very specific for certain ionic species, but for the most part they are unspecific and can attach most metallic ions. In fact, the affinity of the amino, imidazole and carboxyl groups for heavy metals overlap considerably. Chelation can also enhance, decrease or mask affinities by orders of magnitude. Other reactions seem to lie dormant for various periods further obscuring the exact relationships of heavy metals and their species to cellular metabolism. Some of this may in fact be caused by the ionic species becoming involved with genetic replication in actually inhibiting process itself (6).

However, some metals have been observed long enough to have enabled a reasonable information base to emerge and allow for some predictable results based upon some defined parameters. Some generalizations are very broad and are whole organism responses rather than those based upon specific cytochemical etiology. Data on other metals hardly exists at all and much research is needed.

Two heavy metals (also defined as trace elements) that constitute both a metabolic necessity at low concentrations and a toxic substance at higher concentrations are copper and nickel. These heavy metals react in biological systems as previously discussed. They appear in vast quantities in our environment and they are concentrated in and around our society as inexpensive, widely used metals for everything from pocket change to water distribution systems and pots and pans. That these metals end up injested in man is no surprise.

There is much evidence that both of these metals have bioaccumulation characteristics, and that under certain conditions they are carcinogenic, toxic and can damage internal organs. They have also been directly associated with death in certain cases. Given their abundance and heavy usage in our society, it is important that we know exactly what effect they do have down to the cellular level. It is also important that we know how to reduce the opportunities for human consumption.

Of the methods for removing heavy metals from wastewater, activated carbon provides an already exploited resource. Many municipalities either already have or are looking to activated carbon as a unit operation in both waste treatment and water treatment to remove a host of pollutants. The removal efficiencies for this process are now under investigation. The same carbon columns are expected to provide a panacea of solutions for every trace pollutant, but exactly how much of each pollutant and under what conditions they are removed is not fully known.

The purpose of this study was to determine the amounts of copper and nickel removed from water using granulated activated carbon columns under aerobic conditions and multiple pH ranges.

CHAPTER II

LITERATURE REVIEW

Copper (Cu) has an atomic weight of 63.5, atomic number of 29, density of 8.9, melting point of 1083.4°C and boiling point of 2567°C. Copper is second only to silver in conductivity of heat and electricity. World production in 1970 was estimated to be 6 x 10^6 metric tons (7).

In the human body copper is found at 1.4 parts per million (ppm) or a total of approximately 100 mg for a 70 kg man (8). The daily requirement of copper is about 30 µg/kg/body weight for adults and 80 µg/kg/body weight for infants (9).

Copper is an essential part of several human enzymes such as tyrosinase which forms melanin, cytochrome oxidase and uricase. Copper is also essential for the utilization of iron in the formation of hemoglobin. Defficiencies of copper in humans are associated with anemia, structural defects in major arteries and some nervous disorders (7).

Excessive copper concentrations in man can culminate in death although there is some disagreement as to what levels and forms of copper are required to produce evidence of toxicity. The information now available suggests that there is a wide variance of tolerance among individuals and age groups. One case reported the death of an infant apparently due to copper poisioning. The child's water supply was found to contain 675 µg/100 ml copper (10). Nielsen reports a link between excessive copper and hemolytic jaundice (11), hepatic and renal failure, severe anemia, cancer (12, 13, 14, 15), cadriovàcular disease (10), and death (4, 5, 10).

According to a National Research Council report: "Rocks are the primary natural source of most elements that enter the human system," (16). The pathways from the rocks vary. Much is carried from geologic formations within aquifers to the ground water. Other sources include bioabsorption at all levels up the food chain to and including man.

The highest copper bearing minerals are basaltic igneous and shales (16), but in most cases the most direct source of copper to humans is tap water (from distribution lines and fittings), food processing and water treatment chemicals (4, 10). It is also significant to note that most tap water contains enough copper to inhibit many enzyme reactions (6).

Limits to copper concentration, however, were not established from a concern for health but for taste. Copper gives water an astringent taste at concentrations ranging from 1-5 mg/l. The limit for drinking water has been set at 1 mg/l (4).

Nickel (Ni) has an atomic weight of 58.71, atomic number of 28, density of 8.9, melting point of 1453°C, and a boiling point of 2732°C. It comprises .008 percent of the earth's crust. World production of 1963 was 6.6×10^5 tons (17).

In the human body nickel is found at .14 ppm or a total of 10 mg for a 70 kilogram man (8). The daily requirement for nickel has been reported at 50-80 ng/g diet (18) which relates to approximately 90-150 µg nickel per day per adult.

Nickel is, like copper, an essential enzyme constituent and also plays an important role in the development of melanin (19). Nickel has been known to play a vital role in the structural stabilization of nucleic acids and can preserve ribosomal structures against thermal denaturation (18, 20). Nickel serves the purpose of an enzyme activation ion and as an inhibitor of other enzymes (21, 22, 23). Nickel has also been found to play a vital role in the action and sustained function of insulin and the conversion of glucose into glycogen. Deficiencies of nickel in laboratory animals have been associated with growth retardation, dermatitis (19), impaired liver function and birth abnormalities (24).

Reports of excessive nickel concentrations causing toxic effects in man can be traced to the 19th century when a report surfaced that Emperor Franz Josef of Austria had developed an illness due to the use of nickel cooking pots (25). The most profound and widespread toxicity associated with nickel is cancer. A larger base of evidence has linked human cancer with excessive or long term exposure to nickel and its compounds, especially nickel carbonyl (4, 12, 17, 21, 26). Dermatitis, gastrointestinal irritation, renal failure, paralysis, neural membrane degeneration and liver damage have been reported and associated with excessive exposure to nickel (4, 5, 17, 21, 27, 28).

The primary source of nickel in the biological pathways to man occur from food processing equipment (such as the nickel-copper alloy Monel), from fungicides and food. The highest nickel containing food products are Wheaties with 3 ppm, squash with 4.6 ppm, cabbage and mushrooms with 3.3 ppm, tea with 7.6 ppm, cocoa with 5 ppm, black pepper with 3.93 ppm and baking soda with 13.4 ppm (21). One source notes that the consumer may pick up a few milligrams of nickel daily from nickel or nickel alloy cookware (29). Another study reported the mean concentration of nickel in water is 19 µg/l (30). The Governmental Industrial Hygienists (ACGIH) have established the threshold limit value for nickel and its salts in the atmoshpere at 1 mg/m^3 for nickel carbonyl (4).

Now that millions of kilograms of copper and nickel have been released into the biosphere and are moving through the human food and water cycles, it is imperative that their effects, bioaccumulation characteristics, reactivity and methods of removal are clearly understood. These are minute pollutants that require special and specific research methods to find and will also require special and specific methods of removal.

The Environmental Protection Agency has named copper and nickel as two of the 129 priority pollutants that may pose a significant hazard to the environment. These pollutants are listed in section 307 (a)(1) of the 1977 Clean Water Act (33 U.S.C. 466 et seq; Committee Print HR. 3199) (31).

The fate and transport of nickel and copper in the environment, therefore, are receiving special attention. It is important to recognize the most efficient methodology of the removal of these metals from waste water or potable water sources. The metals have been described as "highly associated with hard water" (32), and standard treatment processes to soften water have been shown to be effective in removing the metals (i.e., lime softening) (10). However, a recent study indicates that sorption is a more important removal mechanism than precipitation for copper and that sorption "exerts the major control" over the mobility of nickel (31).

Activated carbon can provide such a sorption removal mechanism under controlled and steady state conditions. Studies have confirmed the viability of activated carbon as a removal mechanism for trace metals including copper and nickel (33, 34, 35, 36). Activated carbon is now used in many industrial and municipal treatment processes. Two such examples are Water Factory-21 in Orange County, California and the city of Pamona, California (37, 38).

Chemical Speciation

Copper exists in natural waters in several forms. The only copper compounds stable under aerobic conditions in water are also highly insoluble (39). Some examples are:

$CuCl$

$CuCN$

However, there are some copper salts that are readily soluble and they are (31):

$CuCl_2$

$Cu(NO_3)_2$

$CuSO_4$

Other examples of copper species present in waters includes (40):

$Cu(OH)_2$

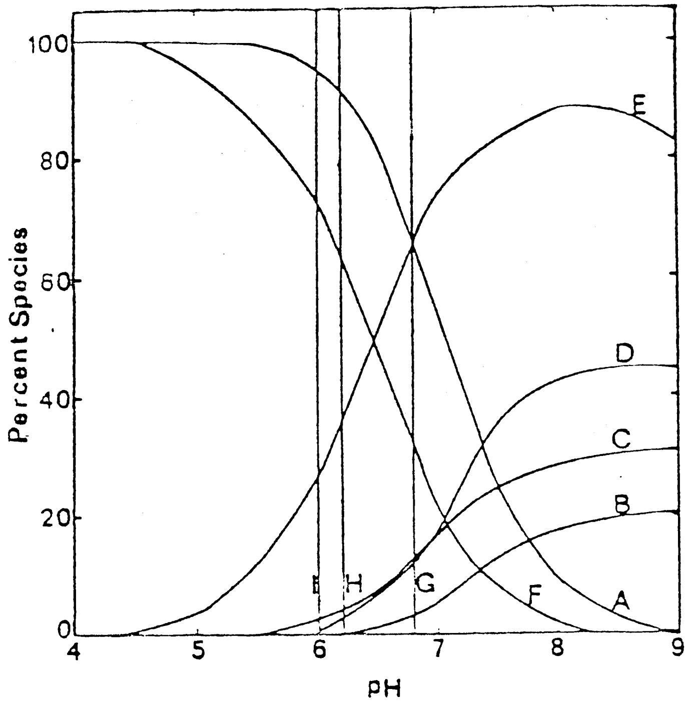
$CuCO_3$

$Cu_2(OH)_2CO_3$

$Cu_3(OH)_2(CO_3)_2$

$Cu_2(OH)_2$

The solubility of the copper species and/or their subsequent precipitation are pH dependent. Figure 1 shows the presence of various species vs. pH (40). The most significant process by which divalent, hydrated copper (II) is removed from unpolluted water is the precipitation of malachite: $Cu_2(OH)_2CO_3$ (41).



Speciation of copper(II)(total concentration 2 ppm) and carbonates as a function of pH. (A) Cu^{+2}. (B) $Cu_2(OH)_2^{+2}$. (C) $CuOH^+$. (D) $CuCO_3$. (E) HCO_3^-. (F) H_2CO_3. (G) pH at which $Cu(OH)_2$ will precipitate. (H) pH at which $Cu_3(OH)_2(CO_3)_2$ (azurite) will precipitate. (I) pH at which $Cu_2(OH)_2CO_3$ (malachite) will precipitate. From Sylva (1976).

Figure 1. Speciation of Copper (II) And Carbonates As A Function of pH

Callahan et al. have found that the predominant species of soluble copper are $Cu(OH)^+$, Cu^{+2}, $CuCO^3$. Their existance in solution occurs in the order of: $Cu(OH)^+ > Cu^{+2} > CuCO^3$. However, another source reports the majority of copper will exist in unpolluted waters as $CuCO_3$ (31).

Callahan et al. also described copper concentrations as being controlled by hydrous oxides of iron and manganese and not by the solubility of the copper compounds.

It is important to note, however, that copper also has a very strong tendency to form complexes and when organic material or organic pollutants are present the soluble copper will consist of almost entirely complexed organic forms (42).

Nickel is also found in several forms in natural waters. Ni^{+2} is the predominant oxidation state in these waters (39) and some of the various species existing under aerobic conditions and at a pH of ≥ 9 are as follows (43):

Ni^{+2}

$Ni(OH)^+$

$Ni(OH)^{+2}$

$NiCO^3$

$NiSO^4$

NiCl

Ni - Si

Ni - Fe

Ni - Mn

Figure 2 shows the nickel species present (moles/l) as a function of pH (43).

The predominant species of soluble nickel exists as follows (43):

$$Ni^{+2} > Ni(OH)_3 > NiSO_4 > NiCl^+$$

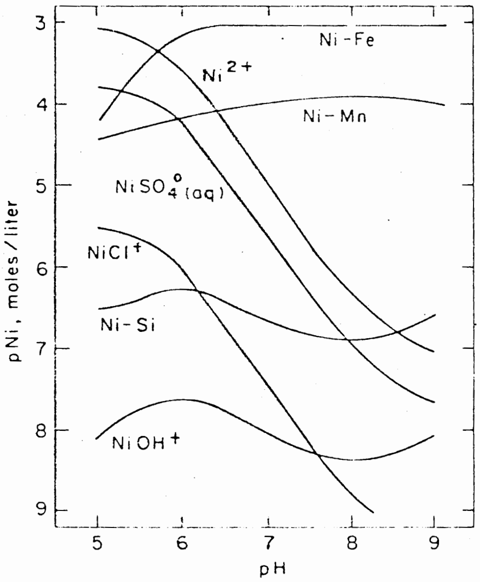
Nickel is a much more highly mobile metal than is copper in the environment. Sorption is a much more important mechnism and organic complexation seems to play a very small role in the fate of nickel in aquatic systems (44).

Adsorption by Activated Carbon

Adsorption is defined as "adherence of materials to the surface of solids in a thin layer" (45). The adherence can be caused by electrostatic attraction of ions between the material (activated carbon) and the solid, by physical entrapment within the carbon pores or crystalline lattice of the surface or by intramollecular attraction by another substance already adhered to the activated carbon. The most tenacious adsorption occurs within the smallest pores and most "active" parts of the carbon's surface from unsatisfied valence bonds and charges (46).

There is but a slight distinction between true adsorption and precipitation on the surface of the adsorbent. The carbon can provide a nucleating force to cause the actual precipitation in a solution that is supersaturated (46).

Adsorption of heavy metals such as copper and nickel onto the surface of activated carbon is dependent on several factors. They are: pH, pore size and distribution, molecular size and distribution, concentration or ionic strength of metal ions in solution and the stoichiometry of the adsorbate molecule (47, 48, 49, 50).



Speciation of nickel as a function of pH.

Figure 2. Speciation of Nickel As A Function of pH

Each factor does affect another, of course, but generally the adsorption capacity of the activated carbon increases as the pH decreases (48). At pH ranges above 6, copper will precipitate. In fact, one study has shown a removal efficiency of copper and nickel by precipitation with lime (followed by recarbonation) of 99 percent at pH's of 8.7 for each metal.

Figure 1 shows the precipitation of $Cu(OH)_2$ at a pH of 6.8, of $Cu_3(OH)_2(CO_3)_2$ at a pH of 6.2 and $Cu(OH)_2CO_3$ (malachite) at a pH of 6 (31). At a pH ≥ 9 nickel will precipitate as the hydroxide or carbonate species. In aerobic environments below a pH of 9 the nickel compounds remain soluble (51). Figure 3 shows the distribution in percent of nickel hydrolysis species as a function of pH (43). A chart summarizing the precipitation ranges of nickel and copper as a function of pH is shown in Figure 4 (48).

Studies done in Japan, a country experiencing severe heavy metal pollution, have shown significant removal of copper with activated carbon columns (52). Another study showed a 95-100 percent removal efficiency of nickel and copper from secondary effluent by activated carbon following a high lime coagulation system. In this study the copper species accumulated in the upper portion of the carbon column and the nickel species in the lower. Table 1 summarizes these findings (53).

This illustration points out and supports an EPA report that nickel is the most mobile of the heavy metals (31). Maruyama et al. notes that the location of nickel far down onthe column appeared to be true adsorption. He also noted that the concentrations of nickel probably would have not been so high if a filtration or a precipitation mechanism were involved (53).

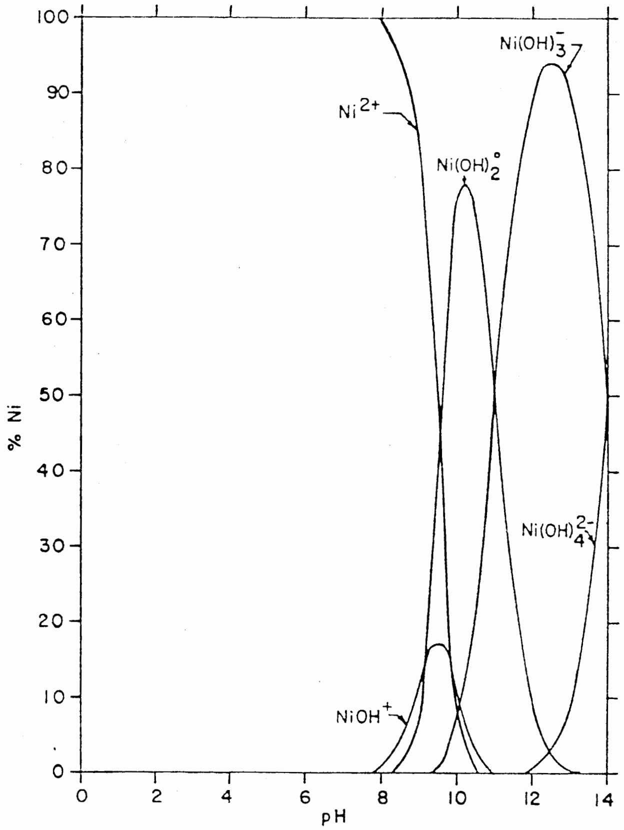


Figure 3. Nickel Hydrolysis Distribution Diagram

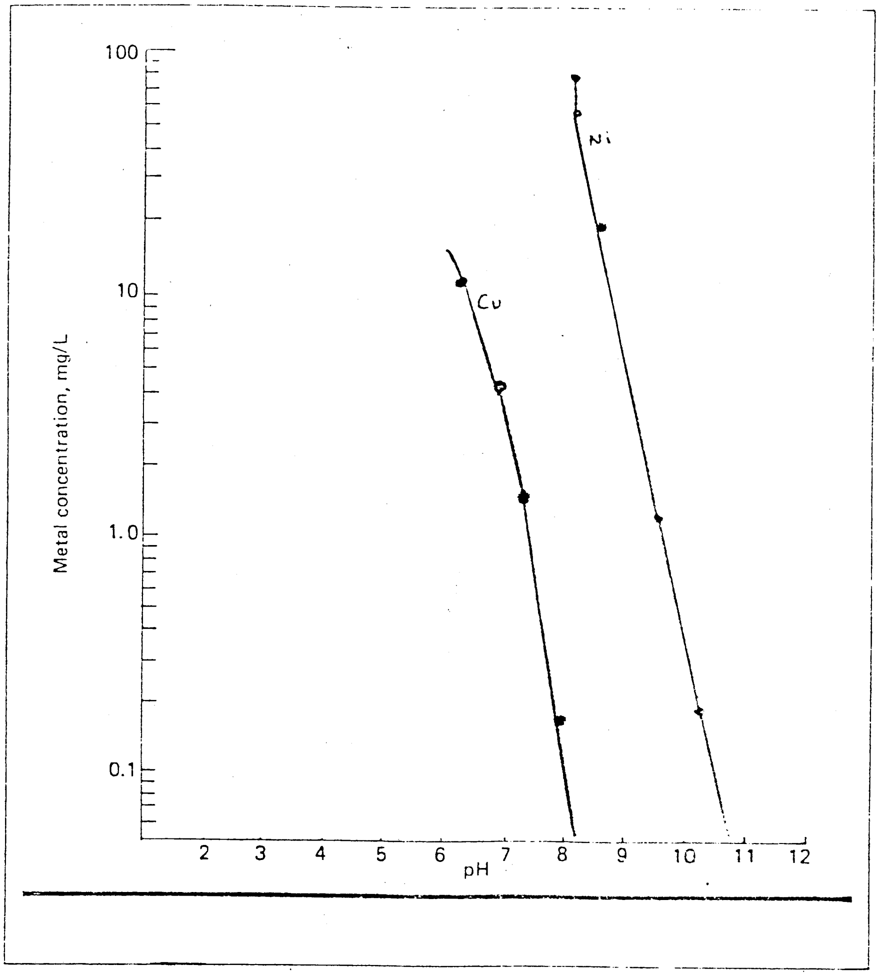


Figure 4. Precipitation of Copper And Nickel As Hydroxides

TABLE I

ADSORPTION OF COPPER AND NICKEL ONTO ACTIVTED CARBON DEPTH (m) VERSUS WEIGHT OF CARBON (mg/100 gr)

Carbon Depth (M)	Copper (mg/l)	Nickel (mg/l)
0.00-0.91	26.4	4.0
0.91-1.83	12.6	8.0
1.83-3.05	11.6	16.0
3.05-4.27	2.4	76.0
4.27-5.49	1.0	114.0

It should be noted again that in the study above, the information regarding the mobility of nickel came from an actual operating waste treatment facility using secondary effluent through a carbon column for four days. The author mentioned the possibility of short term anaerobic conditions developing within the lower portions of the columns and preceipitating the nickel out as sulfides. Again, the backwash failed to change the distribution. However, one cannot totally rule the possibility of anaerobic conditions. Given the tendency of carbon columns to provide a surface for microorganisms and for sulfides to be present downstream in the columns there remain a signficant question (54).

Adsorption Isotherms

The adsorption isotherm for activated carbon is a relationship which defines the mass adsorbed vs. concentration remaining in solution. There are various methods for expressing this relationship and the method selected is the one that most closely approximates a straight line when plotted. With this isotherm data, the following information can be obtained directly about the activated carbon and nature of adsorption of the adsorbate such as:

1. The amount of impurity adsorbed when the adsorbate solution is in equilibrium with the carbon (i.e. $[X/M]/Co$, this represents the ultimate capacity of the carbon for the adsorbate[s]) (54).

2. The efficiency of adsorption per dose of adsorbate.

3. The approximate time of carbon exhaustion (time to equilibrium) per dose.

4. The approximate time to breakthrough when comparing batch systems to dynamic (column) systems.

Indirect information may be obtained such as:

1. The effects of pH, temperature and concentration of adsorbate on the overall efficiency of removal.

2. The effects of competitive adsorption on individual components of a waste water.

3. The extrapolation to dynamic systems in consideration of displacement or rollover, and the effects of regeneration and granular size (55).

These isotherm relationships commonly considered are as follows:

1. X/M vs. C or Langmur for high adsorbate concentrations;
2. 1/(X/M) vs. 1/C or Langmur for low adsorbate concentrations;
3. Log X/M vs. Log C or Freundlich; and
4. C/(X/M) vs. C.

As was stated previously, each of these isotherms demonstrate the relationship to the carbon loading, or X/M as a function of the equilibrium concentration of the adsorbate after treatment (55). The selection of the proper isotherm is based upon the approximation of linearity to most accurately extrapolate the desired information.

CHAPTER III

MATERIALS AND METHODS

This study was designed to obtain the information necessary to formulate isotherms from both batch and column systems of aqueous Cu and Ni. Nuchar (TM) granulated activated carbon (12 x 40) (Westvaco Corp., Covington, VA) was utilized in both the batch and column studies. The copper used for the study was made up from an aqueous solution of $CuSO4$, while the nickel used for the study was made from an aqueous solution of $NiNO3$: $6H2O$. For each metal, a standard solution of 1000 mg/l metal was prepared and used as the stock solution. When it was necessary to adjust the pH, HCL or NaOH was used.

Batch Studies

The purpose of the batch studies was to develop isotherm data on increasing metal concentrations at a given carbon dosage at increasing pH values. The study selected pH values of 2, 4, 6, 8, 10, 12 and metal concentrations of 1, 2, 5, 10, 25, 50, 100, 200, 300, 400, 500, and 600 mg/l. A carbon dosage of 3 grams of Nuchar was selected based upon the maximum amount of carbon that could be continuously suspended in a 100 ml solution on a shaker table. For each run, a 24 hour time period was selected to insure the solutions reached equilibrium.

Initially the flasks and all equipment were cleaned with nitric acid. A volume of pH adjusted, distilled, deionized water was added to the flasks and manually shaken gently to wet the carbon. The metal solution was then added to each 300 ml flask to bring the total liquid volume in the flask to 100 ml. Three grams (dry weight) of activated carbon were added and the flasks were sealed with Parafilm (TM) and subsequently placed on the mechanical shaker table for 24 hours at room temperature (approximately 23 degrees centrigrade). At the end of each run, the solutions were allowed to settle for 10 minutes then filtered through Whatman Glass Fiber Filters, 934 AH. Another set of flasks were prepared and run identically except no carbon was added. These served as control flasks.

Column Studies

The purpose of the column studies was to develop breakthrough curve data on the metals at a given pH, to develop breakthrough curve data on the metals when in secondary municipal waste water and to develop breakthrough curve data of the metals mixed in solution with one another to determine any competition or displacement effects.

Tap water was used for the column studies due to the prohibitive expense of using large volumes of distilled or deionized water. The tapwater, however, was analyzed for Cu and Ni. These metals were not found to be present.

Three inch diameter glass columns were used for each run except the waste water studies. The three inch glass columns were Pyrex (TM), custom blown with nylon stop-cocks. They were mounted vertically to allow gravity flow. Plastic fiber webbing was used in the bottom of the columns to support the carbon bed. A one inch plastic splash-plate was installed between the discharge outlet of the influent tube at the top of the carbon bed to insure uniform distribution of the influent. Nuchar was used as the carbon in 18 inch (860 gram) beds.

For the metals in the secondary municipal wastewater phase of the study, a 1.1 inch inside diameter column was prepared with 100 grams of carbon. A gravity flow system was also used in these trials. These columns were plexiglass columns with rubber stoppered ends, allowing for gravity flow of the wastewater. Glass wool was utilized in the bottom of the columns to support the carbon medium and a 0.25 plastic disc was used for a splashplate.

The smaller columns were used for the wastewater effluent studies because of the amount of time it was predicted for 1.0 mg/l metal to break through and saturate the columns. Negating the effects of competition from the wastewater, it was predicted from the results of the large columns, that in a column of 860 grams of carbon, saturation would have taken approximately 17 hours.

The Nuchar was prepared for each run by soaking in tap water at room temperature for 24 hours. This was done to accomplish degassing and wetting of the carbon. Each run was made at room temperature.

For the three inch glass column studies, two 25 liter bottles connected by a siphoning system were set up above the columns. Siphoning by gravity was used as the input system to the columns. The flow rate was monitored before initiating the run to maintain approximately 1 gpm/ft^2 or 200 ml/min average flow rate over the period of the run. Through several trial runs it was determined that 10 mm diameter tubing was required to maintain this flow rate to the columns.

The selection of the pH and the concentrations for these studies was based upon an informal survey made of various metal plating industries in Oklahoma. It was determined that the pH of metal wastes were acidic in the 3 to 5 pH range and, of course, much more highly concentrated than commonly found in municipal wastes or drinking water supplies. Therefore, the pH and concentrations of this phase of the study were set at those levels associated with metal plating wastes: at a pH of 3.5 and a concentration of 350 mg/l. After startup, the columns were run near the breakthrough times approximated by the batch isotherms and samples were taken for later analyses. Finally, following these studies with individual metals at this concentration, the metals were mixed at 150 mg/l each Cu and Ni, bringing the total metal concentration to 300 mg/l in solution. This was then run in a column using the same procedure as utilized in the individual metal studies.

The wastewater from the secondary clarifier of the Stillwater Municipal Wastewater Treatment facility was filtered through cloth before use to remove a major portion of the large suspended solids. The metal was added to bring the concentration to 1 mg/l. A sample of the wastewater was analyzed for background contamination. The pH of the wastewater was 6.8 as it came from the plant. The carbon was prepared as before and the startup initiated and samples taken for analyses.

To investigate the effects of Biochemical Oxygen Demand (BOD) on the adsorption process for the metals, the small columns were prepared as they were for the metal runs, but the secondary wastewater effluent was run through the columns without metals in solution. This was done to investigate the change in BOD on passage through the column, independent of what effects the metals may have had. The BOD test was performed as specified in Standard Methods for the Examination of Water and Wastewater (56). Abundant evidence exists to support the concept that competition for adsorpitive sites does play a crutial role in the adsorption of metals (36, 54).

Analyses

All samples and blanks were analyzed for copper and nickel using a Perkin-Elmer 5000 Spectrophotometer equipped with a HGA 400 graphite furnace. Both flame and flameless atomic absorption techniques were used. Detection limits for flame were specified by the manufacturer as 0.15 mg/l Ni and 0.09 mg/l Cu. Values below these were analyzed by the HGA 400 graphite furnace. Isotherm data was calculated by computer programs developed by the author for this project and all data was plotted by NEC PC8001 computer on an AMDEK DXY100 plotter.

CHAPTER IV

RESULTS

The batch studies, as discussed previously, investigated the capacity of the carbon for metal adsorption and produced information allowing prediction of column breakthrough and exhaustion. In this study, breaktrhough was defined for both copper and nickel as the point where 10 percent of the original concentration was observed coming through the columns. Exhaustion; or equilibrium, was defined as the point where 90 percent of the original concentration was observed coming through the columns (57).

For the batch studies, a set of control flasks were set up; as described previously, and were shaken during the batch trials without carbon. From these controls, several pieces of information were collected. It was noted that at pH's greater than 6 for copper and greater than 7 for nickel, precipitation was present. It was also observed that the precipitation was quite heavy and clouded the solution significantly at the higher pH values. The controls also allowed a determination of the amount of metal sorbed onto the glass walls of the flasks. All samples including controls were flitered prior to analysis and therefore only soluble metals was analyzed. Control values were subtracted for the corresponding batch runs including carbon to eliminate the effects of precipitation and sorption onto glass from the final answers.

Results from the batch studies were analyzed to determine the effects of pH and concentration on adsorption. In addition, X/M at each pH and concentration was determined. This data is shown in Table II. The X/M ratio defines the amount of contaminate (metal) adsorbed (X) to the amount of carbon in the column (M). Missing values in Table II were those omitted because of loss of sample or experimental error. Table II shows higher X/M values for nickel than for copper, indicating a higher affinity for nickel in the batch studies.

The isotherms developed from the batch studies (Figures 5-16) were plotted as low and high concentration isotherms. This was seen as necessary after several attempts were made to plot them together as a single isotherm. These single isotherms tended to plot the lower points non-uniformly and the higher concentrations as linear.

Isotherms were developed for copper and nickel for concentrations of 100-600 mg/l using the data in Table II and the isotherm relationships of 1/(X/M) vs. 1/c (Langmuir High), where c is the concentration of metal remaining in solution. These isotherms are shown in Figures 5-16. The data for both copper and nickel collected at the high concentrations (Figures 5-16) fit the Langmuir high isotherm very well with linearity apparent at almost every pH studied.

No single isotherm was found to fit the lower concentrations (1-50 mg/l). The data comprising the low isotherms were compiled from metal concentrations that were exceedingly low and approaching the detection limit of the spectrophotometer. In many cases, these values were read in parts per billion. Some of the scatter accounting for the non-linearity observed at the lower concentrations could be due to analytical error or the inherent difficulty in analyzing near the

TABLE II

X/M VALUES VERSUS METAL CONCENTRATIONS

				Copper								
				X/m (mg/gr) Values Vs. Concentration & pH								
Conc	1	2	5	10	25	50	100	200	300	400	500	600
pH 2	0.012	0.001	0.021	0.046	0.236	1.018	–	0.381	2.122	1.989	4.317	6.847
ph 4	0.012	0.003	0.051	0.054	0.166	–	2.033	1.083	7.733	8.800	11.23	13.90
pH 6	0.008	0.006	0.028	0.072	0.145	–	0.525	0.046	0.091	1.116	3.583	6.403
pH 8	0.024	0.005	0.047	0.081	0.137	0.302	0.335	–	0.488	–	3.413	5.160
pH 10	0.017	0.026	0.101	0.103	0.630	0.316	0.425	0.443	1.588	.0905	3.540	–
pH 12	0.026	0.020	0.067	0.060	0.266	0.362	0.417	0.920	2.880	1.107	1.058	3.666
				Nickel								
				X/M (mg/gr) Values Vs. Concentration & pH								
pH 2	0.023	0.039	0.034	0.054	0.100	0.150	0.527	2.243	4.433	7.033	8.667	10.16
pH 4	0.004	0.001	0.0017	0.010	0.093	0.246	0.520	1.337	3.300	5.100	8.567	10.86
pH 6	0.003	0.013	0.007	0.061	0.371	0.612	–	1.543	4.247	7.267	7.500	9.567
pH 8	0.021	–	0.062	0.219	0.401	0.569	0.757	2.480	4.387	8.233	8.733	13.60
pH 10	0.004	0.010	0.020	0.061	0.097	0.230	0.667	2.400	3.467	6.400	9.433	12.70
pH 12	0.033	–	0.066	0.100	0.100	0.406	0.730	5.850	9.717	–	10.30	16.00

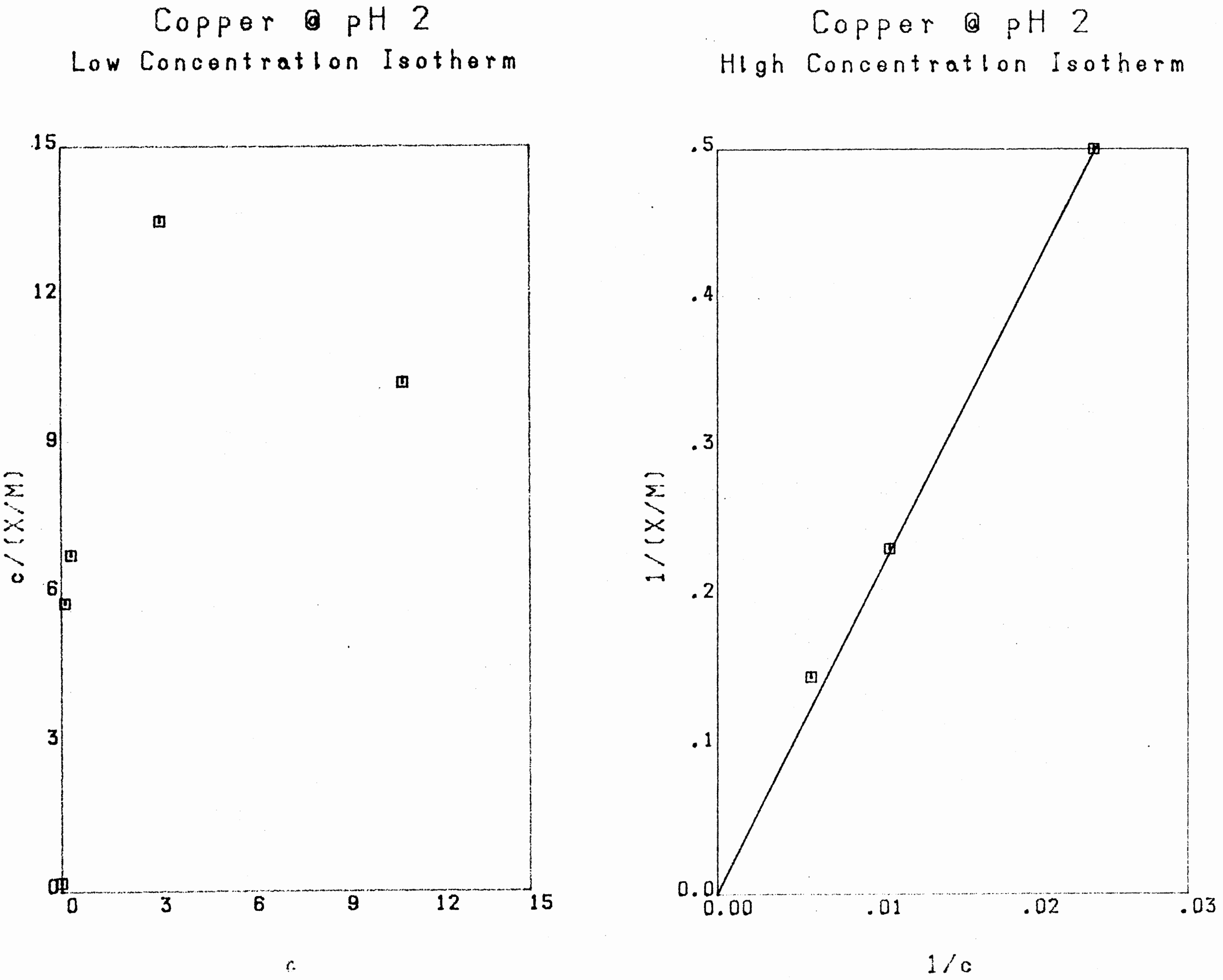


Figure 5. Copper Isotherms At pH 2 - Adsorption Versus Concentration Remaining

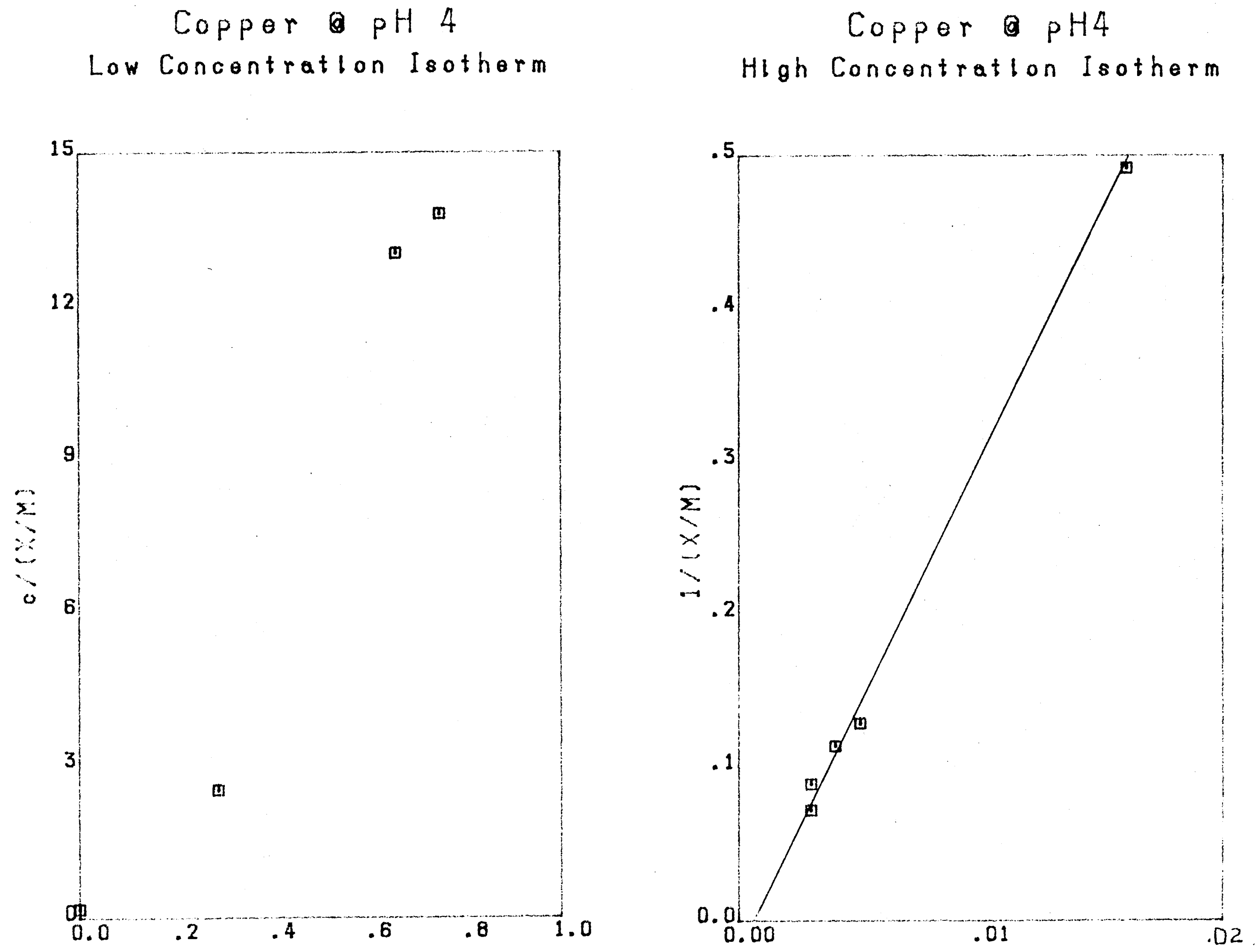


Figure 6. Copper Isotherms At pH 4 - Adsorption Versus Concentration Remaining

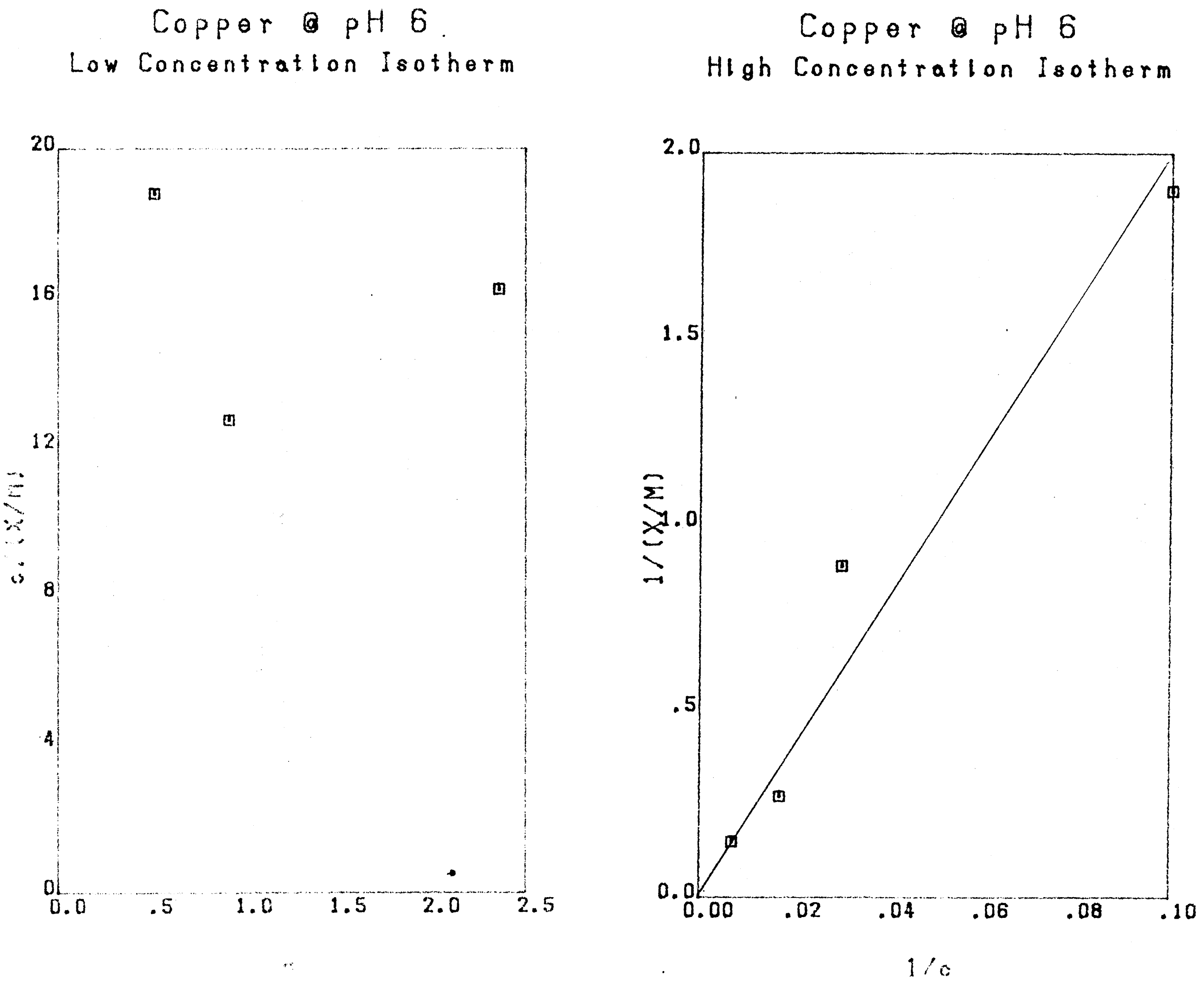


Figure 7. Copper Isotherms At pH 6 - Adsorption Versus Concentration Remaining

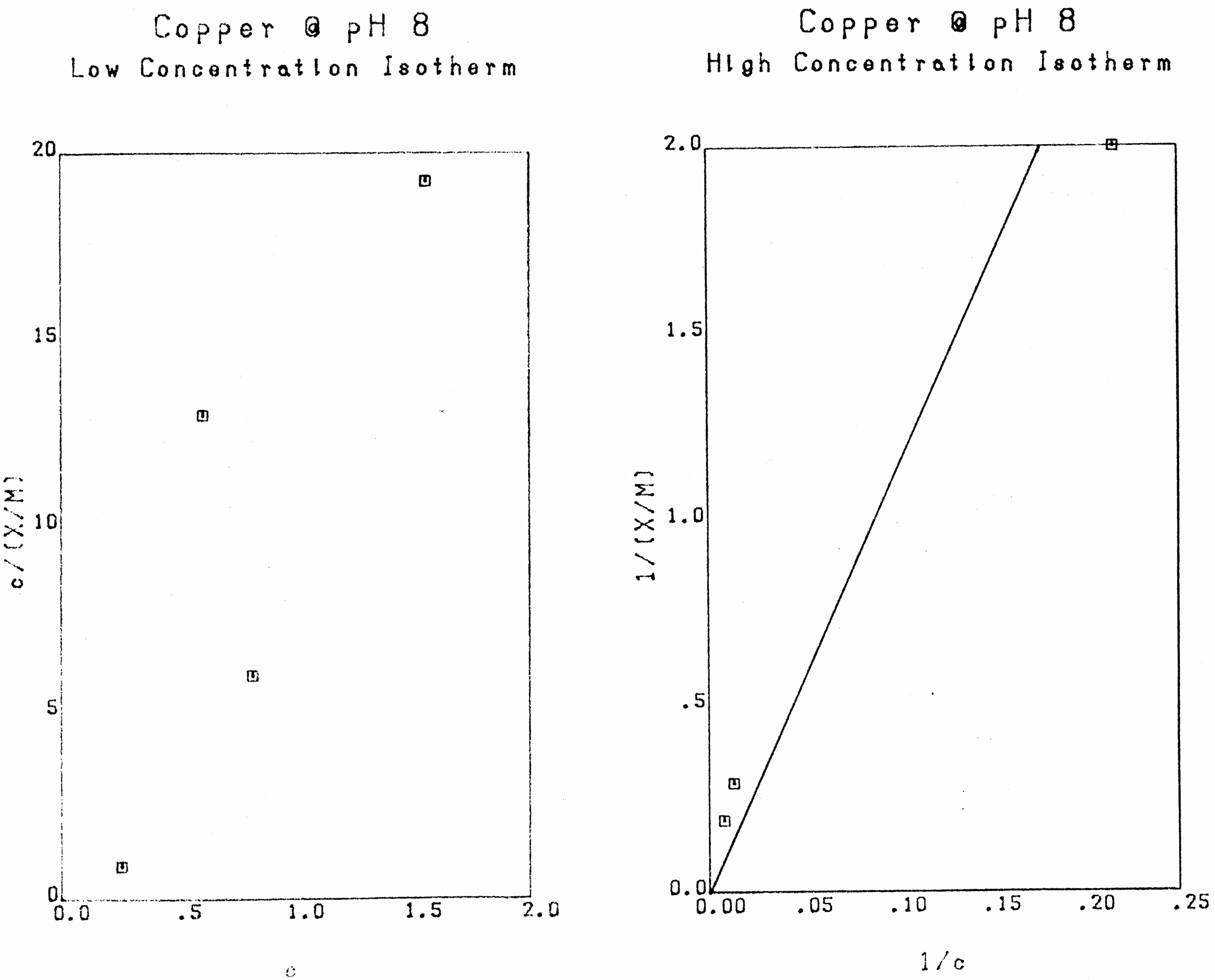
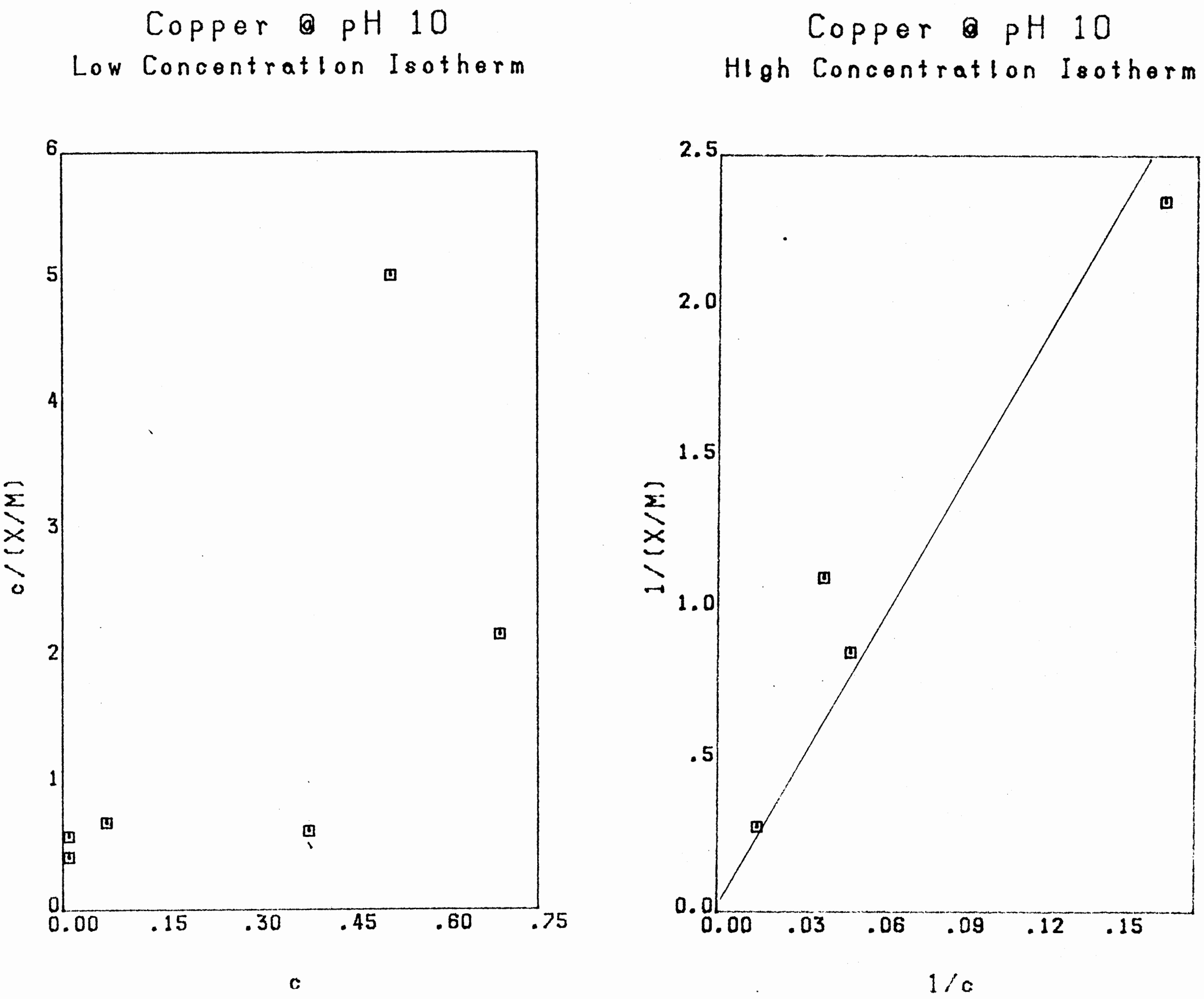


Figure 8. Copper Isotherms At pH 8 - Adsorption Vesrus Concentration Remaining



Copper @ pH 10
Low Concentration Isotherm

Copper @ pH 10
High Concentration Isotherm

Figure 9. Copper Isotherms At pH 10 - Adsorption Versus Concentration Remaining

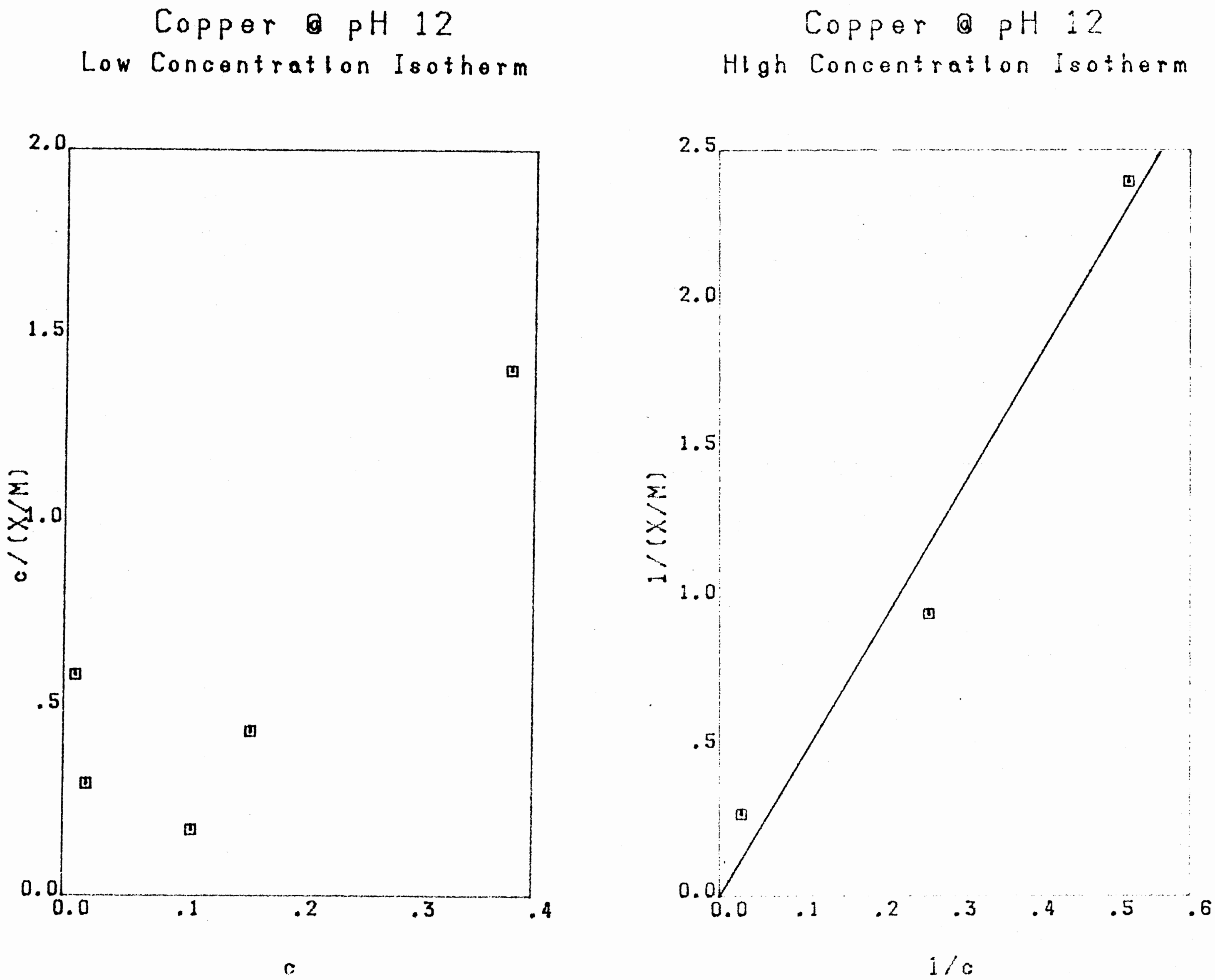


Figure 10. Copper Isotherms At pH 12 - Adsorption Versus Concentration Remaining

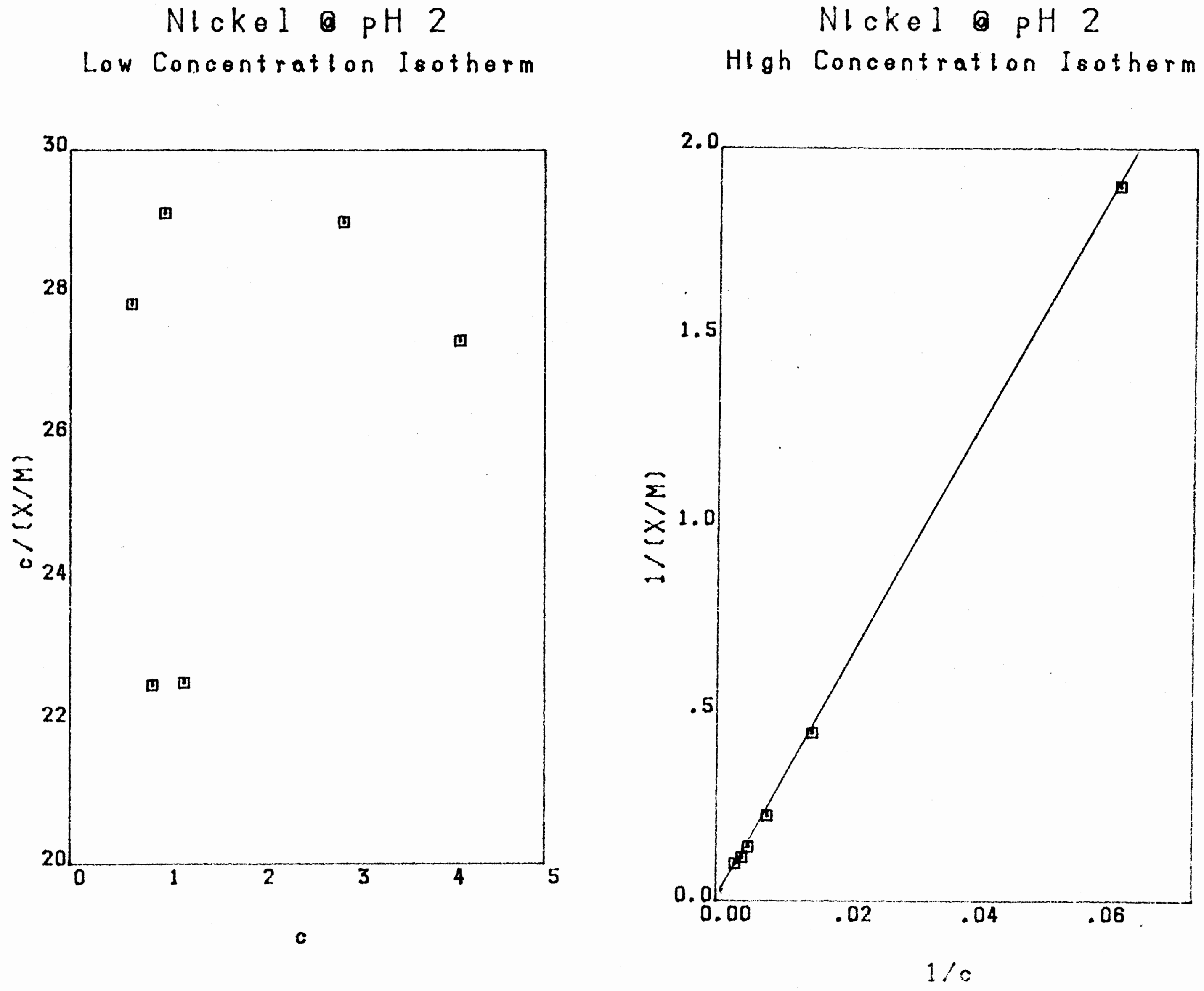


Figure 11. Nickel Isotherms At pH 2 - Adsorption Versus Concentration Remaining

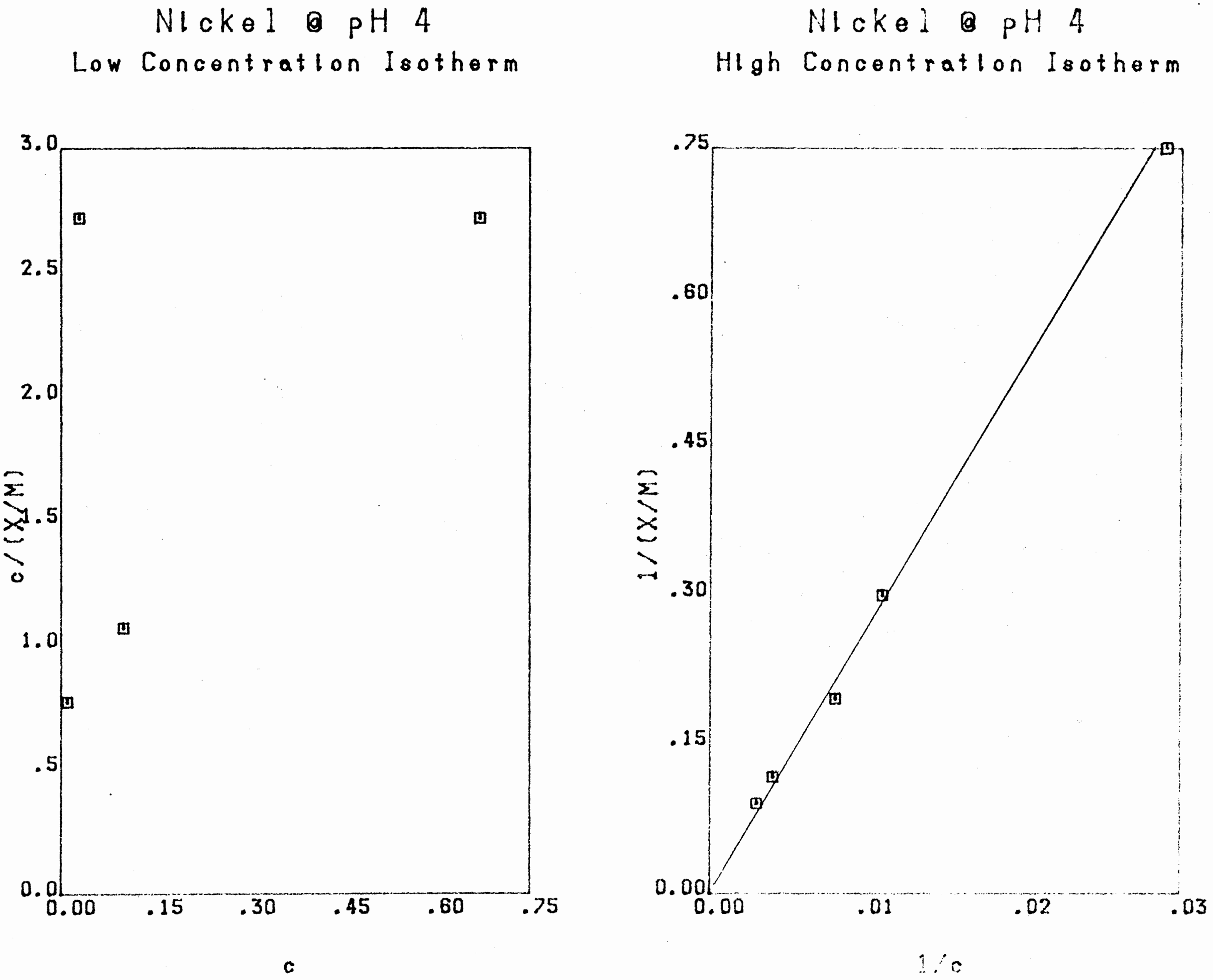


Figure 12. Nickel Isotherms At pH 4 - Adsorption Versus Concentration Remaining

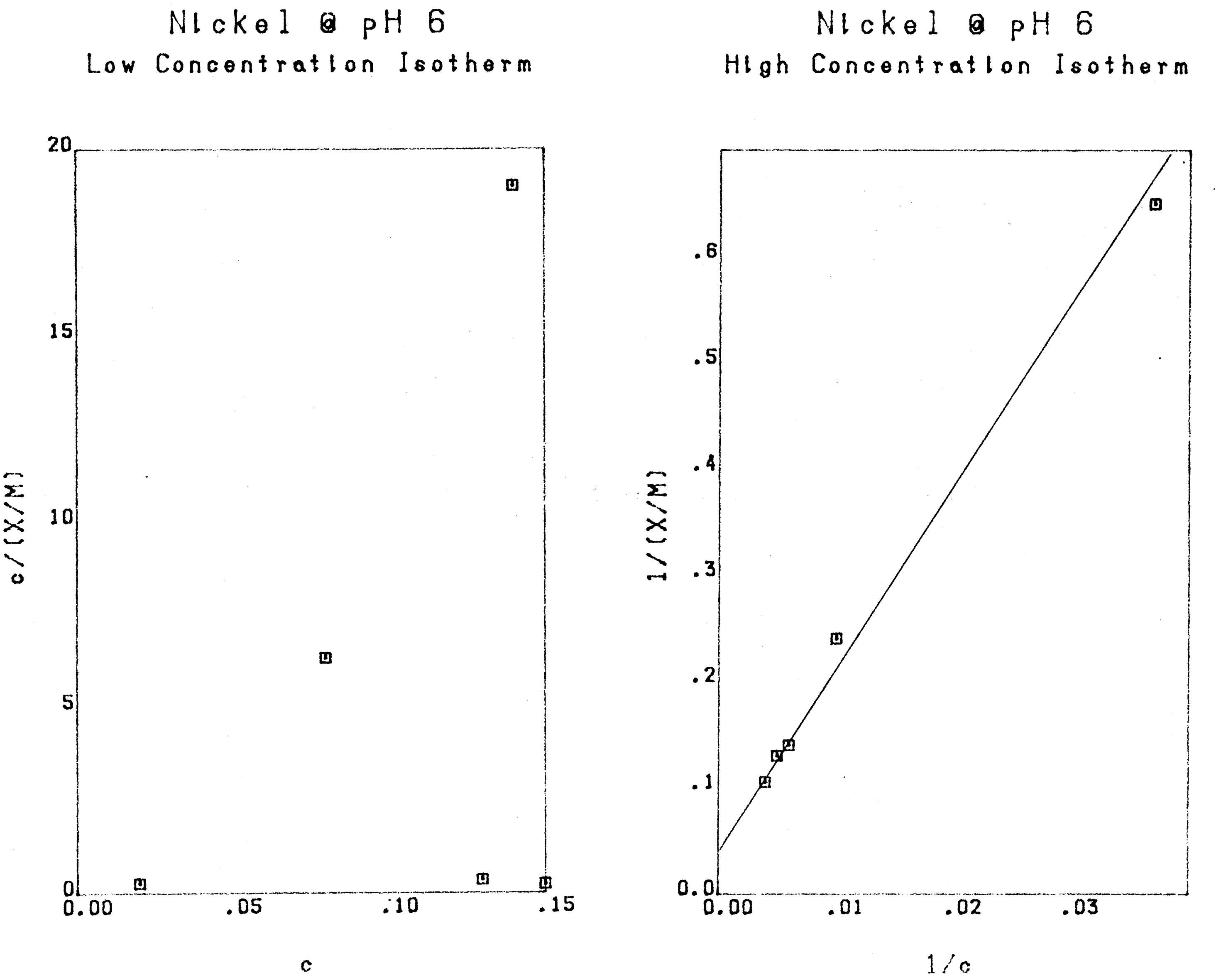


Figure 13. Nickel Isotherms At pH 6 - Adsorption Versus Concentration Remaining

Nickel @ pH 8
Low Concentration Isotherm

Nickel @ pH 8
High Concentration Isotherm

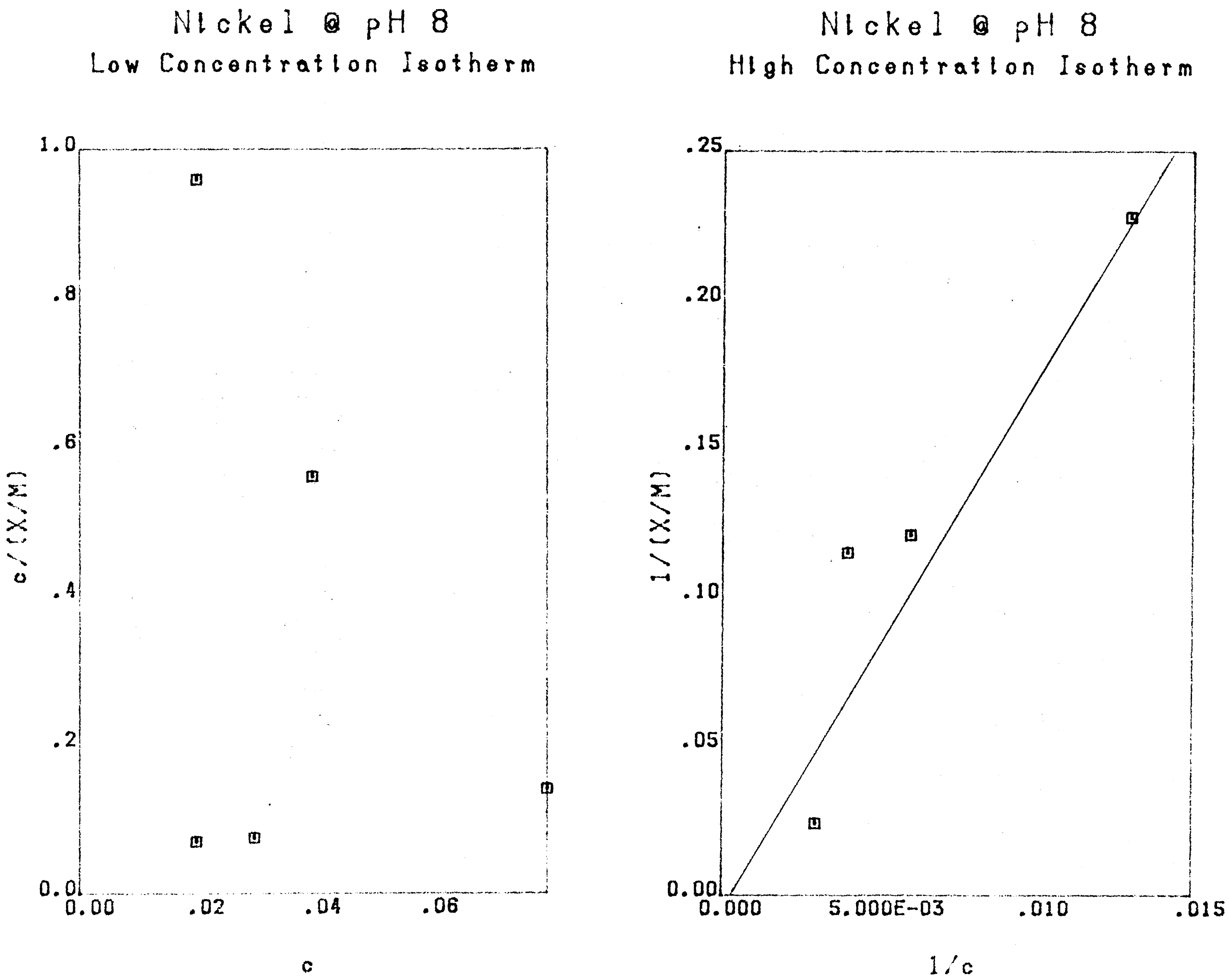
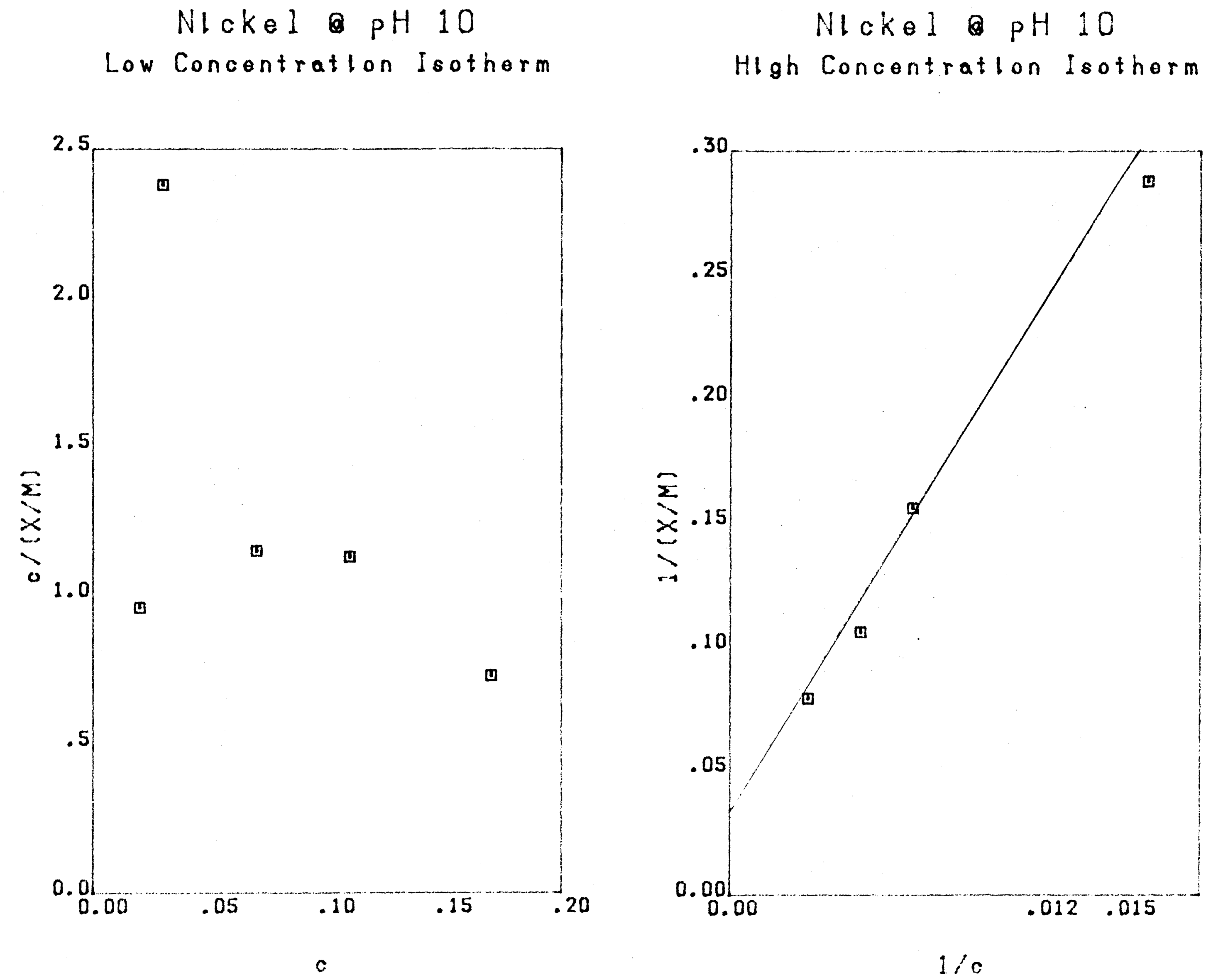


Figure 14. Nickel Isotherms At pH 8 - Adsorption Versus Concentration Remaining



Nickel @ pH 10
Low Concentration Isotherm

Nickel @ pH 10
High Concentration Isotherm

Figure 15. Nickel Isotherms At pH 10 - Adsorption Versus Concentration Remaining

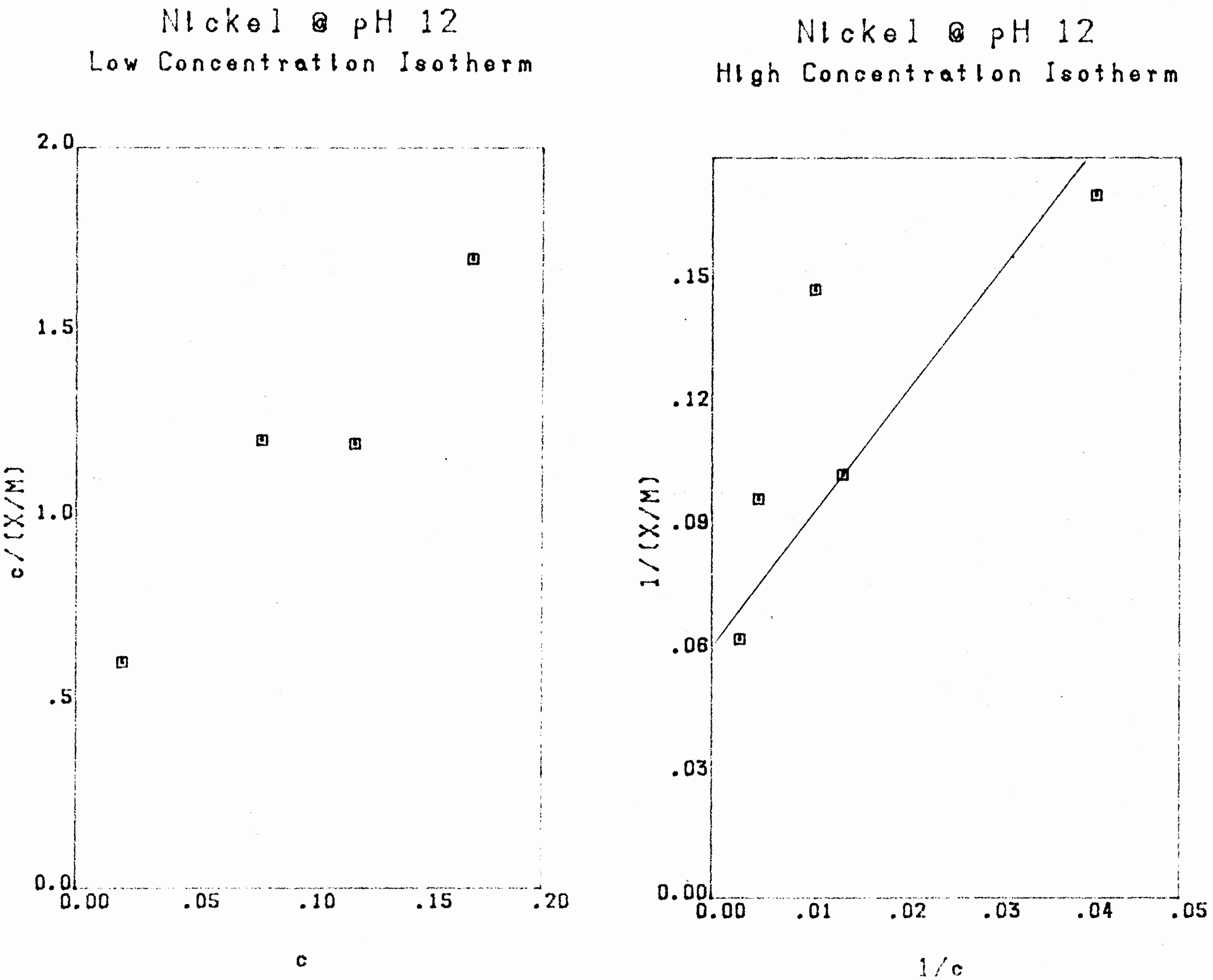


Figure 16. Nickel Isotherms At pH 12 - Adsorption Versus Concentration Remaining

detection limits of the analytical instrument. As an example of the problems encountered in attempting to fit the low concentration range data to an isotherm, Figures 5-16 show the results from the attempt to fit the data to the Langmuir low isotherm.

Figures 17 through 20, plotting effluent concentration versus time, show breakthrough curves for the column studies using both tapwater and wastewater. Tables III and IV show the relationships between column runs, illustrating breakthrough times, saturation times and weight of metal adsorbed given the seperate conditions of each run. In every case nickel breakthrough occurred first in both individual and mixed metal trials. Nickel also reached saturation ahead of copper. Therefore, the carbon demonstrated a greater adsorptive capacity for copper than for nickel in the column studies and nickel demonstrated the greater mobility.

Figure 21 shows the results investigating soluble BOD uptake by the carbon. These results show that the BOD in the effluent from the column increased over time, while the BOD in the influent remained constant at 27 mg/l. It also shows the column adsorbed 1.27 mg/gr soluble, biodegradable organics during the first 120 minutes of the trial.

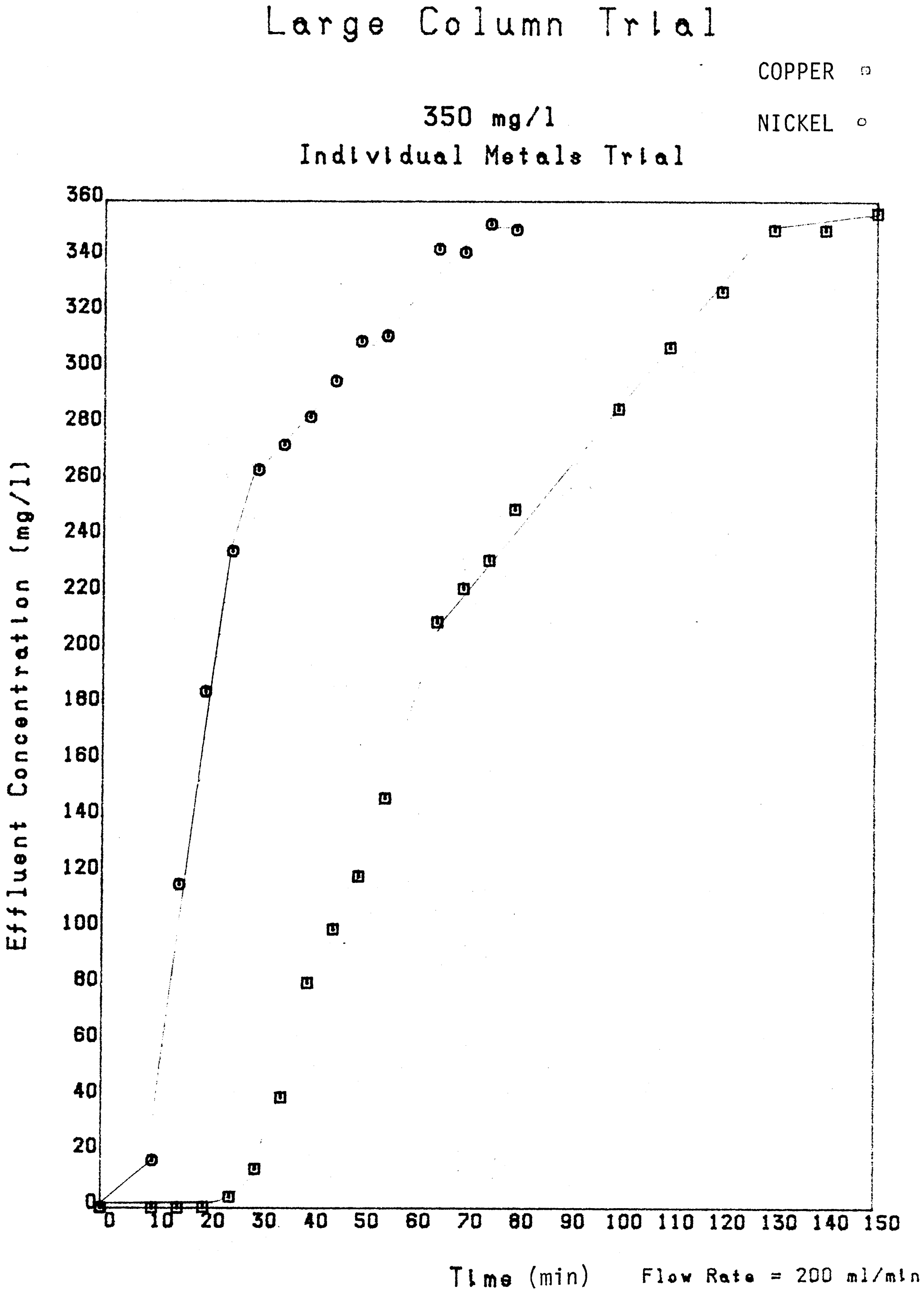


Figure 17. Large Column Trial - 350 mg/l Individual Metals Effluent Concentration Versus Time

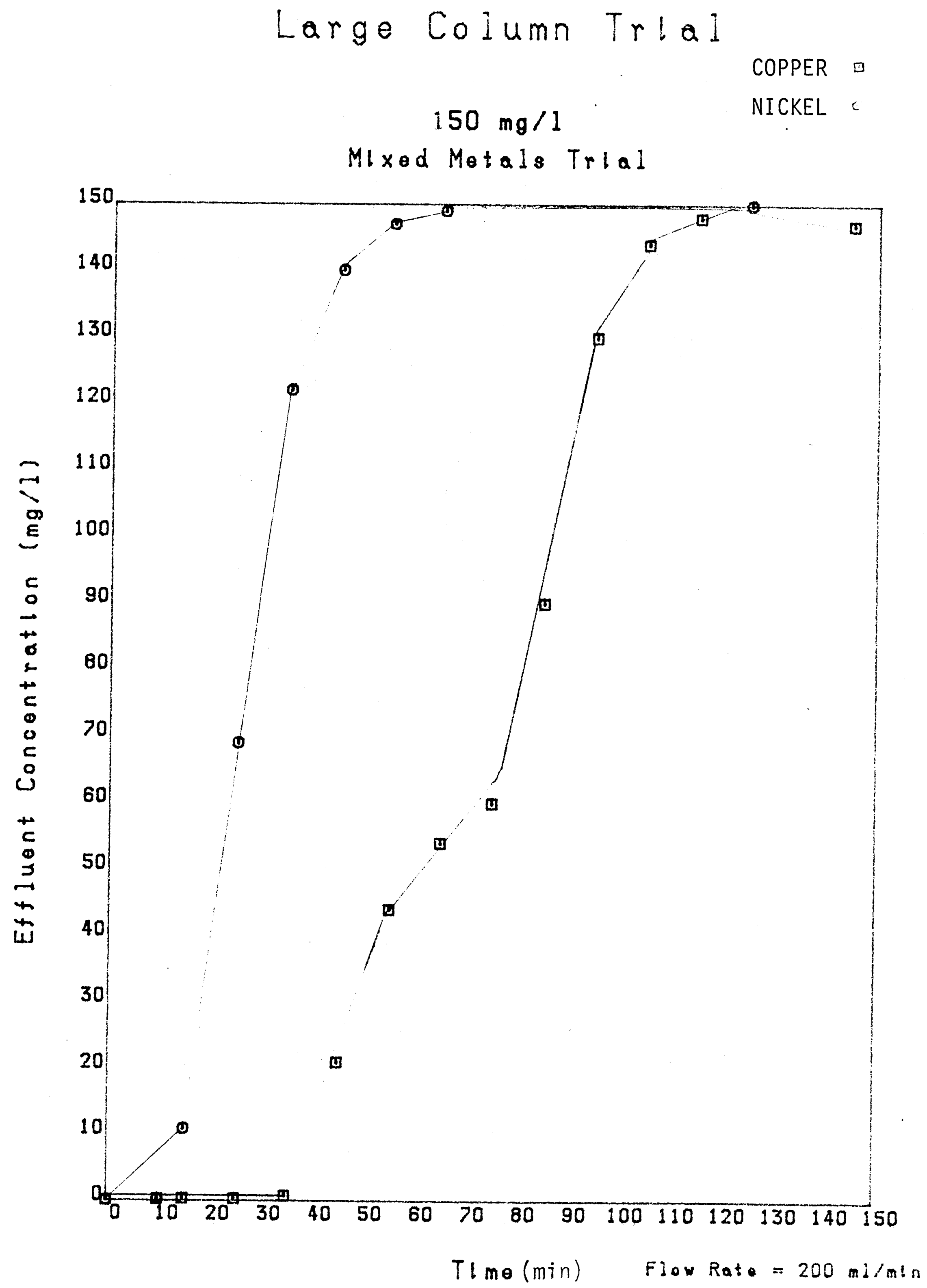


Figure 18. Large Column Trial - 150 mg/l Mixed Metals Effluent Concentration Versus Time

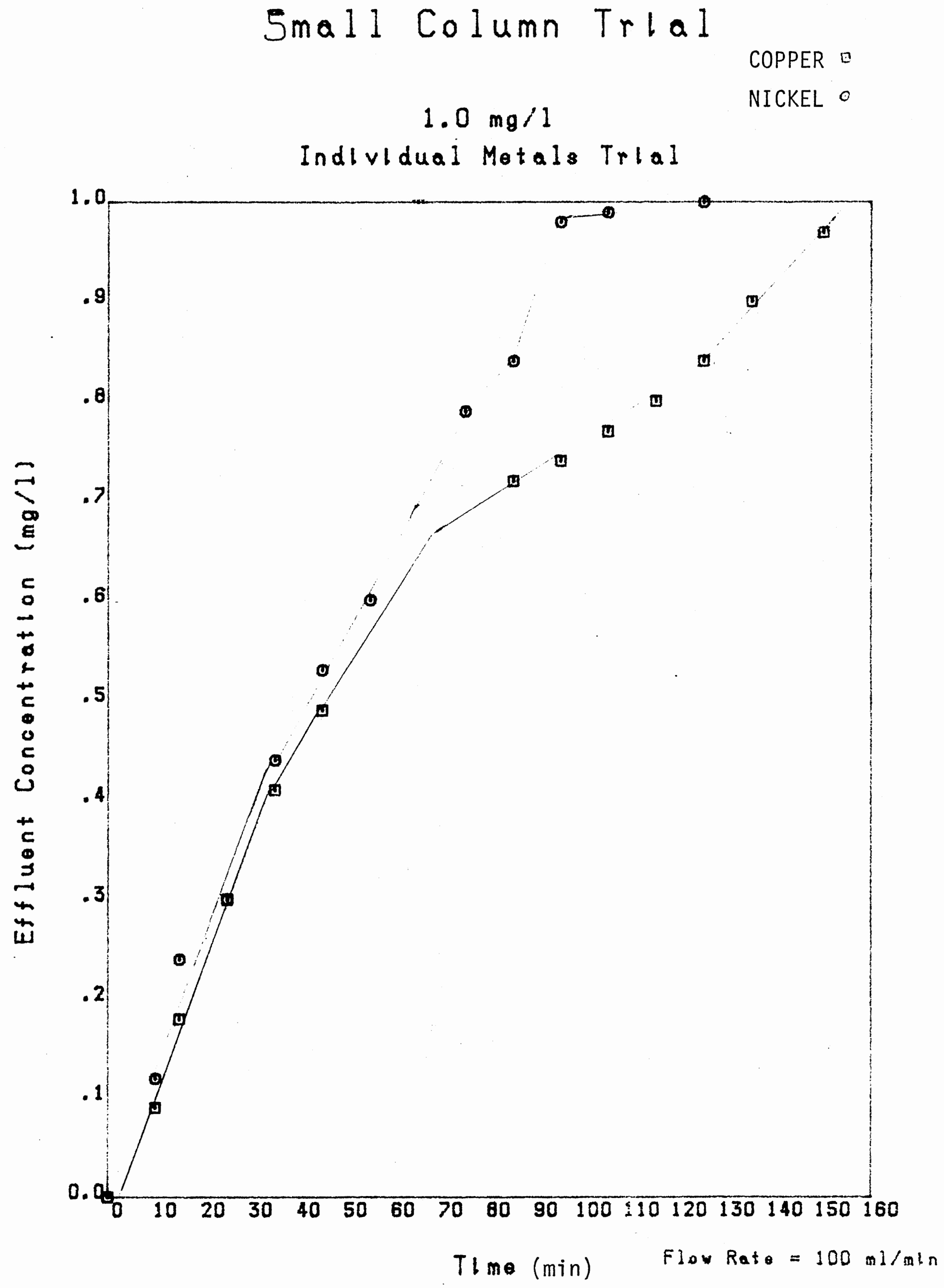


Figure 19. Small Column Trial - 1.0 mg/l Individual Metals Effluent Concentration Versus Time

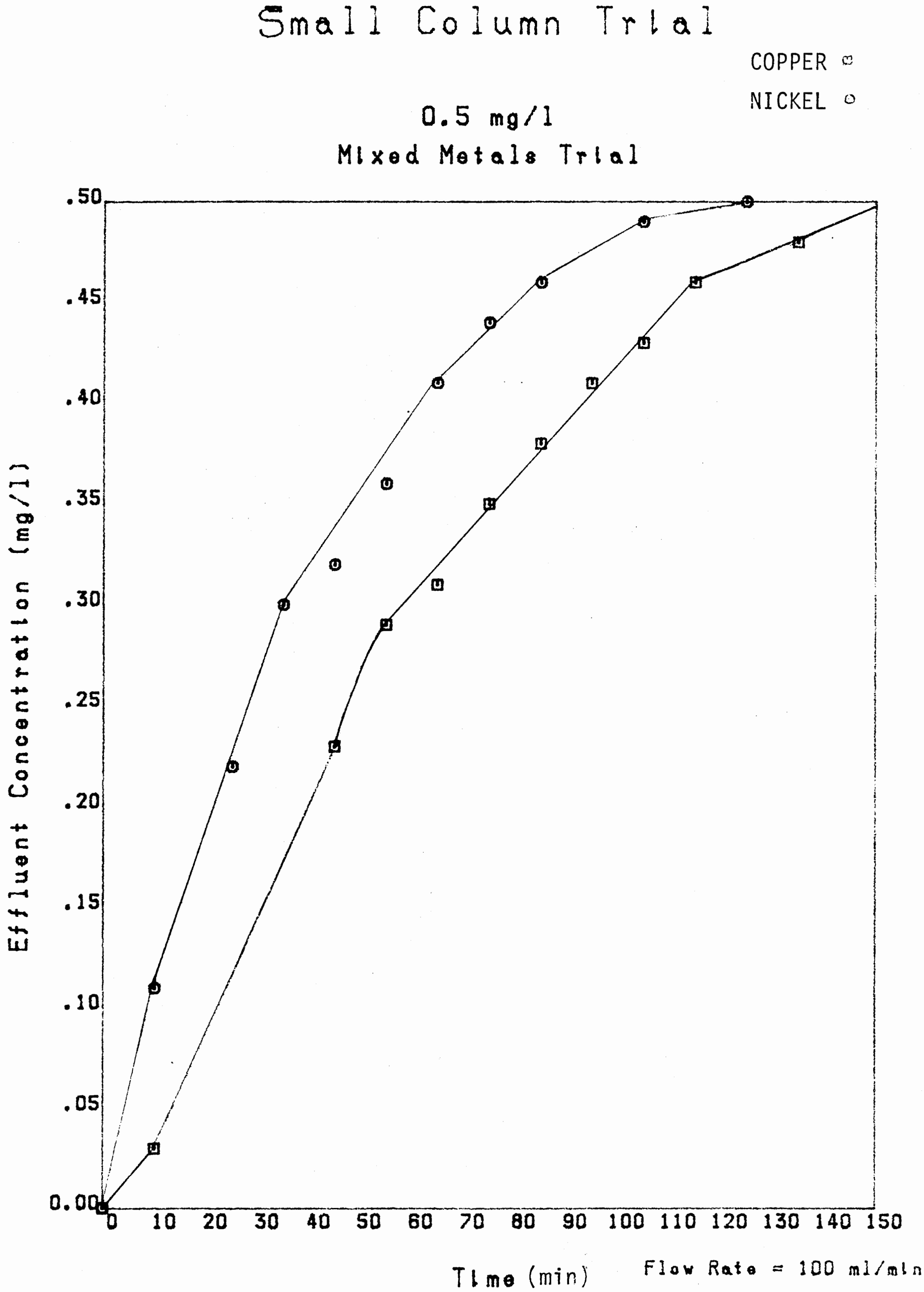


Figure 20. Small Column Trial - 0.5 mg/l Mixed Metals
Effluent Concentration Versus Time

TABLE III

LARGE COLUMN SUMMARY

	Solubilized Metals in Tap Water			
Trial Description	Breakthrough Time (min)	Saturation Time (min)	Weight of Metal Ads at Brkthrgh mg/gr	Weight of Metal Ads at Saturat mg/gr
350 mg/l Ni Individual Metals Trial	12	50	0.97	4.07
350 mg/l Cu Individual Metals Trail	32	105	2.58	8.47
150 mg/l Ni Mixed Metals Trial	12	38	0.41	1.30
150 mg/l Cu Mixed Metals Trial	45	92	1.53	3.14
Mixed Metal Summary 300 mg/l Total	-	-	1.94	4.44

Trial Condition Summary

pH = 3.5
Temp = 23°C
Carbon Weight = 860 grams
Flow Rate = 200 ml/min
Contact Time = 10.50 min

TABLE IV

SMALL COLUMN SUMMARY

Trial Description	Breakthrough Time (min)	Saturation Time (min)	Weight of Metal Ads at Brkthrgh mg/gr	Weight of Metal Ads at Saturat mg/gr
1.0 mg/l Ni Individual Metals Trial	10	85	0.010	0.085
1.0 mg/l Cu Individual Metals Trial	10	140	0.010	0.140
0.5 mg/l Ni Mixed Metals Trial	8	82	0.008	0.082
0.5 mg/l Cu Mixed Metals Trial	12	115	0.012	0.115
Mixed Metal Summary 1.0 mg/l Total	–	–	0.020	0.197

Trial Condition Summary

pH = 6.8
Temp = 23°C
Carbon Weight = 100 grams
Flow Rate = 100 ml/min
Contact Time = 1.860 min

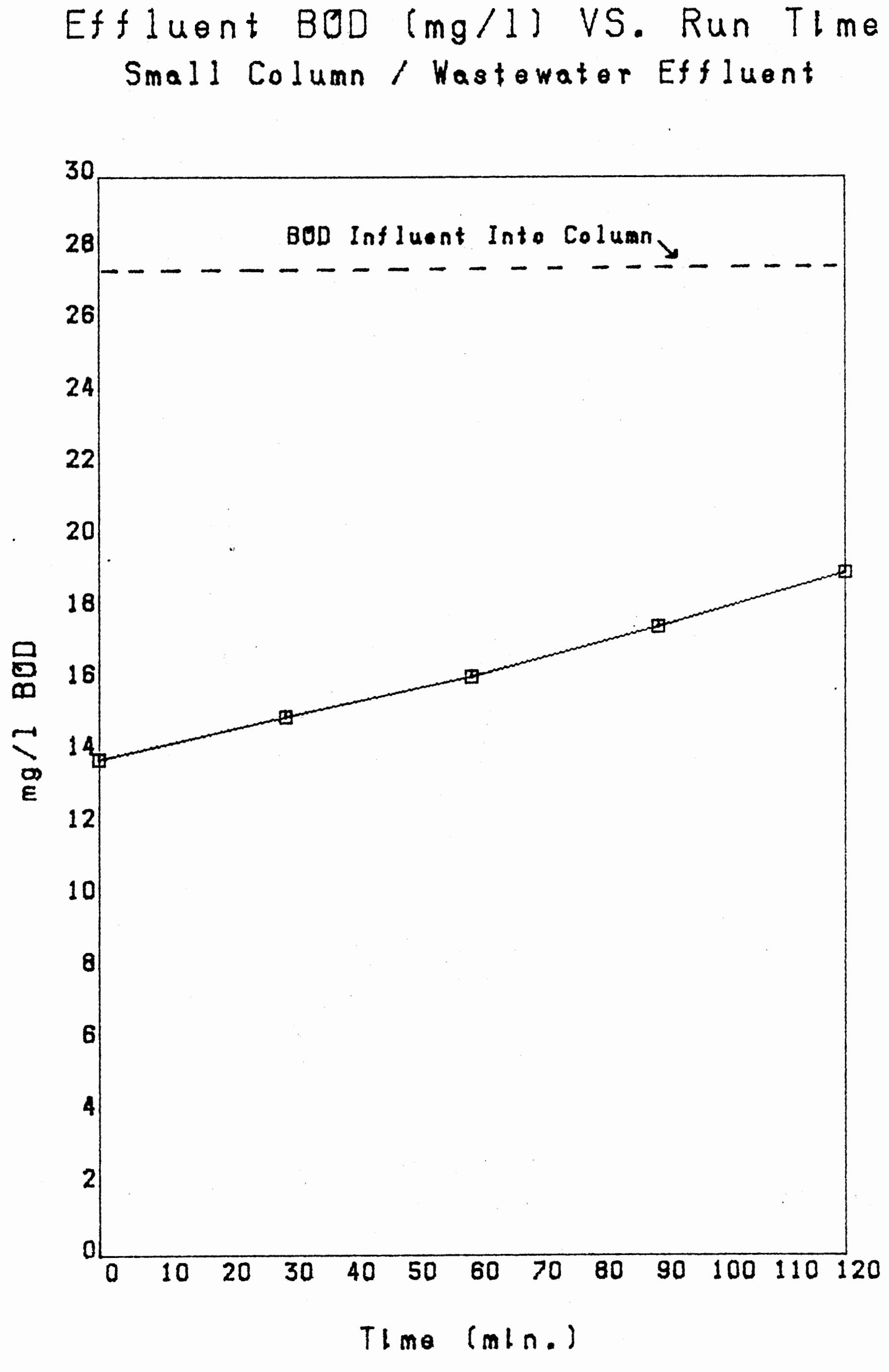


Figure 21. Effluent BOD (mg/l) Versus Run Time - Small Column Secondary Wastewater Effluent - BOD Versus Time

CHAPTER V

DISCUSSION

Simply stated, the purpose of this study was to examine the relative adsorptive properties of copper and nickel on activated carbon. The results, gathered from both batch and column studies, were influenced by the initial concentration of metals, the pH of the solvent, total time of contact with the carbon and type of solvent the metals were mixed with; i.e., deionized water, tap water or secondary municipal wastewater effluent. The significance of each of these factors as related to the practical applications of activated carbon for removal of copper and nickel are appropriate areas for discussion.

Batch Studies

The literature stated that the adsorption capacity of the activated carbon generally increases as the pH decreases (48). However, this effect is influenced heavily by precipitation at pHs above 6 for copper and above 9 for nickel (31, 43, 48). In the concentration range of 1-50 mg/l for both copper and nickel, there was no apparent trend of increasing adsorption with decreasing pH. For copper in the concentration range of 100-600 mg/l, there is an obvious trend of increasing adsorption with decreasing pH for pH values of 12-4. In all cases, X/M at a pH of 2 was less than at a pH of 4. Maximum adsorption of copper in this study occurred at a pH of 4. Decreased sorption of copper at a pH of 2 could have resulted from an increase in competition of copper and H+ for adsorptive sites. This phenomena of metal ion-hydrogen ion competition has been observed in other studies (58). For nickel at concentrations of 100-600 mg/l the observed trend is opposite of that for copper in that maximum sorption occurs at the highest pH values for all cases except the 400 mg/l concentration.

In summary, copper at high concentrations was the only case in which increasing sorption with decreasing pH was observed. There are several possible reasons for this. It should be remembered that precipitation is a competing mechanism at higher pH values and could have affected the sorption reaction. In addition, the relationship between adsorption and pH was described as being general and possibly does not apply to all metals. Cadmium is a notable exception. Huang and Smith (58) and Huang and Wirth (59) have investigated the removal of cadmium from metal plating wastes using activated carbon. In studies conducted to determine the effects of pH on cadmium removal, it was pointed out that because of pH affects the formation and distribution of the various species of cadmium, adsorption characteristics may vary with the pH. Figures 1 and 2 indicate that the species of copper and nickel do definitely vary with pH and therefore, because different species are being sorbed at different pH values, there may be no definitive trend. Similar to the behavior of copper and nickel in this study, the adsorption of cadmium in Huang and Smith's (58) study varied with the pH, yet showed maximum adsorption at a specific pH of 6.7.

The effects of concentration on adsorption were distinct. Table II shows this most graphically as the X/M values increased from the lower to higher concentrations with copper and nickel at all pH ranges.

Huang and Smith (58) also pointed out that increasing the cadmium concentration increased adsorption over the entire pH range (2-10) they studied.

Batch studies using activated carbon not only illustrate the extent of adsorption and factors affecting it, but are also commonly used to predict the usefulness of the carbon in removing a given waste in a "once through" column system. The batch studies accomplish this by the following:

1. Given a general idea of how effectively carbon will adsorb impurities present in a given wastewater.

2. Predicting the maximum quantity of impurities the carbon will adsorb.

3. Giving a rough estimate of the economics of using activated carbon for column removal of impurities by estimating the volume of carbon required per volume of wastewater and predicting the total cost of the required operation in terms of capitol costs and operation/maintenance costs (60).

The batch studies yield the values of X/M for a given concentration and pH (Table II). The X/M value for a given concentration relates to whether or not a column system would be financially feasible to construct. ICI Corporation of Wilmington, Delaware, a company experienced in pilot studies and constructing these columns, has set the following general guidelines for relating X/M values to the economic advisability of building activated carbon columns for removal of a given contaminate.

1. If X/M at a given concentration is greater than 0.10 (10 percent), a carbon system is likely to be economically feasible and carbon column tests should be considered.

2. If X/M at a given concentration is between 0.05 and 1.0, a carbon system is questionable, but the carbon tests should be considered.

3. If X/M at a given concentration is less than 0.05 then a carbon system does not appear to be economically practical (54, 60).

In comparing the X/M values for both copper and nickel at all pH's and concentrations, and relating them to the 0.10 limit as previously discussed, it appears that at concentrations below 25 mg/l for both metals, carbon columns would not appear to be given consideration for column studies, and may not be economically practical. However, at concentrations at the greater than 25 mg/l, column systems appear to be feasible as previously discussed and the concept that this term is used as a general guideline for defining the practicality of future studies as predicted for finally building a system (54, 60).

When discussing the batch systems and the results obtained, it is important to distinguish between how the results are interpreted and how batch and column systems relate to each other. Table V shows the values of c, or concentrations remaining in solution, in the batch systems. Although the X/M was uniformly below 0.10 at low concentrations, a look at the actual adsorption values yields an impressive record with respect to removal by the batch systems. Nearly all the values are below the discharge limitations of 1.00 gm/l (61, 62) and many are below even drinking water limits of 0.1 mg/l (4). These results appear, then, at least on a preliminary basis, to indicate that batch systems for very small volumes and small metal concentrations are possible and quite efficient for removal of copper and nickel, if these systems were to be justified economically and practically on a volume and cost basis.

TABLE V

METAL CONCENTRATION REMAINING VERSUS INITIAL CONCENTRATION AND pH

	Copper Concentration Remaining (c) vs. Init Concentration & pH					
Conc	1	2	5	10	25	50
pH 2	0.00	0.03	0.12	0.32	3.19	10.94
pH 4	0.00	0.01	0.66	0.75	0.29	-
pH 6	0.00	0.05	0.52	0.92	2.36	-
pH 8	0.00	0.01	0.61	1.56	0.82	0.26
pH 10	0.01	0.01	0.07	0.52	0.39	0.60
pH 12	0.00	0.01	0.02	0.11	0.38	-
	Nickel Concentration Remaining (c) Vs. Init Concentration & pH					
pH 2	0.65	0.87	1.00	1.21	2.89	4.11
pH 4	0.03	0.04	-	0.03	0.10	0.67
pH 6	0.07	0.08	0.14	-	0.13	0.15
pH 8	0.02	0.01	0.04	0.02	0.03	0.08
pH 10	0.09	-	-	0.07	0.11	0.17
pH 12	0.02	0.03	0.08	0.17	-	0.19

Column Studies

The most obvious discovery from the results of the column studies was actually a re-confirmation of information found in the literature that states that nickel is much more highly mobile than copper (31, 44, 53). The breakthrough curves (Figures 17, 20) demonstrated that the carbon had an affinity for copper over nickel at a ratio of at least 2:1 in the column studies, even though the ultimate affinity for nickel was shown to be greater than copper in the batch studies.

In the large column individual metals trial (Figure 17), the curves assumed nearly identical shapes for both copper and nickel. However breakthrough for nickel occurred 20 minutes before copper and exhaustion occurred 73 minutes before copper. The results for the mixed metals trial in the large columns (Figure 18) showed that breakthrough occurred for nickel at the 12 minute point and breakthrough for copper occurred at the 40 minute point. In this trial, exhaustion occurred for nickel 54 minutes before copper.

Table III shows the large column summary for individual and mixed metal trials. It shows the carbon adsorbed 2.08 times more copper than nickel in the individual metals run and 2.41 times more copper than nickel in the mixed metals run at saturation. Table III also shows that the carbon adsorbed 1.9 times more metal during the individual metals trial than it did during the mixed metals trial. There are several possible reasons for this behavior. The most obvious reason is, of course, the concentration of each metal during the mixed metals trials was one half that of the concentration during the individual metals trial.

Another possible reason is rollover (54). Rollover is defined as displacement of one contaminant by another on the surface of the carbon.

As two contaminant species flow through a column, a more strongly adsorbed species may displace the less strongly adsorbed component, forcing it deeper into the bed, and utlimately out. If this were occurring, then the competition for sites would result in the nickel breaking through first and at a weight per weight value less than if nickel were in the solution alone. This was in fact observed, although the lower weight to weight value could also have been the result of the lower concentration. Copper should then breakthrough last; and because this competition was occurring at a uniform level (as the metals were equally mixed), and because the copper did not replace every nickel site, the total displacement or rollover would result in a curve roughly equivalent to that of the curve represented by the metal alone in solution (54). This, too, was observed.

Table IV shows the results of the small columns trial in which wastewater was the solvent for the metals. Figure 19 shows the small column with 1.0 mg/l metals run through the columns individually. Breakthrough occurred for both copper and nickel at the 10 minute point, but saturation occurred 55 minutes later for copper than for nickel. The mixed metals trial (Figure 20) showed breakthrough 4 minutes earlier for nickel than copper, and saturation for nickel in the mixed metals trial occurred 33 minutes earlier than for copper.

The weight per weight adsorption for the metals at saturation showed the carbon adsorbing 1.64 more copper than nickel on an individual metals basis and 1.40 times more copper when the metals were mixed. However, when comparing the total metals weight adsorbed between the individual and mixed metals trials, it appeared that the carbon adsorbed slightly more metal in the mixed metals run than when run individually in the small column runs.

It was clear at this point that the adsorption characteristics had changed from the metals at high concentrations applied to the carbon in tap water when compared to the characteristics of the metals applied to the carbon at low concentrations in wastewater effluent. The explanation for this observation is probably that there is competition for sites by the other myriad contaminates in the effluent and it is this point which is essential in considering what is happening in the small columns.

The carbon adsorbs anything that is highly polar or will physically fit into its pores. Its adsorption is also determined by pore size, distribution, total surface area, wetting characteristics, polarity, pH and contact time (57, 63). Given this wide range of variables and the highly complex nature of what is in the waste effluent, it becomes difficult if not impossible to precisely or completely identify the exact processes that are occurring on the surface of the carbon and what is happening to the metals.

However, it is very likely that aside from the billions of individual molecular interactions, several macromolecular processes can be identified with the substantive processes that are finally observed. Thus, it is probably sufficient to maintain an awareness of the micromolecular processes while understanding that in the large sense, though the final results will be highly influenced by these, they will not be completely overshadowed by that primary influence exerted by the summation of all the reactions and the physical priorities finally exhibited.

Figure 21 shows the results of the secondary effluent BOD when run through the small columns. The BOD increased in a linear fashon, removing from 13.5 mg/l BOD at the start of the trial to 10 mg/l at the

120 minute point into the trial. The total BOD adsorbed was 1.27 mg BOD per gram of carbon. This was 9.07 times the amount of copper during its individual run and 6.44 times the total metals adsorbed by the carbon during the mixed metals run. Again, the influent concentration of the BOD must be considered (27 mg/l BOD) and compared to the metals concentrations (1.0 mg/l individually and 0.50 mg/l mixed). But it is clear that the competition exists and given a highly polar, more adsorbable, more concentrated organic loading, the carbon will almost certainly perferentially adsorb the BOD as was observed.

General Analysis of Data

Although the data from each study presented interesting results, it is difficult to make too many comparisons between data from different studies because of widely different conditions of each trial such as pH, concentration, contact time, nature of solvent and competition between metals or other contaminates with the metals for available sites of adsorption.

However, an interesting relationship observed is the comparison of the batch X/M values at the 24 hour point (Table II) to the weight of metal adsorbed at saturation in the carbon column (individual metal at 350 mg/l) as shown on Table III. In an approximate interpolation between the values on Table II (350 mg/l at a pH of 3.5) for both copper and nickel, it is notable that the X/M value in the table approximates what was observed in the columns at 8.47 mg/gr for copper and 4.07 mg/gr for nickel, even though at nearly all other pH ranges and concentrations, the carbon adsorbed nickel at higher values.

Although the contact times accounting for these results were widely different (24 hours in the batch studies and 10.5 minutes in the large column studies), it is significant to note that the adsorption weights were so similar. This indicates that the adsorption process in this case occurred within a very short period of time; at least a majority of the process occurred within 10 minutes.

It is also interesting to note the comparison of uptake of copper and nickel in this study to that of Maruyama et al. (53). In their study, using secondary effluent, the capacity of carbon to adsorb copper was 0.264 mg/gr. In this study, the value was 0.120 mg/gr for nickel, their value for capacity adsorbance was 0.04 mg/gr and our value of 0.085 mg/gr. This comparison, again, is valid only if the conditions of his study were similar to those of this study in pH, concentration and type and quality of solvent.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Both copper and nickel were removed, to some extent, from tap water and secondary municipal wastewater effluent by granular activated carbon in both batch and column systems. The relative removal rates were different, with copper being removed most efficiently by the carbon than nickel in the column systems. However, nickel was removed more efficiently in the batch systems.

Batch systems were shown to be highly effective in removing small concentrations of copper and nickel in given volumes with long contact times. However, column systems were found to be effective, in the short term, in removing large concentrations (350 mg/l) of the metals. Column systems were found to be quite ineffective for removing small concentrations (1.0 mg/l) from secondary wastewater effluent, probably due to the competitive effects of organics and other contaminants in the water.

The predictive abilities of isotherms from the batch studies were found to be quite good as was their ability to predict relative affinity for each metal by the carbon.

Competition for carbon sites was probably present when copper and nickel were mixed in the same solution and introduced into the columns. It was evident by less uptake by the carbon attributed to rollover.

The effects of concentration were most pronounced and deomonstrated that as the concentration increased, the adsorption increased in every case investigated. The effects of pH on the adsorptive process was not so clearly evident, with adsorption occurring more efficiently at different pH's for each metal. This phenomenon was probably due to the effects of the different species of metal present and sorbed at different pH values.

Finally, it should be noted that the feasibility of using activated carbon as the exclusive removal mechanism for these metals may not be attractive or financially acceptable. As stated previously, precipitation occurs at pH values higher than 7 and at concentrations greater than 10 mg/l. This has two primary implications for the adsorptive process using activated carbon.

1. Precipitation could be utilized as a method for metal removal that is less expensive than using activated carbon. After pre-treatment by precipitation, the effluent could be sent to columns or batch reactors for polishing.

2. Improper pH adjustment or monitoring before or within the columns can radically influence uptake by coating the carbon with precipitate or even clogging the carbon itself.

Recommendations

The recommendations are:

1. Examine specific relationships between precipitation and the adsorptive process at all concentrations with both copper and nickel.

2. Examine the effects of Biochemical Oxygen Demand on the adsorption of copper and nickel by relating BOD concentration to the amount of metal adsorbed per unit weight of carbon.

3. Determine the most effective combination of removal of copper or nickel by precipitation followed by adsorption on activated carbon.

4. Determine the exact relationships of adsorption of copper and nickel vs. pH and the effect of precipitation on this process.

5. Perform a series of studies with all conditions kept the same, such as concentration, column size, pH, metal concentration and solvent.

6. Perform studies using column staging with low metal concentrations in secondary effluent to investigate the effects of greater depth and contact time that would perhaps enhance the adsorption of copper and nickel and trap the more polar, concentrated organic contaminants in the lead columns.

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VITA 2

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