HEAVY METALS REMOVAL FROM WASTEWATER BY PEAT ADSORPTION

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ABSTRACT

A constructed wetland is an effective method to remove oil, organic matter, nitrogen, phosphorus and heavy metals from wastewater. Peat is a polar and highly porous plant material formed in wetland areas. Removal of oil, color and treatment of domestic wastewater by peat have been well documented. The mechanisms of pollutant removal by peat include adsorption, complexation, ion exchange and precipitation. Limited research indicates the feasibility of the removal of heavy metals by peat.

The primary objective of this project was to study the peat adsorption of several heavy metals from wastewaters such as landfill leachate and acid mine drainage in which large amounts of heavy metals are typically present. Copper, nickel and zinc were chosen to represent heavy metals in this study.

A series of batch studies were performed to test the peat adsorption capacity of heavy metals. Peat was used as the adsorbent and copper, nickel and zinc, and a mixture of the three metals, were used as the adsorbates. It was found that the three metals were strongly adsorbed by peat, and that adsorption generally followed the Langmuir isotherm and/or the Freundlich isotherm. A dynamic column experiment was conducted by feeding solutions containing fixed concentrations of the mixture of copper, nickel and zinc through a peat column. A continuous removal of 98% of each heavy metal was achieved throughout 66 day column experiment.

A chemical equilibrium model (MINTEQA2) was also applied in the project. It was found that the potential for precipitation existed in a buffered column feed solution but not in an unbuffered feed solution. The model also indicated that heavy metals removal was possibly hindered by the complexation with dissoloved organic matter (DOM).

DEDICATION

To my parents - for always encouraging me to pursue more education

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CHAPTER 1

INTRODUCTION

1.1 Background on Passive Wastewater Treatment Methods

1.1.1 Wetland Overview

Due to the growing requirements of resources and energy conservation in environmental protection and management, engineering of "natural systems" is receiving increased world wide attention for wastewater treatment. "Natural systems" for wastewater treatment generally include composting and direct land application of solid waste (especially yard wastes) and sludges, and large varieties of land treatment systems such as slow-rate irrigation, rapid filtration and grass filtration, ponds, aquaculture and aquatic plant systems, as well as both natural and constructed wetland systems (Bastian et al., 1993). Many research projects have focused on wetland systems during recent years.

Wetlands can be described as areas which are periodically inundated or saturated by surface or groundwater with a frequency and depth sufficient to promote the growth of specific vegetation adapted to life in saturated soil conditions (Hammer et al., 1989; Reed, 1990). Two basic types of wetlands are classified as natural wetlands and constructed wetlands (Reed, 1990).

Natural wetlands are ecosystems which consist of a variety of natural plant assemblages (Reed, 1990). Historically, natural wetlands have been used for receiving wastewater discharges. However, because they are characterized by extreme varieties of functional components, it is difficult to characterize wastewater treatment performance and apply results from one geographical area to another. Therefore, the extent of treatment capacity is often largely unknown. Unlike natural wetlands, constructed wetlands for wastewater treatment can be designed and built according to experimental results and with a much greater degree of control. In addition, they offer several other advantages such as site selection, flexibility in sizing, and most importantly, control over the hydraulic paths and retention time (Brix, 1993).

Constructed wetlands are complex man-made ecosystems which contain a saturated substrate, emergent and submergent vegetation and water. Constructed wetlands are generally specifically designed, constructed, and operated to optimize the physical, chemical and biological processes for wastewater treatment in a more controlled environment and more consistent manner than that occurring in the natural wetland environment (USEPA, 1987, Hammer et al., 1989). In the past few years, constructed wetlands have been widely used as wastewater treatment systems through out the U.S.. More than 140 municipal constructed wetlands systems were inventoried in the U. S. (Freeman, 1993).

Constructed wetlands can be divided into two general types: Free Water Surface (FWS) wetlands and Vegetated Submerged Bed (VSB). In FWS wetlands, the water level is above the ground surface so that the majority of water flow is over the top of sediment and through the above ground plant zone. Vegetation is rooted and emergent above the water surface level, planted, and allowed to colonize freely. However, in VSB wetlands, the water level is below ground, water flow passes through the soil or gravel bed while roots penetrate to the bottom of the bed; this type of wetland is designed to conduct water through the bed of the system in order to make wastewater contact with the plant roots

(Reed, 1990). Soil and soil-like materials are the essential substrates in constructed wetlands. Those substrates can support the growth of wetlands plants and microorganisms. Generally, FWS systems require a base composed of a natural or constructed impermeable layer of clay, compacted *in situ* soil, geotechnical materials or asphalt. The desired permeability of this layer ranges from 10^{-6} to 10^{-7} m/s (USEPA, 1988). Typical materials used as substrate media include natural soils or soil mixtures, sand, gravel, crushed rock, mushroom compost, peat, or any combination of these materials.

Due to the nature of constructed wetlands, they have several advantages compared to conventional secondary and advanced wastewater treatment systems. Particular among these are low cost of construction and maintenance and low energy requirements. Being "low-technology" systems, they can be established and run by relatively untrained personnel, and the systems are usually more flexible and less susceptible to variations in loading rate and decreased performance during winter in temperate regions than conventional systems (Brix, 1993).

1.1.2 Pollutant Removal in Constructed Wetlands

1.1.2.1 Pollutant Removal Mechanisms in Constructed Wetlands

It is well reported that wetlands have the ability to remove pollutants such as acidity, metals, pathogens, trace organics, and to a lesser extent, nitrogen and phosphorus in wastewater, acid mine drainage, and landfill leachate (Witthar, 1993). Mechanisms of pollutant removal in constructed wetlands systems are the combination of physical, chemical and biological processes including sedimentation, adsorption, volatilization, chemical reactions, natural decay and bacterial conversion (Tchobanoglous, 1993).

Suspended solids in wastewater can ultimately settle to the bottom of wetlands. Settling processes can be enhanced by flocculation and hindered by the ambient turbulence (Tchobanoglous, 1993). Not only can suspended solids be removed through sedimentation in wetlands, but organic matter or biochemical oxygen demand (BOD), and pathogens can be accumulated on the sediment surface and therefore removed by sedimentation (Brix, 1993).

Adsorption and precipitation reactions play very important roles in pollutant removal in constructed wetlands. Many chemical compounds tend to attach onto solid substrates in constructed wetlands. Phosphorus reacts with aluminum, iron, calcium and clay minerals in soil and tends to be removed by adsorption and precipitation in constructed wetlands (Brix, 1993). Removal mechanisms for toxic chemicals such as heavy metals, which are present in large amounts in acid mine drainage, landfill leachate and some in groundwater, include adsorption, complexation, and precipitation.

Volatilization may be a major mechanism in systems where liquid and solids vaporize and escape to the atmosphere. In constructed wetlands, for example, ammonium conversion to ammonia gas contributes to the nitrogen removal.

Chemical reactions such as hydrolysis, photolysis and oxidation-reduction are also important in constructed wetlands. Hydrolysis reactions occur between pollutants and water. Solar radiation is known to activate some chemical reactions. Radiation in the near-UV and visible range is known to cause the breakdown of a variety of organic compounds (Tchobanoglous,1993).

Bacterial conversion under aerobic and anaerobic conditions is perhaps the most important process in the transformation of contaminants discharged to constructed wetlands. Organic solids in wastewater can be decomposed by microorganisms resulting in the exertion of carbonaceous BOD and nitrogenous BOD. The bacterial transformation can also remove some toxic organic compounds (Tchobanoglous, 1993).

1.1.2.2 Case Histories of Pollutant Removal in Constructed Wetlands

Case histories of pollutant removal in constructed wetlands are well documented. For example, Litchfield and Schatz (1989) reported the performance of constructed wetlands in treatment of oily wastewater for a refinery plant of Amoco oil company located in Mandan, North Dakota. The parameters detected were BOD, COD (Chemical Oxygen Demand), NH_3-N, sulfides, phenols and TSS (Total Suspended Solids). The processes consisted of primary lagoon and pond systems. Reduction in parameter concentrations of from 36 to 99.9% were obtained in the primary lagoon. Pollutant concentrations were further reduced by 70-100% in the pond system. Another case (Freeman, 1993) which showed the good removal of BOD, TSS, and NH_3 in municipal wastewater was a VSB system located in Bear Creek, Alabama. BOD, TSS and NH_3 were about 13, 60, and 10.7 mg/L, respectively, in inflow and achieved <1, <3, and <1.8mg/L, respectively, in outflow. The excellent removal was attributed to the proper loading of the system, low nutrient application rate and shallow gravel depth.

Heavy metals are often present in acid mine drainage and landfill leachate. Constructed wetlands have demonstrated the successful removal of heavy metals. A case study was reported by Eger et al. (1993). An acid mine drainage located at LTV Steel Mining Company's Dunka Mine in northeastern Minnesota contained high concentrations of nickel, copper, cobalt, and zinc. Nickel was the major trace metal in the acid mine drainage, with a concentration about 3 to 30 mg/L, while copper, cobalt, and zinc were generally less than 5% of the nickel concentration. Over a year of applying wetland treatment to reduce the heavy metals concentrations, overall reduction in nickel mass ranged from 39% to 86%. Concentrations of copper, cobalt, and zinc were also reduced by from 83% to 94% in short-term tests.

1.2 Wastewater Treatment by Peat

Peat is partially fossilized plant matter formed in wetlands where low oxygen levels cause the accumulation of plant matter to occur more rapidly than its decomposition (Couillard, 1994). As a polar and highly porous material, peat can adsorb many elements such as copper, nickel, zinc, lead, and mercury (Couillard, 1994). In addition, it is inexpensive and easy to use. Bench-studies and laboratory experiments have shown efficient metals removal using peat to treat a variety of wastewaters, including municipal and residential sewage, acid mine drainage, industrial discharges, stormwater discharges and landfill leachate.

1.3 Goal of the Project

The objective of this project was to quantify the adsorption capacity of a Canadian sphagnum peat for heavy metals. Copper (Cu), nickel (Ni), and zinc (Zn) were selected as representative heavy metals in this study, because they are the common heavy metals existed in industrial wastewater and landfill leachate. All tests were conducted on bench-scale. Batch studies were performed to analyze the adsorption capacity of peat for each different metal separately and for the three metals mixed. Different pH values in the initial solution were used to test the influence of pH on the peat adsorption capacity for heavy metals. Adsorption isotherms were developed for each batch study.

Column studies were performed to test a dynamic system with the inflow feed solution containing the same concentration (approximately 5 mg/L) of each of the three metals. The feed solution was designed to ensure that adsorption was the main removal mechanism for heavy metals by maintaining pH of from 4.5 to 5.5. Influent and effluent pH and heavy metals concentrations were measured on a daily basis during the entire column run. Total Organic Carbon (TOC) was measured selectively on samples from the batch study as well as inflow and outflow from the column study to determine how much humic acid was released during the peat adsorption processes and to quantify the effect of complexation on heavy metals removal.

A chemical equilibrium model MINTEQA2 - was also applied in this project. It was used to evaluate the distribution of chemical species in the column feed solution with buffer and without buffer and the batch studies with different metal concentrations and DOM (Dissolved Organic Matter).

The application of this project can be extended to the peat adsorption of heavy metals in wastewater treatment such as acid mine drainage, landfill leachate and industrial wastewater. The bench-study results should be valuable as a guide in any further research or in the operation of full-scale peat adsorption processes.

CHAPTER TWO

LITERATURE REVIEW

2.1 Properties of Peat

Peat is partially fossilized plant matter, generally with dark brown color. It is formed in poorly oxygenated wetlands, where the plant accumulation is greater than decomposition (Couillard, 1994). High-moor peat deposits in the area where water system was higher than the groundwater system of mineral soils. The peat used in this project was a peat mosses (Sphagnum), which is one type of high-moor peat. The two other types of high-moor peat are cottongrass (Eriophorum) and health plants (various genera of the Ericaceae) (Fuchsman, 1980). Peat mosses (Sphagnum) are the most common type of high-moor peat. The composition of peat differs from one peat bog to another, and even with the same location and depth in a given bog (Fuchsman, 1980). Generally, peat has at least 20% of organic matter content and less than 50% of ash content (Crum, 1988). The properties of peat depend on several factors, including the ambient conditions existing during its formation, the extent of its decomposition, and the method of harvesting. Although composition is essentially unchanged, a great change occurs in some properties of peat when it is removed from its natural state in the bog and is drained, air or mechanically dried, and milled or comminuted. Table 2.1 shows the elemental composition of peat based on percent of dry organic material.

Peat is a rather complex material with the principal organic components of cellulose, lignin, and colloidal humic substances resulting from incomplete decay in wetlands (Fuchsman, 1980). Lignin is defined only as the substance left after treatment

Table 2.1 Elemental Composition of Peat (% of dry organic material)

Organic element	*slightly decomposed sphagnum peat*	*Highly decomposed sphagnum peat*
Carbon	48-53	56-58
Hydrogen	5.0-6.1	5.5-6.1
Oxygen	40-46	34-39
Nitrogen	0.5-1.0	0.8-1.1
Sulfur	0.1-0.2	0.1-0.3

Source: Fuchsman, 1980

with strong sulfuric acid. Sphagnum peat in various degrees of decay may contain 20-30 percent of lignin. In general, the lignin content increases with decomposition because of its resistance to microbial action (Crum, 1988). The polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers are involved in the formation of chemical bonds (Couillard, 1994).

Humic substances consist of humic and fulvic acids. Sphagnum peat contains 5-20 percent of humic acids (Crum, 1988). Some researchers think humic acid can be regarded as originating directly from lignin, while others consider it as a microbial product derived largely from other components in the decomposing plant. Like lignin, humic acids have phenolic elements in their structure, but unlike lignin, humic acids have a high carboxylic acid content and contain significant amounts of nitrogen (Crum, 1988; Fuchsman, 1980). The characteristics of humic substances are extremely complex and their structure is not very well defined. They are a mixture of poorly biodegradable decomposition products and by-products of natural organic matter produced by both plants and animals and give a brown, yellow-brown, or black color. Humic substances have been arbitrarily divided into three diverse groups of compounds on the basis of their solubility in dilute acid and dilute base. Fulvic acids are soluble in both dilute acid and dilute base. Humic acids are soluble in dilute base but are precipitated by dilute acid. Humin is insoluble in both dilute acid and dilute base (Snoeyink & Jenkins, 1980). The gross chemical and physical properties of humic acids and fulvic acids are presented in Table 2.2. The major functional groups present in humic substances are carboxyl, carbonyl, phenolic, ether, alcohol, methoxyl, and ester.

Peat can be modeled as an organic soil which is capable of exchanging cations. The specific surface area of a sphagnum peat ranged from 11.8 m^2/g to 122.2 m^2/g for the particle size range of 150-250 μm. Microscopic studies also have revealed that partially decomposed peat is a highly polar and porous material with a porosity of approximately 95% (Couillard, 1994).

Table 2.2 Physical and Chemical Properties of Humic and Fulvic Acids

Property	*Humic Acids*	*Fulvic Acids*
Elemental composition (% by weight)		
C	50-60	40-50
H	4-6	4-6
O	30-35	44-50
N	2-4	<1-3
S	1-2	0-2
Solubility in strong acid (pH1)	Not soluble	Soluble
Molecular weight range	Few 100 to Several million	180-10,000
Functional group distribution	*Percent of oxygen in indicated functional group*	
carboxyl	14-45	58-65
phenol	10-38	9-19
alcohol	13-15	11-16
carbonyl	4-23	4-11
methoxyl	1-5	1-2

Source: Snoeyink & Jenkins, 1980

2.2 Mechanisms of Pollutant Removal by Peat

2.2.1 General Introduction

The adsorption process plays an important role in pollutant removal by peat. When the peat adsorption process is applied to large scale treatment, it is important to consider the modes of contact between solid adsorbent and the aqueous solutions. There are four primary stages in the adsorption process when using porous peat (Couillard, 1994):

1. transport of pollutants from the bulk of solution to the external surface of the peat;
2. movement of pollutant across the interface and adsorption onto external surface sites;
3. movement of pollutant molecules within the pores of the peat; and
4. interaction of pollutant molecules with the available sites on the interior surfaces bounding the pore and capillary spaces of the peat.

Several investigators have also suggested many possible interactions between heavy metals and peat, including (Couillard, 1994):

1. metallic cation exchange with H^+ ions found in the carboxyl, phenolic hydroxyl and heterocyclic groups;
2. the interaction of metallic cations to form chelate complexes with humic substance; and
3. the formation of hydrogen bonds between polyvalent cations and the hydroxyl, lignin, cellulose and hemicellulose groups within the porous structure.

Other than the adsorption process, the two main pollutant removal mechanisms are ion exchange and chelation. Chelation is the chemical process by which other complexes are formed by chemical bonds during the adsorption process. However, these interactions depend on the characteristics of the peat and those of the impurities.

2.2.2 Adsorption - Description

Adsorption is the physical-chemical process which involves the interphase accumulation or concentration of substances at a surface of interface. The process can occur at an interface between any two phase such as liquid-liquid, gas-liquid, gas-solid or liquid-solid interfaces. The material being concentrated or adsorbed is defined as the adsorbate and the adsorbing phase is defined as the adsorbent (Weber, 1972).

2.2.3 Adsorption Isotherms

Data collected during an adsorption test can be used to describe the performance of the adsorbent and yields valuable information if properly interpreted. This information can be developed from mathematical relationships which describe the equilibrium distribution of adsorbate between the two phases in solution and helps in the interpretation of adsorption data. These relationships are referred to as adsorption isotherms, since the test is normally conducted at a constant temperature (Benefield, 1982). Three most common isotherms are the Langmuir isotherm; Freundlich isotherm and Brunaur-Emmett-Teller (BET) isotherm.

2.2.3.1 Langmuir Isotherm Equation

The Langmuir isotherm equation was developed based on the assumption that each adsorption site is capable of adsorbing one molecule and maximum adsorption capacity corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface. Additional assumptions include constant adsorption energy, and no transmigration of adsorbate in the plane of the surface. That is all the adsorption sites have equal affinities for molecules of the adsorbate and the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. This model is valid for single-layer adsorption (Weber,1972; Benefield, 1982). The Langmuir isotherm can be derived directly from either kinetic considerations or the thermodynamics of adsorption for monolayer adsorption with constant adsorption energy.

Langmuir isotherm equation can be described as follows:

$$q = x/m = (QbC) / (1 + bC) \tag{2-1}$$

where: $q = x/m$ = amount of adsorbate adsorbed per unit mass of adsorbent,
mass of adsorbate / mass of adsorbent;
C = equilibrium concentration of adsorbate in solution after adsorption,
mass of adsorbate (mg) / L;
Q = maximum adsorption capacity of adsorbent,
mass of adsorbate / mass of adsorbent;
b = empirical constant, 1 / concentration (L/mg).

Figure 2.1 shows the typical isotherm of Langmuir equation. The Equation 2-1 can be rewritten in linear form as:

$$C/q = 1/(Qb) + C/Q \tag{2-2}$$

Q and b can be determined by knowing the slope 1/Q and the intercept 1/(Qb) from a plot of the linearized form (C/q versus C). Dividing both sides of equation by C, an alternative equation will be formed as follows:

$$1/q = [1/(Qb)][1/C] + 1/Q \tag{2-3}$$

Q and b in this case can also be determined by knowing the slope 1/(Qb) and the intercept 1/Q from the plot of the linearized form (1/q versus 1/C).

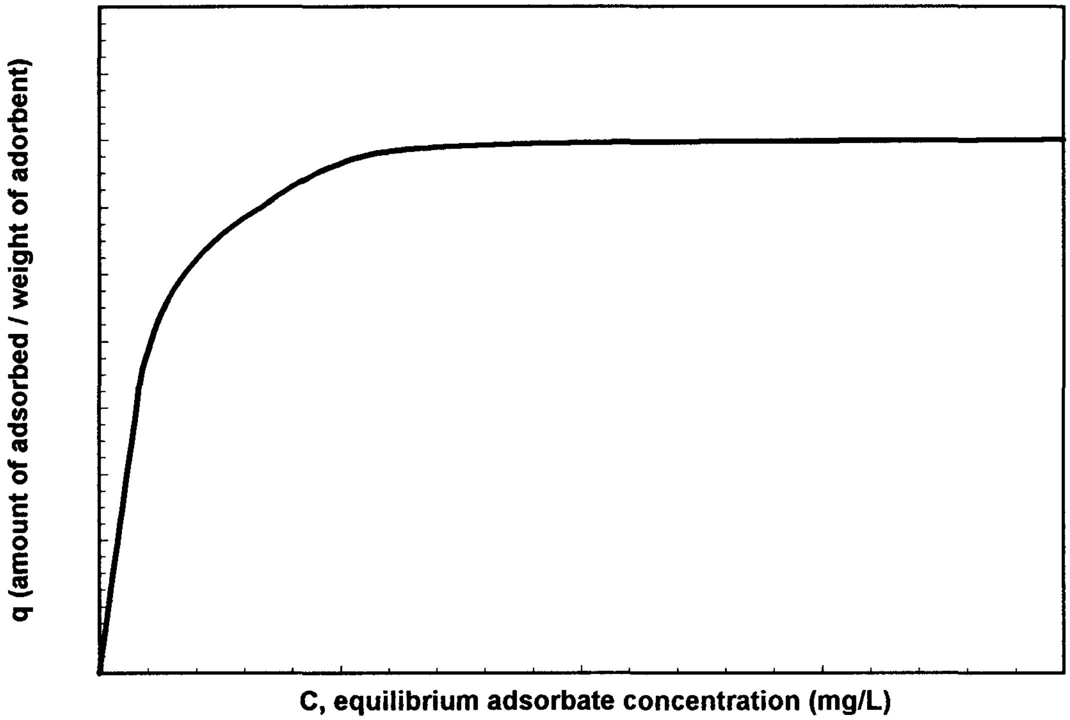

Figure 2.1 Typical Langmuir Isotherm (Source: Weber, 1972)

2.2.3.2 Freundlich Isotherm Equation

The Freundlich isotherm equation is an empirical equation to describe adsorption equilibrium. The equation is developed based on the assumption that the adsorbent has a heterogeneous surface which is composed of different classes of adsorption sites, and that adsorption on each class of site follows the Langmuir equation (Benefield, 1982). The Freundlich isotherm equation is empirical and cannot be derived from kinetic and thermodynamic theory; nevertheless it is often useful for data description (Weber, 1972). The general form of Freundlich equation is:

$$q = x/m = KC^{1/n} \qquad (2\text{-}4)$$

where: $q = x/m$ = amount of adsorbate adsorbed per unit mass of adsorbent,

mass of adsorbate / mass of adsorbent;

C = equilibrium concentration of adsorbate in solution after

adsorption, mass of adsorbate (mg) / L

K, n are empirical constants

The linearized form shown in Equation 2-5 can be developed by taking the log of both sides which is:

$$\log q = \log K + (1/n) \log C \qquad (2\text{-}5)$$

Constants K and n can be determined by knowing the slope 1/n and the intercept log K from a plot of the linearized form (log q versus log C). Figure 2.2 describes the general form of the Freundlich equation.

2.2.3.3 BET Isotherm Equation

The BET isotherm equation was developed based on the assumption that molecules can be adsorbed in more than one layer, therefore it extends the Langmuir model from a monolayer to several molecular layers. Above the monolayer, each additional layer of adsorbate molecules is assumed to equilibrate with the layer below it, and the adsorption at one site does not affect adsorption at neighboring sites. The energies of adsorption for each layer beyond the first are equivalent (Benefield, 1982; Montgomery, 1985). The general form of the BET isotherm can be described by Equation 2-6:

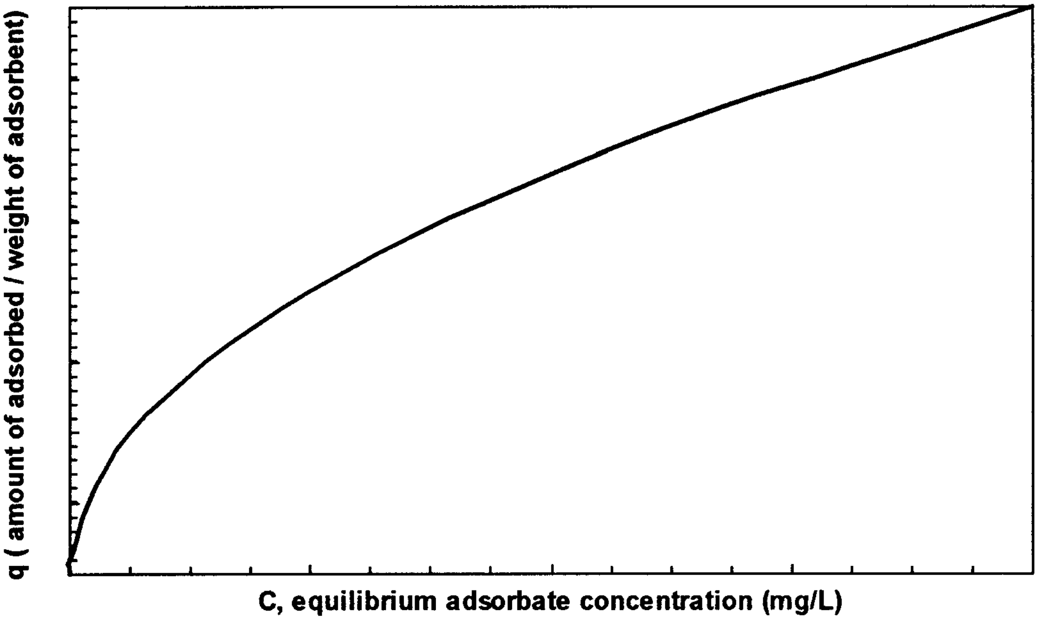

Figure 2.2 Typical Freundlich Isotherm (Source: Weber, 1972)

$$q = x/m = (CbQ) / \{(Cs-C)[1 + (b-1)\, C/Cs]\} \qquad (2\text{-}6)$$

where q = x/m = amount of adsorbate adsorbed per unit mass of adsorbent,

mass of adsorbate / mass of adsorbent;

C = equilibrium concentration of adsorbate in solution after adsorption,

mass of adsorbate (mg) / L;

Q = maximum adsorption capacity of adsorbent,

mass of adsorbate / mass of adsorbent;

Cs = saturation concentration for adsorbate in solution, mg/L;

b = empirical constant, 1 / concentration (L/mg)

Figure 2.3 shows the typical BET isotherm equation. Equation 2-6 can be rewritten in linear form as shown in Equation 2-7:

$$C / [(Cs - C)] = 1/(bQ) + \{[(b-1) / (bQ)](C/Cs)\} \tag{2-7}$$

Again, Q and b can be found from the slope and intercept of the linear form.

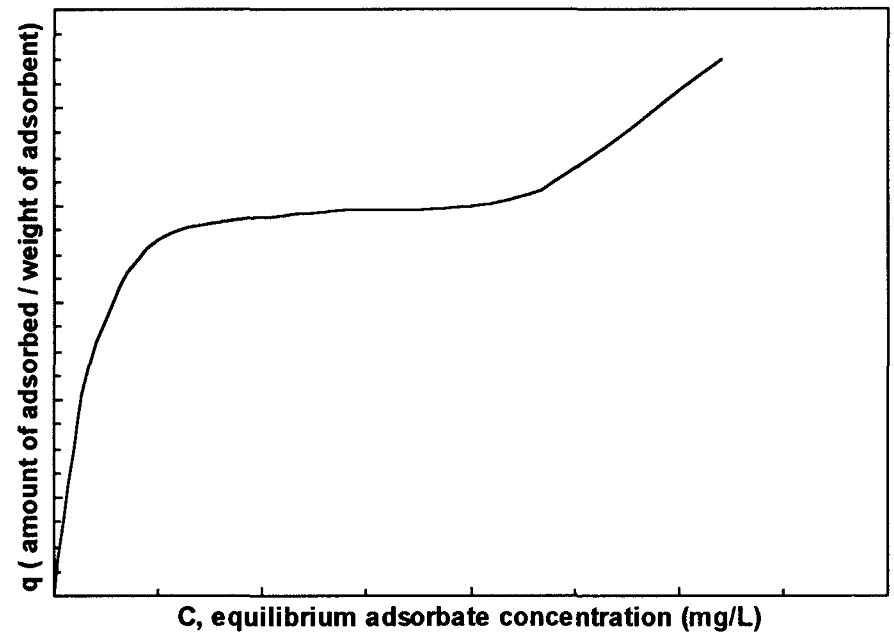

Figure 2.3 Typical BET isotherm (Source: James M. Montgomery, Inc., 1985)

2.3 Application of Peat to Wastewater Treatment

2.3.1 Removal of Oil

Chemical and refinery plants produce large amounts of oil wastewater. Oil water is also present in groundwater due to groundwater pollution. Removal of oil by peat has been well documented. Generally, the average oil removal capacity of activated peat was 83 to 97% compared to 89 to 97% of a synthetic adsorbent (Couillard, 1993). An experiment showed that by using horticultural Sphagnum peat, oil removal efficiency reached to a high of 80% under the 12-48 mL/min flow rate during the 8 hours of the experiment (Viravaghavan & Mathavan, 1989).

Four different oil-in-water emulsion samples were used in the experiments performed by Viraraghavan & Mathavan (1989) - refinery effluent (RE); cutting oil (CO); low viscosity Midale crude oil (MCO) and medium viscosity Standard mineral oil (SMO). Horticultural peat was used to adsorb oil. The characteristics of the oil samples and the characteristics of horticultural peat used in the experiments are listed in Table 2.3 and Table 2.4, respectively. The results showed that depending on the nature of the oil used and the emulsion stability, equilibrium was reached within 1 to 3 hours of contact between peat and oil-in-water emulsions according to the kinetic study. The oil removal efficiency from oil-in-water emulsions investigated varied between 21% and 98% based on the batch kinetic study. Adsorption followed the BET isotherm equation most closely.

Table 2.3 Characteristics of Oil-in-Water Emulsions

Description	*SMO*	*MCO*	*CO*	*RE*
Influent oil concentration mg/l	300-228	196-142	890	12.10
Influent pH	7.5	8.5	8.25	8.5
Viscosity of oil	130	50	-	-

Source: Viraraghavan & Mathavan, 1989

Table 2.4 Characteristics of Horticultural Peat

Characteristics	*Range*
Particle size range	
(a) Foreign matter	0
(b) Coarse fibre (>2.36mm) %	14.1
(c) Medium fibre (2.36-0.85mm) %	26.1
(d) Fines (<0.85mm) %	59.8
pH at 21^{o}C	
(a) In distilled water	6.0
(b) In $CaCl_2$	5.5
Moisture content (%)	
(a) Method I	50-70
(b) Method II (at 21^{o}C)	58.60
Sand content %	2.0
ash content %	4.8
Organic matter content %	37.5

Source: Mathavan & Viraraghavan, 1989

2.3.2 Removal of Color

The most significant components of pulp industrial effluent are organic compounds which consist of lignins and their derivatives, along with tannins. The latter components are principally responsible for the blackish-brown color (Hammer et al., 1993). Many dyes used in the textile industry are especially hard to remove from effluent streams by conventional waste treatment method because they are stable to light and oxidizing agents, and are resistant to aerobic digestion (McKay & Allen, 1980). An investigation of peat use for adsorption of acid blue dye found that approximately 80% of (McKay & Allen, 1980; Viraraghavan & Ayyaswami, 1989). It was found that color was reduced as much as 99.6%.

2.3.3 Removal of Heavy Metals

Heavy metals represent a major risk to the environment and can be removed by a traditional wastewater treatment process such as ion exchange, activated carbon adsorption and chemical precipitation. Peat adsorption of heavy metals has been investigated by several researchers in recent years. This research has shown that peat is effective in removing a number of elements, such as copper, cadmium, lead, mercury, nickel, and zinc from a variety of wastewaters. The reports showed that heavy metals are selectively adsorbed by peat (Couillard, 1993). Research by Smith et al. (1977) also showed that peat treated with sulfuric acid had considerable potential for the removal of cationic species from water over a wide range of concentrations. Also, pH has been found to have a dramatic effect on metal ion adsorption (Dissanayake and Weerasooriya, 1981). They found that at pH of 2.8-3.0, copper was strongly adsorbed by peat, while at a pH of 6.5-7.0, precipitation of copper occurred owing to the solubility product of $Cu(OH)_2$.

A batch study of zinc removal using peat adsorption (Lehocine, 1989) showed that, at acid to neutral pHs, the effectiveness of zinc removal by peat is 93-96%, and the main removal mechanism is adsorption. The adsorption isotherm followed the Langmuir isotherm equation. The method of the batch experiment involved preparing the initial solutions which contained different concentrations of zinc, adding about 2.7 grams of peat and shaking together with the zinc solution for about 24 hours. The experiment tested different pH of inflow, and showed that, at pH higher than 6 and at concentration of zinc of 5-10 mg/L, zinc was precipitated. It also showed that removal of zinc by peat increased with an increase in the pH of the zinc solution. Since the main constituent of peat is humic acid, the increase in zinc removal by peat at higher pH can be attributed to complexing of zinc with humic acid or possibly increasing in zinc precipitation. Kinetic and thermodynamic studies of batch metal removal showed that if the pH is in the range of 0-6.5, in a metal cation solution which contained Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}, the four cation binding reactions behaved differently, demonstrating that the metal binding equilibrium constant decreases in the order of $Ni^{2+} > Cu^{2+} > Cd^{2+} = Zn^{2+}$ (Gosset et al, 1986).

Another study (Rock et al.,1985) confirmed the capacity of peat to remove metals like lead, copper, iron, and zinc from sanitary landfill leachate. The leachate examined were from Augusta landfill and Freeport landfill, both located in Maine. The composition of untreated sanitary landfill leachate is listed in Table 2.5. After ten weeks of treatment, results showed that the effluent concentration of lead was less than 0.01 mg/L and the effluent concentrations of copper, zinc, and iron were zero.

Table 2.5 Characteristics of Untreated Landfill Leachate

Parameter	*Unit*	*Augusta Landfill*	*Freeport Landfill*
pH	-	7.9	5.6
TS (Total Solids)	mg/L	15,700	510
Hardness (as $CaCO_3$)	mg/L	1,200	180
Total P	mg/L	9.80	0.25
NH_4-N	mg/L	0.50	0.004
NO_3-N + NO_2-N	mg/L	0.03	0.0
Cl	mg/L	12.5	0.05
Na	mg/L	509	39.9
SO_4	mg/L	0.24	0.01
Mn	mg/L	8.43	1.84
Fe	mg/L	151	722
Zn	mg/L	11.8	0.44
Cu	mg/L	33.4	0.08
Pb	mg/L	2.98	0.35
Cd	mg/L	0.041	0.003
Hg	mg/L	0.002	<0.0005
As	mg/L	0.005	0.001

Source: Rock et al., 1985

2.4 Chemical Equilibrium Modeling - Description of MINTEQA2 Capabilities

2.4.1 General Description of MINTEQA2

MINTEQA2 is a chemical equilibrium model which is used to calculate the equilibrium species concentrations under a given set of interacting chemical components whose total concentrations are known. MINTEQA2 is the modified version of MINTEQ and MINTEQA1. MINTEQ is the EPA approved version of MINEQL and REDEQL which were originally developed by James Morgan, and John Westall (Allison, 1995). The currently available version of MINTEQA2 is version 3.11.

2.4.1.1 Components and Species

In the MINTEQA2 modeling approach, components are analogous to reactants and species are represented by products. The model accounts for 61 inorganic components and 28 organic components listed in Table 2.6, as well as three special purpose components - adsorption sites, electrostatic potentials, and dissolved organic matter (DOM). Over 900 dissolved species, 500 solid species and 21 gas species can be generated at chemical equilibrium.

2.4.1.2 MINTEQA2 Calculations

After the total concentrations of a set of components to represent the system are specified by MINTEQA2 users, the calculations inside the MINTEQA2 program will basically run through the following steps:

1. Calculation of the equilibrium aqueous solution concentration based on the input total concentrations and thermodynamic data;

2. Adjustment of the equilibrium calculations by checking for the supersaturation and undersaturation, and repetition of calculations until the system reaches equilibrium;
3. Summary calculation of the distribution of total dissolved, adsorbed and precipitated concentrations at equilibrium.

The mass action equation (Eqn. 2-8) is used in MINTEQA2 to calculate the concentrations of species in the solution.

$$C_i = (K_i / \gamma_i) \prod_{j=1}^{n} X_j^{a_{ij}} \tag{2-8}$$

where C_i = concentration of species *i*

K_i = formation constant for species *i*

γ_i = activity coefficient of species *i*

X_j = activity of component *j*

a_{ij} = stoichiometry of component *j* in species *i*

n = number of components

Table 2.6 Components Available in MINTEQA2 Version 3.11

Inorganic components:

e^-	H_2O	Ag^+	Al^{3+}	$H_3AsO_3^0$	$H_3AsO_4^0$
$H_3BO_3^0$	Ba^{2+}	Br^-	CO_3^{2-}	CN^-	OCN^-
Ca^{2+}	Cd^{2+}	Cl^-	Cr^{2+}	$Cr(OH)_2^+$	CrO_4^{2-}
Cu^+	Cu^{2+}	F^-	Mn^{3+}	NH_4^+	NO_2^-
NO^{3-}	Na^+	Ni^{2+}	PO_4^{3-}	Pb^{2+}	Rb^+
HS^-	S^0	SO_4^{2-}	$Sb(OH)_3^0$	$Sb(OH)_6^-$	HSe^-
$HseO_3^-$	SeO_4^{2-}	$H_4SiO_4^0$	Sr^{2+}	TI^+	$TI(OH)_3^0$
Fe^{2+}	Fe^{3+}	H^+	Hg_2^{2+}	$Hg(OH)_2^0$	I^-
K^+	Li^+	Mg^{2+}	Mn^{2+}	U^{4+}	U^{3+}
UO_2^{+1}	UO_2^{+2}	V^{+2}	V^{+3}	VO^{+2}	VO_2^{+1}
Zn^{+2}					

Organic components:			
diethylamine	n-butylamine	methylamine	dimethylamine
tributylphosphate	hexylamine	ethylenediamine	n-propylamine
iso-propylamine	tri-methylamine	citrate	nitrilotriacetate3-
EDTA4-	propanoate	butyrate	iso-butyrate
2-methyl pyridine	3-methyl pyridine	4-methyl pyridine	formate
iso-valerate	valerate	acetate	tartrate
glycine	salicylate	glutamate	phthalate

Special purpose components for:			
	Adsorption sites,	electrostatic potentials,	dissolved organic matter (DOM)

The iterative solution method is used in MINTEQA2 in order to calculate the equilibrium concentrations of species. Mass balance equation (Eqn. 2-9) is used to calculate the mass imbalance of components in the system.

$$Y_j = \sum_{i=1}^{m} a_{ij}C_i - T_j \qquad (2\text{-}9)$$

where T_j = measured dissolved concentration of component *j*

Y_j = mass imbalance of component *j*

m = number of species

Equations 2-8 and 2-9 are the principal equations used for the iterative solution method. MINTEQA2 runs through the following procedures before reaching equilibrium:

1. Users supply the T_j values for each of the n components;
2. MINTEQA2 database has K_i and $a_{i,j}$ values;
3. MINTEQA2 makes the initial estimate of X_j values;
4. MINTEQA2 evaluate mass action equation (Eqn. 2-8) to get C_i values;
5. MINTEQA2 evaluate mass balance equations to get Y_j values;

6. If Y_j is greater than convergence criteria (which is 1/10,000 times the total initial concentration), use Newton-Raphson method with nxn matrix to improve n and X_j values and return to step (4);
7. If Y_j is equal to zero, problem is finished;

2.4.1.8 MINTEQA2 Assumptions and Limitations

MINTEQA2 is best used under the assumptions of aqueous systems with ionic strength less than 0.5 M and at temperature of 25^0C, although temperature correction can be made between approximately to 0^0C and to 100^0C. Some equilibrium systems such as precipitation of clays will not come into equilibrium quickly as the other systems do. The applying of MINTEQA2 is also limited on database quality and some additional assumptions which need to be referred to specialized sub-models for adsorption and organic matter.

2.4.2 MINTEQA2 Input and Output Files

2.4.2.3 Input

Input files must be created before running the MINTEQA2 model. The program provides four levels for the user to input or edit data for the initial system. In editing Level I, the user can change ionic strength, pH, Eh, temperature, adsorption parameters, number of iterations, precipitation option, etc. Components such as gas, redox, aqueous and mineral species can be specified by editing Level II. The system is assumed to be closed unless gas pressure is specified. Some adsorption sites and reactions, and all types of new species which are not shown in MINTEQA2 database, are defined by editing Level II as well. Level III is used for checking whether all entries are correct and allowing the user to individually edit all entries. Level IV can be used to sweep range of pH, pe or dissolved concentrations or to design an auxiliary MINTEQA2 output file to receive equilibrated output for spreadsheet import.

2.4.2.2 Output

The main output file is divided into five parts:

1. Part 1 is a replay and interpretation of the input file;
2. Part 2 is a report on all species found in the thermodynamic database;
3. Part 3 gives the calculated concentration, activity, activity coefficient, and adjusted log K for each species;
4. Part 4 gives a percentage distribution of each component among aqueous and adsorbed species;
5. Part 5 gives the mass distribution of each component among dissolved, adsorbed, and precipitated phases; charge balance, computed ionic strength, computed pH (if applicable), and computed pe (if applicable); electrostatic parameter values; and saturation indices of all solid phases.

Auxiliary output is used with the titration option or multiproblem option to generate data that can easily be imported by a spreadsheet program and analyzed or plotted (Allison, 1995).

2.4.3 Application of MINTEQA2

As mentioned previously, MINTEQA2 can be used to compute equilibrium pH and concentrations for acid-base reactions. Other useful features of this model include the computation of: amount of component reduced and oxidized in oxidation-reduction reactions; amount of gas with fixed partial pressure for dissolved into or evolved from the system; amount of solid dissolved or precipitated; temperature and ionic strength corrections; choice of seven adsorption models; composite-ligand model and availability of a preprocessor.

2.4.3.1 Modeling Oxidation-Reduction Reactions (Redox) in MINTEQA2

MINTEQA2 represents redox reactions in terms of reduction half-reactions:

$$\text{ox} + ne^{-} \leftrightarrow \text{red} \qquad (2\text{-}10)$$

where ox and red are oxidized and reduced forms of the same component. MINTEQA2 can calculate the E_h and pe based on the definition of the following equations:

$$K = \{\text{red}\}/(\{\text{ox}\}\{e^{-}\}^{n}) \qquad (2\text{-}11)$$

$$pe = (1/n)\,(\log K - \log \{\text{red}\}/\{\text{ox}\}) \qquad (2\text{-}12)$$

$$E_h = 2.303(RT/F)pe \qquad (2\text{-}13)$$

$$\text{at } 25^{0}\text{C},\ E_h = 0.05916pe \qquad (2\text{-}14)$$

where Eh = potential of a cell (volts);

F = Faraday constant, 23061cal/mole-volt;

K = equilibrium constant.

Elements in various oxidation states represented by MINTEQA2 components are listed in Table 2-7.

Table 2-7 Elements in various oxidation states in MINTEQA2 components

As(III)	N(-III)	Mn(II)	Cr(II)	Fe(II)	U(III)	V(II)
As (II)	N(III)	Mn(III)	Cr(III)	Fe(III)	U(IV)	V(III)
	N(V)		Cr(VI)		U(V)	V(IV)
					U(VI)	V(V)
Cu(I)	S(-II)	Se(-II)	Sb(III)	Hg(I)	TI(I)	
Cu(II)	S(0)	Se(IV)	Sb(V)	Hg(II)	TI(III)	
	S(VI)	Se(VI)				

2.4.3.2 Modeling Adsorption in MINTEQA2

For components undergoing adsorption reactions, MINTEQA2 can calculate the distribution coefficient between adsorbed and dissolved phases. The adsorption models available in MINTEQA2 are linear K_d model; Freundlich isotherm; Langmuir isotherm; surface complexation models which include constant capacitance, diffused layer and triple layer; and ion exchange model.

2.4.3.3 Modeling Metal Complexation with DOM in MINTEQA2

There are two methods for modeling metal complexation with dissolved organic matter (DOM) in MINTEQA2. One is a discretized representation of natural DOM ligands; another is a composite ligand model. In the discretized representation of natural DOM ligands, two or more ligands are selected to reproduce the metal binding capacity of DOM. If the discrete ligands are real, then equilibrium constants are available. If the discrete ligands are hypothetical, equilibrium constants are derived using an optimizing fitting procedure. In the composite ligands model, it is assumed that DOM consists of a population of binding sites in which the probability of occurrence of a binding site is normally distributed with respect to its log K value for proton or metal binding. The advantage of this model is that it is very easy to use. By entering DOM concentration in units of mole/L in the input file, the output will show the distribution of DOM at equilibrium. MINTEQA2 has a database of metal-DOM reactions that includes H^+, Ca^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+}, Ba^{2+}, Be^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}.

Furthermore, MINTEQA2 can be applied for two systems: laboratory systems and natural systems. In laboratory systems, it can be used to calculate the concentrations of individual species, such as the equilibrium pH or free metal activity, or to determine whether a solid will precipitate or dissolve. In natural systems, MINTEQA2 can determine mobile concentrations of metals and soil cleanup levels, compute the acid neutralizing capacity of soils and other materials, and compute the bioavailable metal concentration.

CHAPTER THREE

PROCEDURES

3.1 General Description and Analytical Method

All the experiments were conducted in the Environmental Engineering Lab at Youngstown State University. Copper, nickel and zinc were selected to represent heavy metals in these experiments. Synthetic solutions were made containing Cu, Ni and Zn by using metal reference solutions and as well as dry chemicals. Peat used in this study was Canadian Sphagnum peat moss which was originally purchased from a local lawn and garden supply center. Six batch adsorption experiments were performed for the determination of adsorption isotherms for each metal. Also, a peat column was set up and run with continuous feed to stimulate the dynamic system. The column feed rate was varied in order to evaluate the adsorption capacity of peat to metals at different hydraulic residence times.

The pH of batch solutions and influent and effluent of the column experiment were measured by using a Accumet® pH meter Model 810, Allied Fisher Scientific. The concentrations of heavy metals were analyzed by Atomic Absorption Spectroscopy (AA) performed on a Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer in flame mode. Total Organic Carbon (TOC) measurements were conducted in the Instruments Lab in the Chemistry Department at Youngstown State University using a Shimadzu Model TOC-500 Total Organic Carbon Analyzer and Shimadzu Model ASI-502 Auto Sample Injector. The operation mode of the TOC analyzer was set to TC (Total Carbon), and the Autosparge Unit was used to purge the inorganic carbon from the sample. Therefore, Total Carbon (TC) which was measured in the samples equals Total Organic

Carbon (TOC). Heavy metal standard solutions containing Cu, Ni and Zn were prepared for the measurements of heavy metals by dilution of 1000 mg/L standard reference solutions. A 300 mg/L TOC standard solution was prepared by dissolving Reagent Grade potassium hydrogen phthalate in deionized water. Table 3.1 lists the operating parameters used in AA analysis. Table 3.2 lists the operating parameters used in TOC analysis.

Table 3.1 Atomic Adsorption Operating Parameters

Metal Analyzed	Wavelength	Silt Width	Flame Type
Cu	324.8 nm	0.7 nm	air-acetylene
Ni	232.0 nm	0.2 nm	air-acetylene
Zn	213.9 nm	0.7 nm	air-acetylene

Table 3.2 TOC Operating Parameters

Operation mode	Total Carbon
Calibration method	1
High standard	300 mg/L
Low standard	0 mg/L
Volume of Stroke each analysis	20 μL
Repeat measuring times	3
Dilution times (x1)	1
SD/CV	1.0

All of the glassware and containers which were used to the storage of standard solution and samples had been acid washed by 2:1 nitric acid and air-dried in inverted position on a clean paper towel.

3.2 Batch Adsorption Experiments

Batch experiments were performed in order to determine the peat adsorption isotherms of the three heavy metals. The method used in these experiments was to place a fixed amount of adsorbent into each of several flasks (or bottles) containing a certain volume of solution, but with different concentrations of adsorbates. Dried Canadian Sphagnum peat moss was used as the adsorbent. The solutions were made of deionized water and the different concentrations of adsorbate. The adsorbates used in the batch experiments were Cu, Ni, and Zn individually, and the mixture of the three metals. In order to test the peat adsorption capacity for heavy metals at different pH, batch studies were performed at pH values of 5 and 7-8 for both Ni and Zn. A buffer (KH_2PO_4) was used to maintain the solution at stable pH. NaOH was added to adjust pH to the same initial value for all samples.

The general procedure of batch experiments was to first rinse and drain the peat to remove fine (<2 mm) particles. Next, the peat was dried in a laboratory oven at 103^0C for more than 12 hours. Then, 100 mL solutions of adsorbate were prepared by adding the KH_2PO_4 buffer (usually 0.1M) and desired heavy metal concentrations to deionized water. Solutions were poured into clean, dry 250 mL erlenmeyer flasks or 125 mL plastic bottles and 0.1g or 0.5g dried peat was added. The flasks or bottles containing the peat and heavy metals were placed on a Lab-Line shaker shaking about approximately 24 hours at a speed of 200 rpm. The final solutions were filtered through the Whatman GF/C glass fiber filters to separate the peat from the solution. Final pH was measured on all samples. Filtrates were then acidified with approximately 1 mL of concentrated nitric acid and stored in the 125 mL plastic bottles. Subsamples (before acidification) were saved in 50 mL glass vials for the TOC measurements. The final concentrations of heavy metals were measured on the filtrate and recorded. Table 3.3 summarizes the experimental conditions for these six batch experiments.

Table 3.3 Summary of Conditions for Batch Experiments

Batch #	*1*	*2*	*3*	*4*	*5*	*6*
Adsorbate / Adsorbent	Ni / Peat	Ni / Peat	Zn / Peat	Zn / Peat	Cu / Peat	Mixed Cu, Ni & Zn / Peat
Buffer	0.02M K_2HPO_4	0.1M KH_2PO_4	0.1M KH_2PO_4	0.1M KH_2PO_4	0.1M KH_2PO_4	0.1M KH_2PO_4
NaOH pH adjustment	1.0N	1.0N	1.0N	none	1.0N	1.0N
Initial Adjust pH	around 7.0	around 5.0	7.5 - 8.0	4.3 - 4.5	5.0 - 5.2	5.0 - 5.7
Shake Time	24 hours	24 hours	24 hours	24 hours	24 hours	24 hours
Soil:Solution Ratio	1 : 200	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000
Initial Adsorbate concentration	Variable 1.0 mg/L 5.0 mg/L 10.0 mg/L 20.0 mg/L 50.0 mg/L	Variable 2.0 mg/L 5.0 mg/L 10.0 mg/L 20.0 mg/L 30.0 mg/L 50.0 mg/L	Variable 2.0 mg/L 5.0 mg/L 10.0 mg/L 20.0 mg/L 30.0 mg/L 50.0 mg/L	Variable 2.0 mg/L 5.0 mg/L 10.0 mg/L 20.0 mg/L 30.0 mg/L 50.0 mg/L	Variable 2.0 mg/L 5.0 mg/L 10.0 mg/L 20.0 mg/L 30.0 mg/L 50.0 mg/L	Variable 1.0 mg/L 2.0 mg/L 5.0 mg/L 9.0 mg/L 15.0 mg/L 20.0 mg/L of each
Volume of Reaction Container	250 mL Erlenmeyer flask	125 mL Plastic Bottle	125 mL Plastic Bottle	125 mL Plastic Bottle	125 mL Plastic Bottle	125 mL Plastic Bottle

The amount of heavy metal(s) which has been adsorbed by the peat was calculated by Equations 3-1 and 3-2.

$$x = (C_0 - C) \times V \qquad (3\text{-}1)$$

$$q = x/m = (C_0 - C)\ V/m \qquad (3\text{-}2)$$

where: C_0 = initial concentration of adsorbate (mg/L);

C = equilibrium concentration of adsorbate (mg/L);

V = volume of solution (L);

x = mass of adsorbate adsorbed (mg);

m = mass of oven-dried adsorbent (mg);

q = amount of adsorbate to be adsorbed per unit mass of adsorbent (mg/kg).

3.3 Column Experiment

Column experiment was performed in order to simulate adsorption of heavy metals by peat in a dynamic system. The configuration of the column is shown in Figure 3.1. The column consisted of two nontransparent sections of 6-inch diameter Schedule 40 PVC pipe. The top was 6 inches in height and the bottom was 24.25 inches high. Flat pieces of Plexiglas (8 × 8 × 0.25 inch) were attached to each end of the column to provide the effective closure as well as a stable platform (Patterson, 1996). The two sections were banded together with a rubber sleeve.

Peat was placed in a 2 mm stainless steel sieve and washed with tap water before placing it into the column. In order to keep the peat from floating inside the column, a circular screen was placed in the column on top of the peat layer. The total column height was 30.25 inches while the peat was filled up to 22.25 inches before starting the column experiment.

A 22 L Nalgene® carboy was utilized as a reservoir for the feed solution of heavy metals. The carboy was elevated above the top of the column so that the feed solution could pass through the column by gravity. The discharge rate was controlled manually by adjusting a valve (clamp) on the column outflow-line.

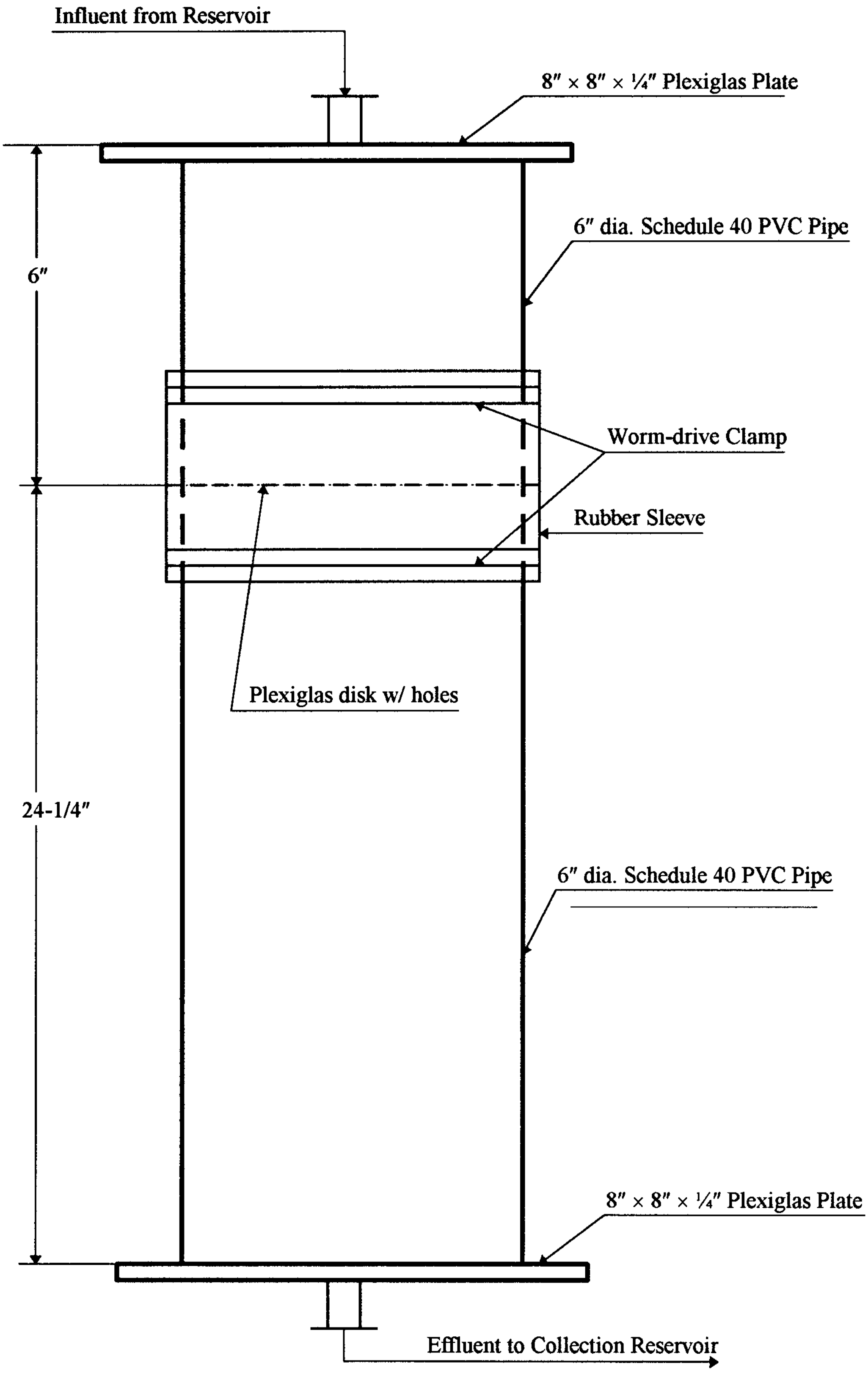

Figure 3.1 Diagram of Column Apparatus (not in scale)

One full reservoir of distilled water containing no heavy metals was passed through the entire column at an average feed rate of 11 mL/min for the purpose of flushing out loose colloidal material of the humic acid inside the peat as much as possible. After that, flow of the feed solution containing mixed heavy metals of Cu, Ni and Zn was started at a desired average feed rate of 4 mL/min. The target concentration of each heavy metal was 5 mg/L. The column was run for a total period of 1584 hours (66 days) with periodical interruptions. A total of about 380 L (19 carboys) of feed solution was run through the column.

Table 3.4 lists the target concentrations of heavy metals and different buffers used to prepare each carboy of feed solution run through the column. Different buffers were used in the column feed solution to keep the feed solution pH between 5.0 and 7.0 in order to avoid precipitation inside the reservoir. It was desired that adsorption be the primary mechanism of heavy metals removal by the peat.

The heavy metals in the first three reservoirs of feed solution were obtained by addition of 1000 mg/L (± 1%) standard reference solutions of Cu, Ni, and Zn. The rest of the feed solutions were prepared by dissolving dried chemicals in the 20 L carboys. Table 3.5 lists the characteristics of chemicals used to make these column feed solutions.

The target concentration values of heavy metal was reasonably maintained during most of the column experiment. However, it should be noted that a light blue color indicating copper precipitation was found in the reservoir a week after starting the column experiment. A magnetic stirring bar was used to agitate the feed solution to ensure complete mixing during the whole period of the column experiment. After about the first half of the experiment (799 hours, or 141 L of feed solution), a light green colored precipitate indicating the mixed metal precipitation was observed inside the reservoir, along with a decrease in the measured heavy metals concentrations in the feed solution.

Table 3.4 General Overview of Column Experiment

No. of Carboy	*Target Metals Concentration*			*Buffer Solution*
	Cu (mg/L)	*Ni (mg/L)*	*Zn (mg/L)*	
1	5	5	5	0.01M KH_2PO_4 + 0.01M K_2HPO_4
2	5	5	5	0.01M K_2HPO_4 + NaOH (1.8g)
3	5	5	5	0.02M K_2HPO_4
4	5	5	5	0.01M Na_2HPO_4
5	5	5	5	0.005M Na_2HPO_4
6	5	5	5	0.005M Na_2HPO_4
7	5	5	5	0.005M Na_2HPO_4
8	5	5	5	None
9	5	5	5	None
10	5	5	5	None
11	5	5	5	None
12	5	5	5	None
13	5	5	5	None
14	5	5	5	None
15	5	5	5	None
16	5	5	5	None
17	5	5	5	None
18	5	5	5	None
19	5	5	5	None

Table 3.5 Chemicals Characteristic used for making Column feed solution

Name	Formula	Formula Weight
Cupric Sulfate	$CuSO_4.5H_2O$	249.68
Zinc Chloride	$ZnCl_2$	136.28
Nickel Sulfate	$NiSO_4.6H_2O$	262.86

The measured concentration of each of the three metals dropped to less than 2 mg/L. The magnetic stirring bar did not perform well in breaking up the precipitate. To avoid the precipitation in the reservoir, the decision was made to add no buffer to the feed solution. For the remaining half period of about 785 hours, column experiments was run with no buffer added in the feed solution and the concentrations of heavy metals in the feed solution remained reasonably steady around 5 mg/L. pH of the feed solution were controlled between 5.0 and 7.0 for all feed solutions.

The target feed rate was 4 mL/min for the first 1351 hours, 10 mL/min for the next 161 hours and 14 mL/min for the last 72 hours. Since the feed rate was controlled manually, it is somewhat difficult to maintain a steady flow rate; therefore, during the initial phase of the column experiment, the feed rate fluctuated between 2-5 mL/min. Samples of feed solution were taken one or two times from each batch for pH and metals analyses. Outflow samples were taken once a day except the last three days (high flow period) in which samples were taken once every three hours. pH and the heavy metal concentrations were measured for each outflow sample. Approximately one in three outflow samples were selected for TOC measurement.

The column was disconnected after 1584 hours of operation. After stopping the experiment, a measurement of the porosity of peat was performed. First, the solution inside the column was drained as much as possible and the amount of water removed was 6305 g. Then, the wet peat was removed from the column and weighed at 8535g. The wet peat was placed into a laboratory oven to be dried for 24 hours at temperature of 90^0C. The total weight of dry peat was 1795g. The total amount of water in the peat, therefore, was 13045g. The porosity of 93% was obtained for the peat column. Since the total volume of 380L of water run through the column for the whole period of 1584 hours. The hydraulic residence times of the three phases of the experiment were calculated to be about 73 hours for the first 56 days (1351 hours), 26 hours for the next 7 days (161hours), 16 hours for the last 3 days (72 hours).

3.4 MINTEQA2 Application

The chemical equilibrium model program MINTEQA2 (Allison, 1995) was used in this study to model the column feed solution and batch adsorption experiments.

3.4.1 MINTEQA2 Model of Column Feed Solution

MINTEQA2 was used to model the column feed solution with only heavy metals and buffer (carboy #1 to #7) and without buffer (carboy #8-12). The input information for the model is listed in Table 3.6. It should be noted that the target concentrations of chemical components in the feed solution are not exactly the same as the measured concentration. All the details are discussed in Section 4.3.1. Open system was applied to model the CO_2 effect to the chemical equilibrium system.

3.4.2 MINTEQA2 Model of Batch Experiments

In batch experiments, as well as in the column outflow, significant amounts of colloidal organic matter were leached from the peat into solution. MINTEQA2 was used to model the batch study considering the humic acid added into the system. Organic acid concentration is expressed as DOM (Dissolved Organic Matter) when using MINTEQA2. Because of the complex structure of organic acids which exist in peat, it is difficult to estimate the formula weight of these compounds. Maximum 10^{-5} M of DOM was used in MINTEQA2 for modeling of batch experiments. In order to determine the relationship

Table 3.6 MINTEQA2 Basic Input Information for Column Feed Solution

Carboy #	*Description*	*Target Concentration of Chemical Components in Feed Solution (M)*	*Temperature (^0C)*	*Precipitation Allowed*
1	Feed solution containing 5 mg/L of each Cu, Ni and Zn with 0.01M KH2PO4 + 0.01M K2HPO4	$[Cu^{2+}] = 7.869\times10^{-5}$ $[Ni^{2+}] = 8.516\times10^{-5}$ $[Zn^{2+}] = 7.649\times10^{-5}$ $[K^+] = 0.03$ $[H_2PO_4^-] = 0.01$ $[HPO_4^{2-}] = 0.01$	25^0C	Yes
2	Feed solution containing 5 mg/L of each Cu, Ni and Zn with 0.01M K_2HPO_4 + 1.8 g NaOH	$[Cu^{2+}] = 7.869\times10^{-5}$ $[Ni^{2+}] = 8.516\times10^{-5}$ $[Zn^{2+}] = 7.649\times10^{-5}$ $[K^+] = 0.02$ $[HPO_4^{2-}] = 0.01$ $[Na^+] = 2.25\times10^{-3}$ $[OH^-] = 2.25\times10^{-3}$	25^0C	Yes
3	Feed solution containing 5 mg/L of each Cu, Ni and Zn with 0.02M K_2HPO_4	$[Cu^{2+}] = 7.869\times10^{-5}$ $[Ni^{2+}] = 8.516\times10^{-5}$ $[Zn^{2+}] = 7.649\times10^{-5}$ $[K^+] = 0.04$ $[HPO_4^{2-}] = 0.02$	25^0C	Yes
4	Feed solution containing 5 mg/L of each Cu, Ni and Zn with 0.01M Na_2HPO_4	$[Cu^{2+}] = 7.869\times10^{-5}$ $[Ni^{2+}] = 8.516\times10^{-5}$ $[Zn^{2+}] = 7.649\times10^{-5}$ $[SO_4^{2-}] = 1.641\times10^{-4}$ $[Cl^-] = 1.538\times10^{-4}$ $[Na^+] = 0.02$ $[HPO_4^{2-}] = 0.01$	25^0C	Yes
5,6,7	Feed solution containing 5 mg/L of each Cu, Ni and Zn with 0.005M Na_2HPO_4	$[Cu^{2+}] = 7.869\times10^{-5}$ $[Ni^{2+}] = 8.516\times10^{-5}$ $[Zn^{2+}] = 7.649\times10^{-5}$ $[SO_4^{2-}] = 1.641\times10^{-4}$ $[Cl^-] = 1.538\times10^{-4}$ $[Na^+] = 0.01$ $[HPO_4^{2-}] = 0.005$	25^0C	Yes
8-19	Feed solution containing 5 mg/L of each Cu, Ni and Zn without any buffer	$[Cu^{2+}] = 7.869\times10^{-5}$ $[Ni^{2+}] = 8.516\times10^{-5}$ $[Zn^{2+}] = 7.649\times10^{-5}$ $[SO_4^{2-}] = 1.641\times10^{-4}$ $[Cl^-] = 1.538\times10^{-4}$	25^0C	Yes

between the heavy metal concentrations and the percent bound to organic matter at the equilibrium, heavy metals and organic matter were simplified to be the only components inthe MINTEQA2 input. The heavy metal concentrations used were 0.1, 1, 5, 20 mg/L.

The output basically listed the concentrations of each species at equilibrium at each different condition. When DOM is considered in the input, the output shows the percentage of heavy metals bound to DOM at equilibrium.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Batch Adsorption Experiments

Six batch adsorption experiments were conducted in this project. Peat was used as the adsorbent in all the batch experiments. All the peat used in these batch experiments was washed and oven dried for about 12 hours at 103^{0}C. In the first five batch experiments, copper, nickel, or zinc was used separately as the adsorbate, while a mixture of the three metals was used as the adsorbate in the sixth batch experiment. In batch experiment #1, the soil : solution ratio was 1 : 200, while a ratio of 1 : 1000 was used in batch experiments #2 to #6. The Langmuir and Freundlich isotherms were developed to analyze the peat adsorption capacity for each metal.

The concentration of heavy metals adsorbed by peat can be described as follows:

$$C_a = C_o - C_c - C \qquad (4\text{-}1)$$

where C_a = concentration of heavy metal adsorbed by peat, (mg/L);

C_o = initial heavy metal concentration, (mg/L);

C_c = concentration of heavy metal adsorbed by container, (mg/L);

C = equilibrium heavy metal concentration, (mg/L)

The amount of heavy metals adsorbed per unit mass of peat can be calculated in Equation 4-2:

$$q = x/m = VC_a/m \qquad (4\text{-}2)$$

where all the other parameters were defined in Section 2.2.3 and 3.2.

4.1.1 Batch Experiment #1

4.1.1.1 Procedure of Experiment #1

Nickel was used as the adsorbate in experiment #1. A stock solution of 100 mg/L nickel was made by diluting the 1000 ppm ± 1% nickel reference solution. The 100 mL initial solutions containing nickel concentration of 1mg/L, 5mg/L, 10 mg/L, 20 mg/L, and 50 mg/L were made by diluting the stock solution into 0.02 M K_2HPO_4 buffer. The solutions were poured into clean 250 mL erlenmeyer flasks. The initial pH was measured for each of the samples, and 1.0 N NaOH was added to adjust the initial pH of all samples to about 7. Approximately 0.5 g dried peat was added to each of the flasks to obtain soil : solution ratio of 1 : 200. One blank sample containing 10 mg/L nickel without any peat was prepared to test the container (glass) adsorption of heavy metal under the same experimental conditions. The samples were shaken for 24 hours at a speed of 200 rpm. Final solutions were filtered through Whatman GF/C glass fiber filter to filter out the peat. The equilibrium pH was measured on all the samples. Subsamples were saved in 50 mL glass vials for TOC measurements. Filtrates were then acidified with approximately 1 mL of concentrated nitric acid and stored in 125 mL plastic bottles. Concentrations of nickel in the filtrates were measured and recorded. Final TOC concentrations of all samples were also analyzed.

4.1.1.2 Results and Analysis of Experiment #1

Since no measurement of nickel concentration in the initial solution was conducted in this batch experiment, it was assumed that the measured nickel concentration was the same as the nominal nickel concentrations in the initial solutions. Since the measured concentration of nickel in the control sample (nominal concentration of 10 mg/L) was 9.95

mg/L, it was assumed that the 0.05 mg/L of nickel was adsorbed by the container. It was also assumed that the amount of nickel adsorbed by the container for all other samples was directly proportional to the final concentration in the sample. The color of the filtrates in batch experiment #1 were very light brown, indicating that some amount of humic acid leached from the peat into the solution.

A summary of results from batch experiment #1 is presented in Table 4.1.

Table 4.1 Summary of Batch Experiment #1 - Nickel / Peat

Initial metal concentration, C_0 (mg/L)	1	5	10	20	50
Initial pH	1.71	1.97	3.75	2.80	3.30
Adjusted pH	7.05	7.10	7.03	7.03	7.11
Peat weight, m (g)	0.5044	0.5039	0.5103	0.5047	0.5069
Volume of Solution, V (mL)	100	100	100	100	100
Soil : Solution ratio	1 : 200	1 : 200	1 : 200	1 : 200	1 : 200
Equilibrium pH	6.53	6.59	6.49	6.54	6.57
Equilibrium metal concentration, C (mg/L)	0.15	0.24	0.35	0.73	3.66
Container adsorbed, C_c (mg/L)	0.021	0.034	0.05	0.104	0.522
Amount of adsorbed, Ca (mg/L)	0.829	4.73	9.60	19.2	45.8
Percent of adsorbed (%)	82.90	94.52	96.00	95.83	91.64
Amount of adsorbed, q (mg metal/kg peat)	164.4	937.9	1881	3798	9039
TOC concentration (mg/L)	48	43	37	40	32

A plot of equilibrium nickel concentration versus amount of nickel adsorbed by peat is shown in Figure 4.1. The Langmuir and Freundlich isotherms were developed accordingly. The linearized form of the Langmuir isotherm is shown in Figure 4.2 and the best fit line is described by equation 4-3:

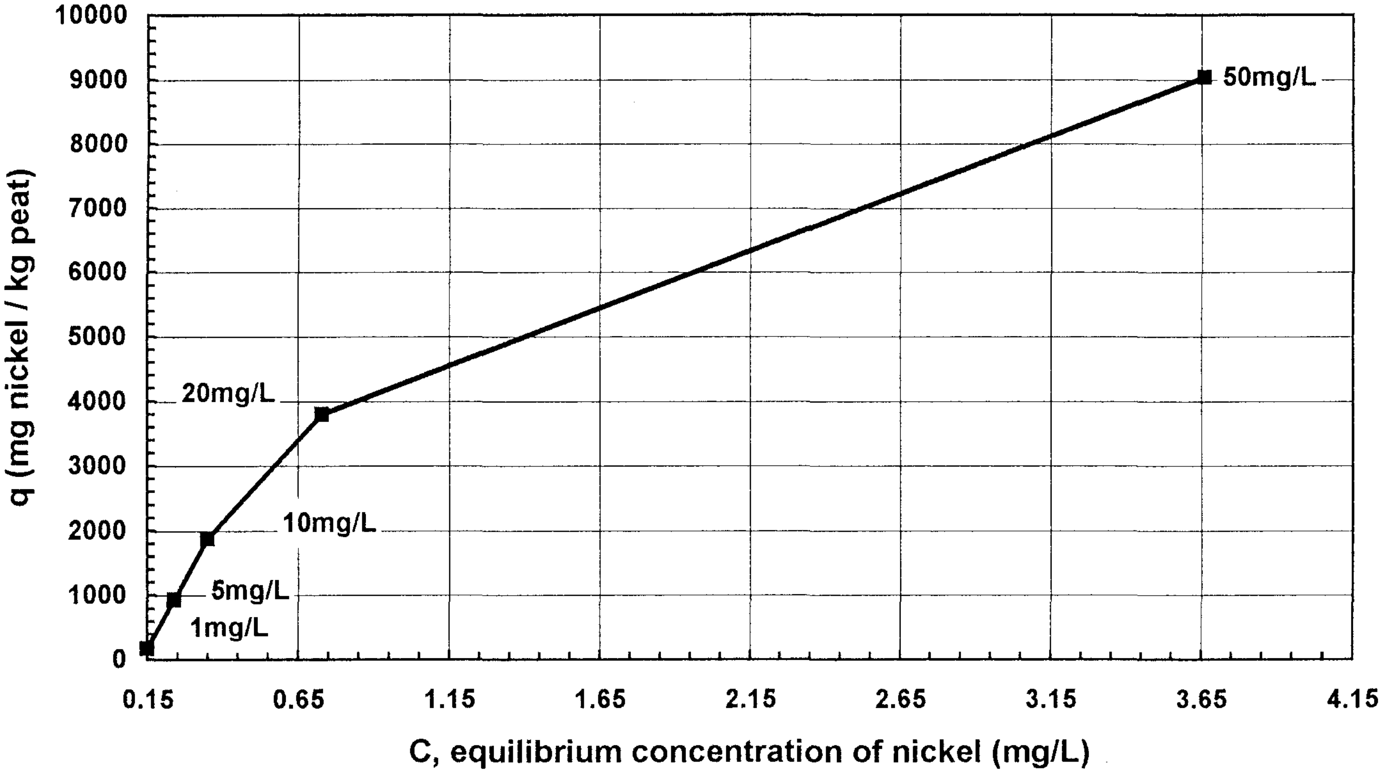

Figure 4.1 Batch Experiment #1 - Nickel / Peat (pH = 7 - 8)

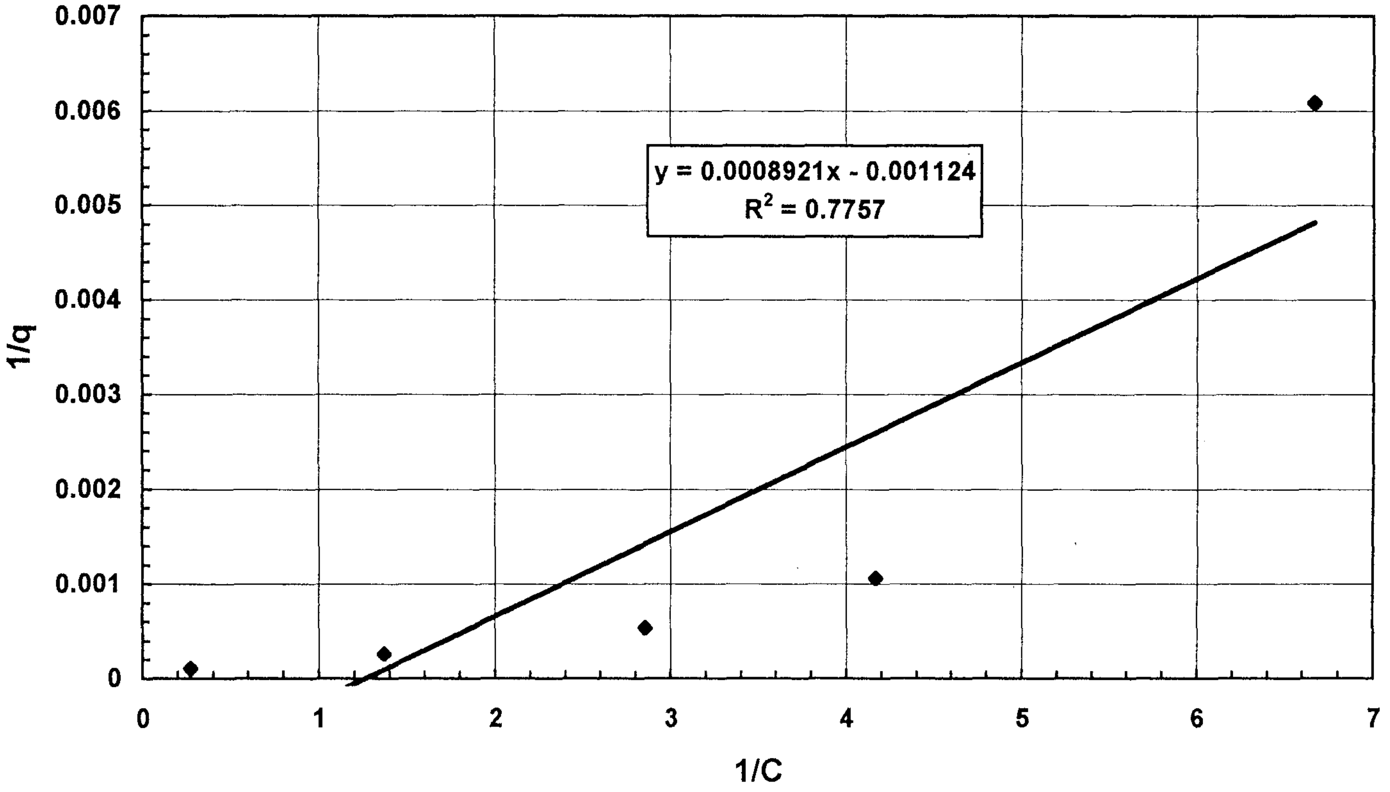

Figure 4.2 Batch experiment #1 - Langmuir Isotherm

$$1/q = 0.0008921/C - 0.001124 \qquad (R^2 = 0.7757) \qquad (4\text{-}3)$$

The intercept of the linearized Langmuir isotherm represents the maximum adsorption capacity of peat (Q). Since the intercept of the above equation is negative, an accurate value cannot be obtained for this parameter.

The linearized form of the Freundlich isotherm is shown in Figure 4.3, and the best fit straight line is described by Equation 4-4:

$$\log q = 1.101 \log C + 3.524 \quad (R^2 = 0.8166) \qquad (4\text{-}4)$$

The slope (1/n) and intercept (log K) were 1.101 and 3.524, respectively. So, K was found to be 3342 and 1/n was 1.101. The Freundlich isotherm can also be expressed as:

$$q = 3342\ C^{1.101} \qquad (4\text{-}5)$$

However, R^2 was 0.8166, indicating the data did not fit the Freundlich equation very well.

It should be noted that the measured TOC was zero in the blank sample. This means that peat was the only material which could release organic acids in the batch experiments. The equilibrium pH was lower than the initial adjusted pH, which indicates that during the adsorption process, organic acid was leached into the solutions. This was also caused the source of color in the solutions.

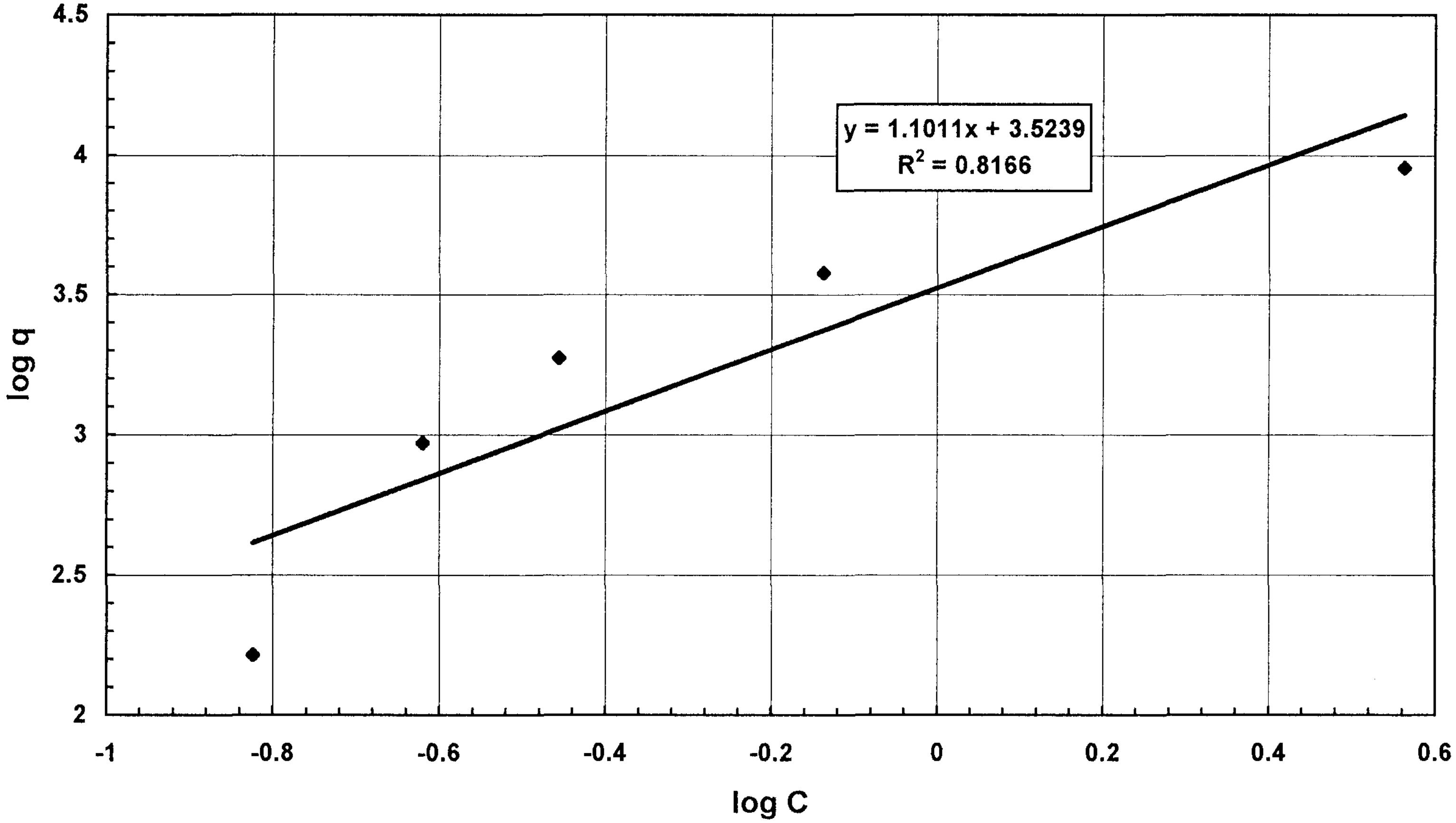

Figure 4.3 Batch experiment #1 - Freundlich Isotherm

4.1.2 Batch Experiment #2

4.1.2.1 Procedure of Experiment #2

Nickel was used as the adsorbate in the experiment #2. A stock solution of 1000 mg/L nickel was prepared by dissolving 0.4477g nickel sulfate ($NiSO_4.6H_2O$) into 1L deionized water. The 100 mL initial solutions containing nickel concentrations of 2 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, and 50 mg/L were prepared by diluting the stock solution into 0.1 M KH_2PO_4 buffer. The nickel concentrations in the initial solutions were determined by a measurement on the 100 mg/L nickel stock solution. The solutions were poured into clean 125 mL plastic bottles. The initial pH was measured for each of the samples, and 1.0 N NaOH was used to adjust the initial pH to 5.0 - 5.5 in all samples compared to 7-8 in the experiment #1. Approximately 0.1 g dried peat was added to each of the bottle to obtain a soil : solution ratio of 1 : 1000. One blank sample containing 10 mg/L nickel without any peat was prepared to test the container (plastic) adsorption of heavy metal under the same experimental conditions. The samples were shaken for about 24 hours at a speed of 200 rpm in order to reach equilibrium. Final solutions were filtered through Whatman GF/C glass fiber filters to filter out the peat. The equilibrium pH was measured on all samples. No subsamples were saved in 50 mL glass vials for the TOC measurement in experiment #2. Filtrates were acidified with approximately 1 mL concentrated nitric acid and stored in 125 mL plastic bottles. Concentrations of nickel in the filtrates were measured and recorded.

4.1.2.2 Results and Analysis of Experiment #2

The detected concentration of nickel was 96 mg/L in the stock solution. It was assumed that all the nickel concentrations in the initial samples were directly proportional to this measured value. Since the measured concentration of nickel in the control sample was 9.27 mg/L, it was assumed that 0.33 mg/L of nickel was adsorbed by the container. It was also assumed that the amount of nickel adsorbed by container was directly proportional to the final concentration in the sample.

A summary of results from batch experiment #2 is presented in Table 4.2.

Table 4.2 Summary of Batch Experiment #2 - Nickel / Peat

Nominal initial metal concentration, (mg/L)	2	5	10	20	30	50
Measured initial metal concentration, C_o (mg/L)	1.92	4.80	9.60	19.2	28.8	48
Initial pH	4.45	4.58	4.47	4.45	4.47	4.46
Adjusted pH	5.16	5.17	5.11	5.13	5.15	5.17
Peat weight, m (g)	0.1	0.1	0.1	0.1	0.1	0.1
Volume of Solution, V (mL)	100	100	100	100	100	100
Soil : Solution ratio	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000
Equilibrium pH	4.94	4.96	4.91	4.93	4.96	4.95
Equilibrium metal concentration, C (mg/L)	1.28	2.94	6.88	13.72	20.05	33.51
Container adsorbed, C_c (mg/L)	0.061	0.141	0.33	0.658	0.962	1.607
Amount of adsorbed, Ca (mg/L)	0.58	1.72	2.40	4.83	7.79	12.9
Percent of adsorbed (%)	30.16	35.81	24.95	25.14	27.04	26.85
Amount of adsorbed, q (mg metal/kg peat)	579.0	1719	2395	4827	7788	12888
TOC (mg/L)	N/A	N/A	N/A	N/A	N/A	N/A

A plot of nickel concentration at equilibrium versus the amount of nickel adsorbed by peat is shown in Figure 4.4. The linearized form of the Langmuir equation is shown in Figure 4.5 and the best fit straight line is described by equation 4-6:

$$1/q = 0.002116/C + 0.00002260 \qquad (R^2 = 0.9807) \qquad (4\text{-}6)$$

According to the above equation, the slope (1/bQ) and the intercept (1/Q) were 0.002116 and 0.00002260, respectively. Therefore, a theoretical maximum adsorption capacity of 44,248 mg nickel per kg peat was obtained, while the constant b was 0.01068. R^2 equals to 0.9807 indicating a good fit to the data.

The linearized form of the Freundlich isotherm is shown in Figure 4.6, and the best fit straight line is described by equation 4-7:

$$\log q = 0.9030 \log C + 2.7011 \qquad (R^2 = 0.9807) \qquad (4\text{-}7)$$

The slope (1/n) and the intercept (log K) were 0.9030 and 2.7011, respectively. So, n was found to be 1.107 and K was 502.5, while R^2 was 0.9807 indicating a good fit to the data. The Freundlich isotherm can also be written as follows:

$$q = 502.5\ C^{0.9030} \qquad (4\text{-}8)$$

The measurement of TOC was not performed in batch experiment #2, because the color of the filtrate was not different from the initial solution. Therefore, it was assumed that the amount of organic acids released was very low in this experiment. This is supported by the observation that the equilibrium pH was very close to the initial adjusted pH.

The adsorption data from batch experiment #2 fit much better to the isotherm equations compared to those in the batch experiment #1. However, the amount of nickel adsorbed were lower in the batch experiment #2 due to the lower initial pH. The percentage of adsorption increases with an increase in initial pH, possibly due to nickel precipitation.

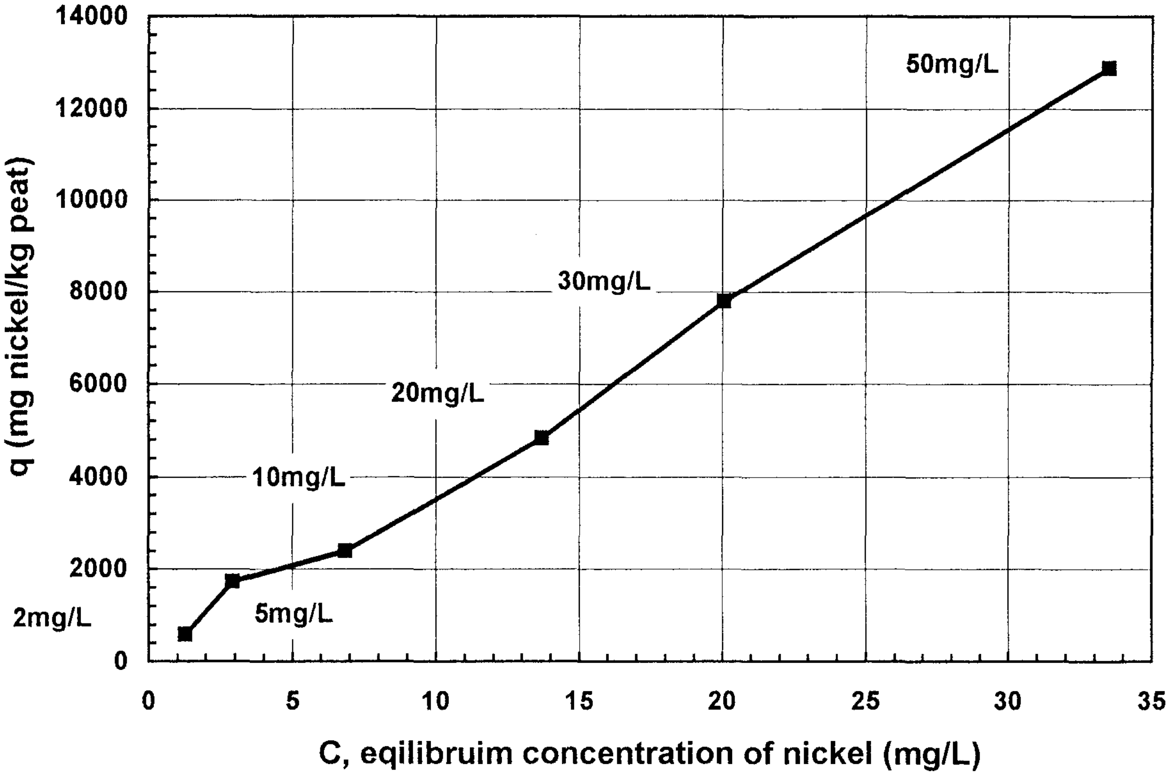

Figure 4.4 Batch Experiment #2 - Nickel / peat (pH = 5.0 - 5.5)

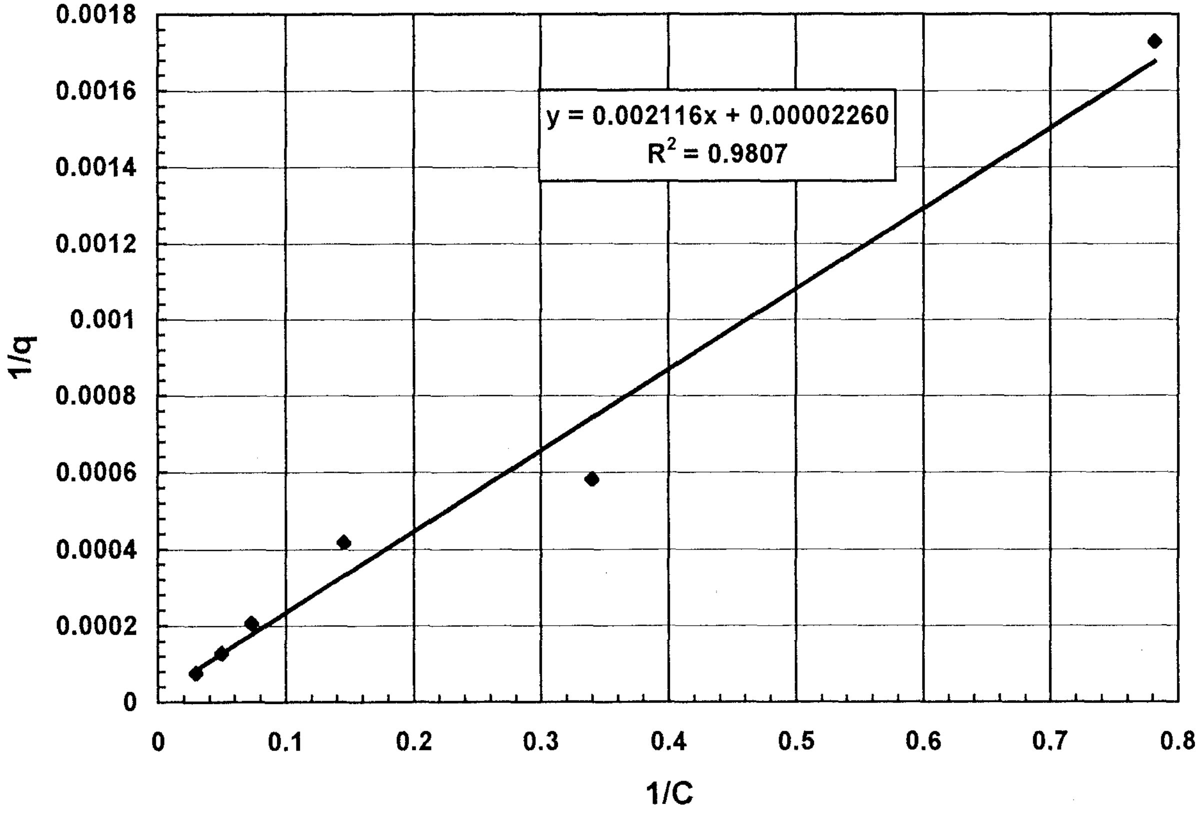

Figure 4.5 Batch Experiment #2 - Langmuir Isotherm

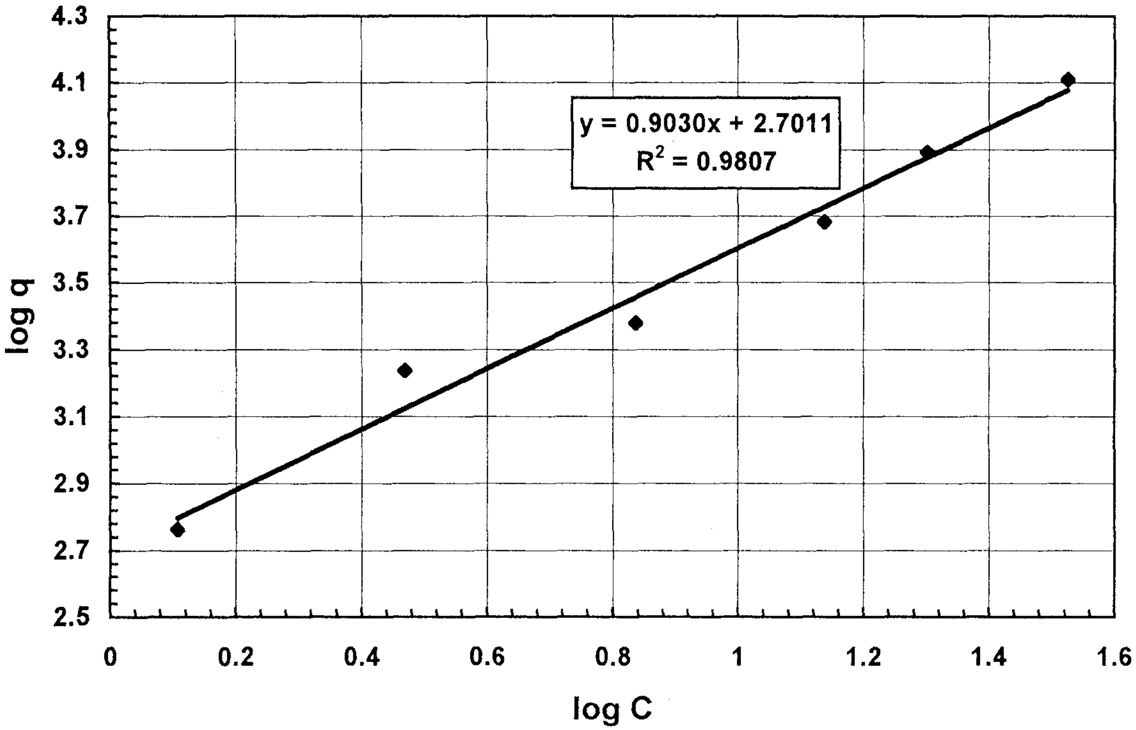

Figure 4.6 Batch Experiment #2 - Freundlich Isotherm

4.1.3 Batch Experiment #3

4.1.3.1 Procedure of Experiment #3

Batch experiment #3 was performed to detect peat adsorption of zinc. The experimental conditions were similar to batch experiment #1. Zinc was used as the adsorbate in this experiment. A 100 mg/L zinc stock solution was prepared by dissolving 0.2084g zinc chloride ($ZnCl_2$) in 1L deionized water. The 100 mL initial solutions containing zinc concentrations of 2 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, and 50 mg/L were made by diluting the stock solution into 0.1 M KH_2PO_4 buffer. The initial zinc concentration was measured on the 100 mg/L zinc stock solution. The solutions were poured into clean 125 mL plastic bottles. The initial pH was measured on each of the samples, and 1.0 N NaOH was used to adjust the initial pH to 7.5 - 8.0 for all the samples. Approximately 0.1 g dried peat was added to each flask to give a soil : solution ratio of 1 : 1000. One blank sample containing 10 mg/L zinc without any peat was prepared to test the container (plastic) adsorption of heavy metal under the same experimental conditions. The samples containing peat and different concentrations of zinc were shaken for about 24 hours at a speed of 200 rpm. Final solution were filtered through Whatman GF/C glass fiber filters to filter out the peat. The equilibrium pH was measured on all the samples. Subsamples were saved in 50 mL glass vials for TOC measurements. Filtrates were acidified with approximately 1 mL concentrated nitric acid and stored in 125 mL plastic bottles. Concentrations of zinc in the filtrates were measured and recorded. Final TOC concentrations in the samples were also analyzed.

4.1.3.2 Results and Analysis of Experiment #3

The detected concentration of zinc was 95 mg/L zinc in the stock solution. It was assumed that the zinc concentration in each initial solutions was directly proportional to this measured value. Since the measured concentration of zinc in the control sample was 9.46 mg/L, it was assumed that 0.04 mg/L zinc was adsorbed by the container. It was also assumed that the amount of zinc adsorbed by each container was directly proportional to the final concentration in the sample.

A summary of results from batch experiment #3 is presented in Table 4.3.

Table 4.3 Summary of Batch Experiment #3 - Zinc / Peat

Nominal initial metal concentration, (mg/L)	2	5	10	20	30	50
Measured initial metal concentration, C_o (mg/L)	1.9	4.75	9.5	19	28.5	47.5
Initial pH	4.56	4.45	4.54	4.51	4.46	4.34
Adjusted pH	7.70	7.79	7.41	7.71	7.69	7.69
Peat weight, m (g)	0.1	0.1	0.1	0.1	0.1	0.1
Volume of Solution, V (mL)	100	100	100	100	100	100
Soil : Solution ratio	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000
Equilibrium pH	7.66	7.44	7.24	7.61	7.48	7.50
Equilibrium metal concentration, C (mg/L)	0.97	2.02	2.46	2.74	2.60	1.41
Container adsorbed, C_c (mg/L)	0.016	0.033	0.04	0.045	0.042	0.023
Amount of adsorbed, Ca (mg/L)	0.914	0.269	0.700	1.62	2.59	4.61
Percent of adsorbed (%)	48.11	56.78	73.68	85.34	90.73	96.98
Amount of adsorbed, q (mg metal/kg peat)	914	2697	7000	16215	25858	46067
TOC (mg/L)	29	24	21	23	24	28

It should be noted that some light green precipitate was observed on the filter when separating the peat from the solutions for the 30 mg/L and 50 mg/L samples. This precipitation caused the equilibrium concentrations of zinc to be extremely low in these two samples. No adsorption isotherms were developed for this batch experiments. However, measurement of TOC was performed on all the samples, because the color of the filtrate was light brown. The concentrations of TOC were slightly lower than those measured in batch experiment #1. In order to avoid precipitation, an initial pH range of 4-5 was used in the next batch experiment.

4.1.4 Batch Experiment #4

4.1.4.1 Procedure of Experiment #4

The procedure of batch experiment #4 was the same as batch experiment #3, except no pH adjustments were performed in this experiment. The initial pH was around 4-5 without any 1.0 N NaOH adjustment. The objective was to prevent any precipitation during the adsorption experiment.

4.1.4.2 Results and Analysis of Experiment #4

The same initial zinc concentrations and the container adsorption concentrations (batch experiment #3) were used in batch experiment #4.

A summary of results from batch experiment #4 is presented in Table 4.4.

A plot of zinc concentration at equilibrium versus amount of zinc adsorbed by peat is shown in Figure 4.7. A plot of the linearized form of the Langmuir equation is shown in Figure 4.8; the best fit straight line is described by equation 4-9:

$$1/q = 0.002051/C + 0.0002755 \qquad (R^2 = 0.8861) \qquad (4\text{-}9)$$

The slope (1/Qb) and the intercept (1/Q) are 0.002051 and 0.0002755, respectively, which gave Q of 3629.8 and constant b of 0.1343. So, a theoretical maximum peat adsorption capacity for zinc was found to be 3639.8 mg zinc per kg peat. R^2 was 0.8816 indicating a fair fit to the data.

The linearized form of the Freundlich isotherm is shown in Figure 4.9; the best straight line fit is given by equation 4-10:

$$\log q = 0.7298 \log C + 2.5926 \qquad (R^2 = 0.9709) \qquad (4\text{-}10)$$

where the slope (1/n) and the intercept (log K) are 0.7298 and 2.5926 respectively.

Table 4.4 Summary of Batch Experiment #4 - Zinc / Peat

Nominal initial metal concentration, (mg/L)	2	5	10	20	30	50
Measured initial metal concentration, C_o (mg/L)	1.9	4.75	9.5	19	28.5	47.5
Initial pH	4.35	4.33	4.36	4.34	4.41	4.32
Adjusted pH	N/A	N/A	N/A	N/A	N/A	N/A
Peat weight, m (g)	0.1	0.1	0.1	0.1	0.1	0.1
Volume of Solution, V (mL)	100	100	100	100	100	100
Soil : Solution ratio	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000
Equilibrium pH	4.20	4.31	4.30	4.28	4.31	4.24
Equilibrium metal concentration, C (mg/L)	1.31	3.88	7.91	16.09	23.85	41.04
Container adsorbed, C_c (mg/L)	0.01	0.02	0.04	0.08	0.12	0.20
Amount of adsorbed, Ca (mg/L)	0.583	0.850	1.55	2.83	4.53	6.26
Percent of adsorbed (%)	30.70	17.90	16.32	14.89	15.89	13.16
Amount of adsorbed, q (mg metal/kg peat)	583.4	850.4	1550	2829	4529	6252
TOC (mg/L)	N/A	N/A	N/A	N/A	N/A	N/A

So, it is found that K was 391.4 and n was 1.370. R^2 was 0.9709 indicating a good fit, and slightly better than the Langmuir isotherm. The Freundlich isotherm can be rewritten as follows:

$$q = 391.4\, C^{0.7298} \qquad (4\text{-}11)$$

The percentage of zinc adsorbed by peat ranged from 30.70% to 13.16% in the batch experiment #4, while this percentage ranged from 48.11% to 96.98% in batch experiment #3. The amount of zinc adsorbed to peat ranged from 914 mg/kg to 46067 mg/kg in the batch experiment #3 and 583.4 mg/kg to 6252 mg/kg in batch experiment #4

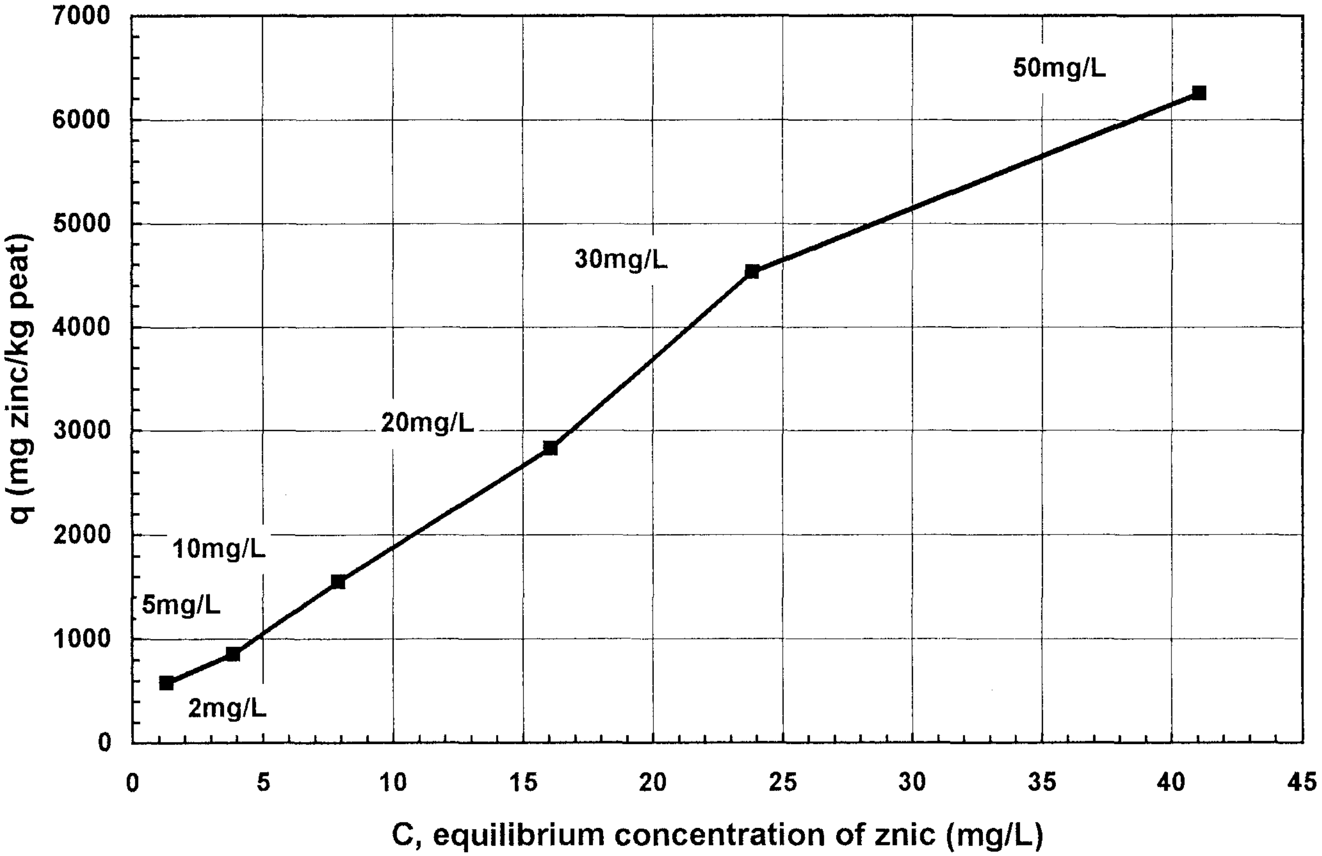

Figure 4.7 Batch Experiment #4 - Zinc / Peat (pH = 4- 5)

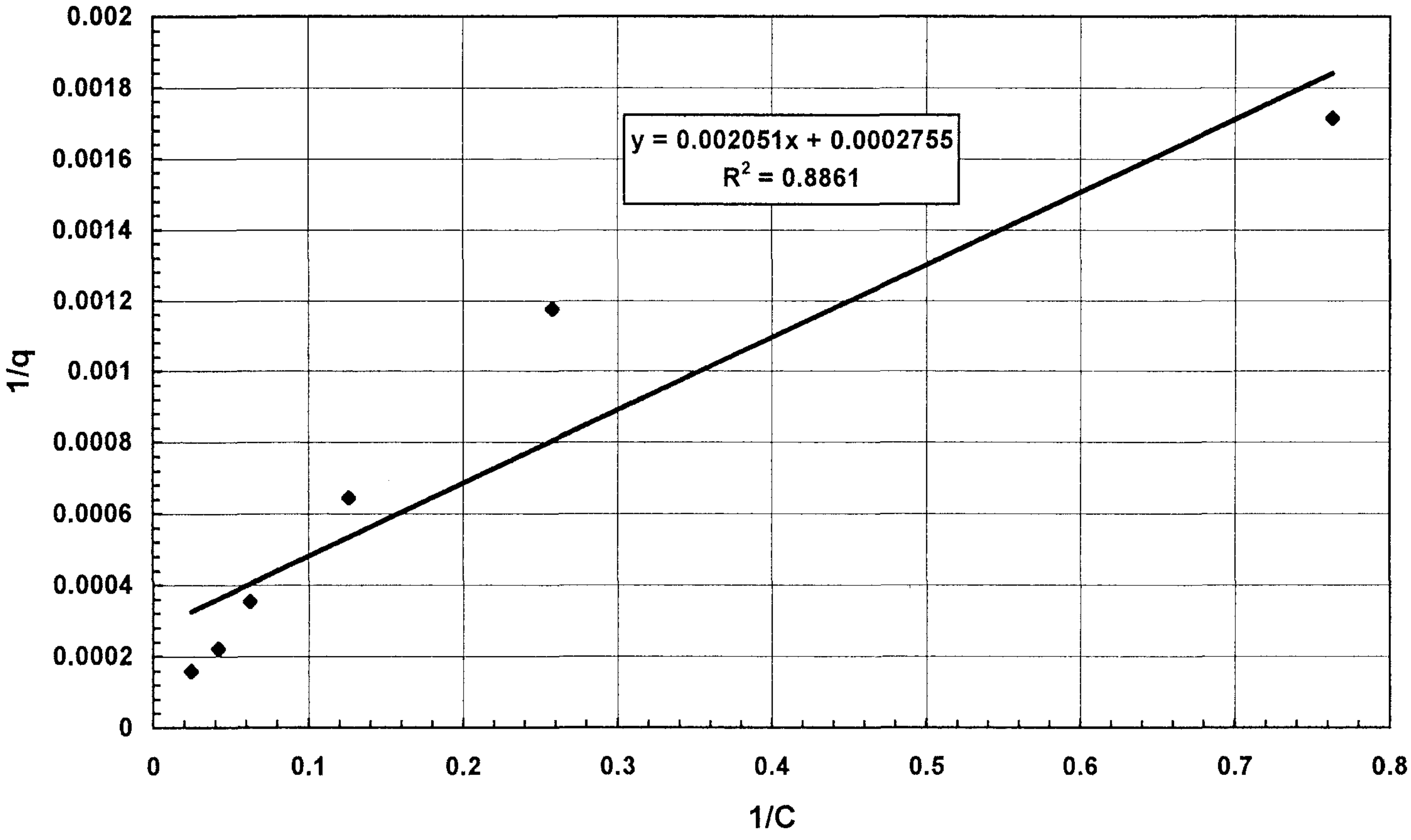

Figure 4.8 Batch Experiment #4 - Langmuir Isotherm

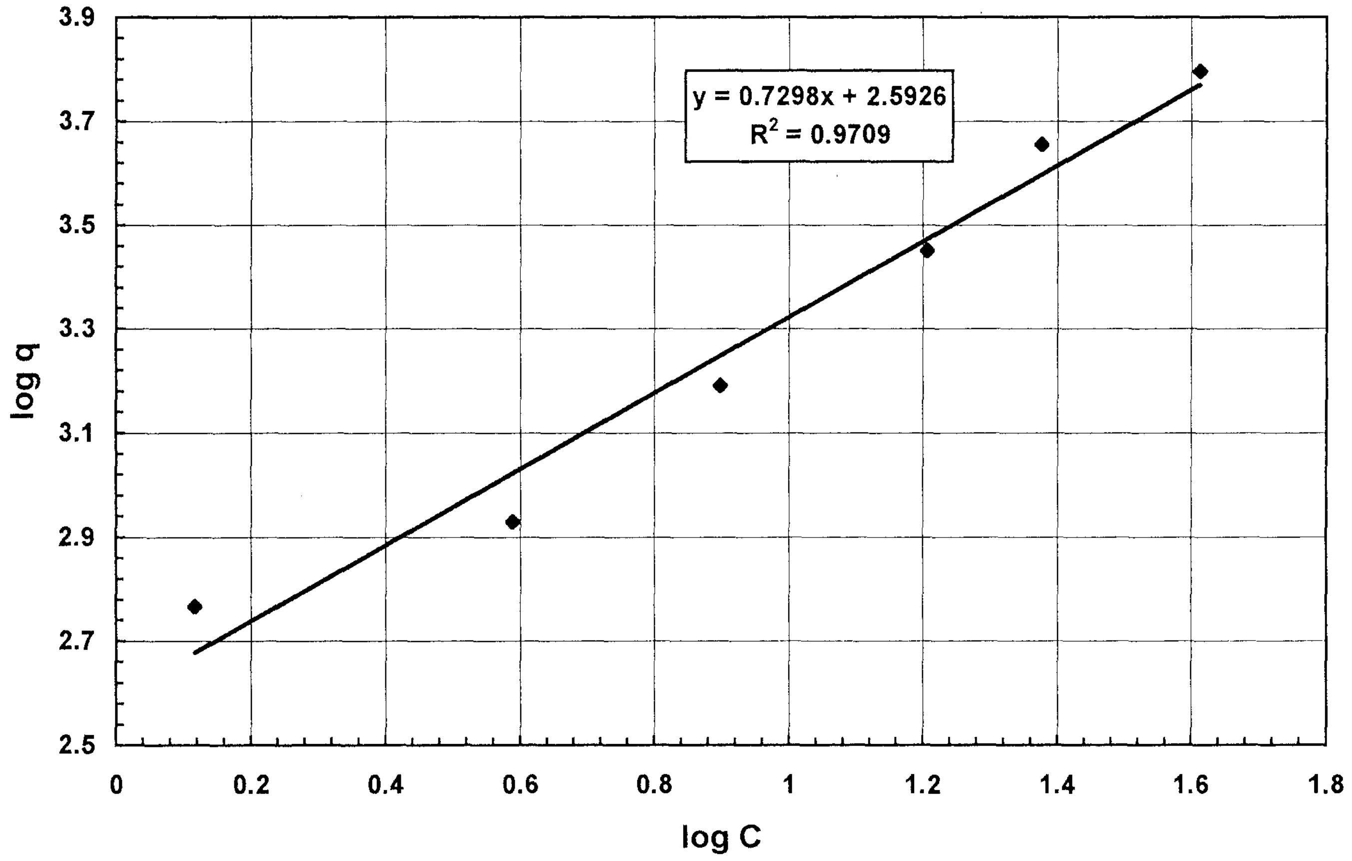

Figure 4.9 Batch Experiment #4 - Freundlich Isotherm

at the same soil : solution ratio and initial zinc concentrations. The results showed greater zinc adsorption at higher initial pH, possibly because the precipitation and metal - peat complexation were much stronger.

The measurement of TOC was not performed in batch experiment #4, because the color of the filtrate was not different from the initial solution. Therefore, it was assumed that the amount organic acids released was very low in this experiment. This is also supported by the observation that the equilibrium pH was very close to the initial pH.

4.1.5 Batch Experiment #5

4.1.5.1 Procedure of Experiment #5

Batch experiment #5 was performed to detect peat adsorption of copper. The experimental conditions were similar to batch experiment #4. Copper was used as the adsorbate in this experiment. A 100 mg/L copper stock solution was prepared by dissolving 0.3930g copper sulfate ($CuSO_4.5H_2O$) in 1L deionized water. The 100 mL initial solutions containing copper concentration of 2 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, and 50 mg/L were prepared by diluting the stock solution into 0.1 M KH_2PO_4 buffer. The initial copper concentration was determined by a measurement on the 100 mg/L copper stock solution. The solutions were poured into clean 125 mL plastic bottles. The initial pH was measured on each of the samples, and 1.0 N NaOH was used to adjust the initial pH to around 5 for all the samples. Approximately 0.1 g dried peat was added to each flask to give a soil : solution ratio of 1 : 1000. One control sample containing 10 mg/L copper without any peat was prepared to test the container (plastic) adsorption of copper under the same experimental conditions. The samples containing peat and different concentrations of copper were shaken for about 24 hours at a speed of 200 rpm. Final solution were filtered through Whatman GF/C glass fiber filters to filter out the peat. The equilibrium pH was measured on all the samples. No subsamples were saved for the TOC measurement. Filtrates were acidified with approximately 1 mL of concentrated nitric acid and stored in 125 mL plastic bottles. Concentrations of copper in the filtrates were measured and recorded.

4.1.5.2 Results and Analysis of Experiment #5

The detected concentration of copper was 94 mg/L in the nominal 100 mg/L copper stock solution. It was assumed that the initial copper concentrations were directly proportional to the this measured value. Since the measured concentration of copper in the control sample was 9.34 mg/L, it was assumed that 0.06 mg/L copper was adsorbed by the container. It was also assumed that the amount of copper adsorbed by the containers was directly proportional to the initial concentration in the sample.

A summary of results from batch experiment #5 is presented in Table 4.5.

Table 4.5 Summary of Batch Experiment #5 - Copper / Peat

Nominal initial metal concentration, (mg/L)	2	5	10	20	30	50
Measured initial metal concentration, C_o (mg/L)	1.88	4.70	9.40	18.80	28.20	47.00
Initial pH	4.44	4.42	4.39	4.42	4.41	4.35
Adjusted pH	5.15	5.17	5.21	5.17	5.11	5.09
Peat weight, m (g)	0.1	0.1	0.1	0.1	0.1	0.1
Volume of Solution, V (mL)	100	100	100	100	100	100
Soil : Solution ratio	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000
Equilibrium pH	5.13	5.13	5.10	5.10	5.01	4.90
Equilibrium metal concentration, C (mg/L)	0.329	0.993	3.497	9.455	11.21	9.965
Container adsorbed, C_c (mg/L)	0.0056	0.017	0.06	0.16	0.19	0.18
Amount of adsorbed, Ca (mg/L)	1.545	3.690	5.844	9.185	16.80	36.86
Percent of adsorbed (%)	82.20	78.51	62.16	48.86	59.57	78.41
Amount of adsorbed, q (mg metal/kg peat)	1545	3690	5844	9185	16800	36855
TOC (mg/L)	N/A	N/A	N/A	N/A	N/A	N/A

The equilibrium concentration of copper in the 50mg/L sample was extremely low, possibly because copper precipitates at pH around 5. Therefore, a plot of copper concentration at equilibrium versus amount of copper adsorbed by peat was developed based on the first five samples and was shown in Figure 4.10. A plot of the data in the linearized form of the Langmuir equation is shown in Figure 4.11; the best fit straight line is described by equation 4-12:

$$1/q = 0.0001866/C + 0.00008260 \qquad (R^2 = 0.9870) \tag{4-12}$$

The slope (1/Qb) and the intercept (1/Q) are 0.0001866 and 0.00008260, respectively, which give Q of 12107 mg copper / kg peat and constant b of 0.4427. So, the theoretical maximum peat adsorption capacity is 12107 mg copper per kg peat. R^2 was 0.9870 indicating a good fit to the data.

A plot in the linearized form of the Freundlich isotherm is shown in Figure 4.12; the best fit line is described by to equation 4-13:

$$\log q = 0.5853 \log C + 3.4984 \qquad (R^2 = 0.9481) \tag{4-13}$$

The slope (1/n) and the intercept (log K) were 0.5853 and 3.4984 respectively. So, it was found that the K was 3151 and n was 1.7085. R^2 was 0.9481 indicating a good fit to the data. The Langmuir isotherm fits slightly better compared to the Freundlich isotherm in this experiment. The Freundlich isotherm can be rewritten as follows:

$$q = 3151\ C^{0.5853} \tag{4-14}$$

There was almost no color in the filtrates in this batch experiment which means there were less organic acids leached into the solution. The percentage of copper adsorbed ranged from 48.86% to 82.80%, while the amount adsorption ranged from 1545 to 36855 mg copper per kg peat.

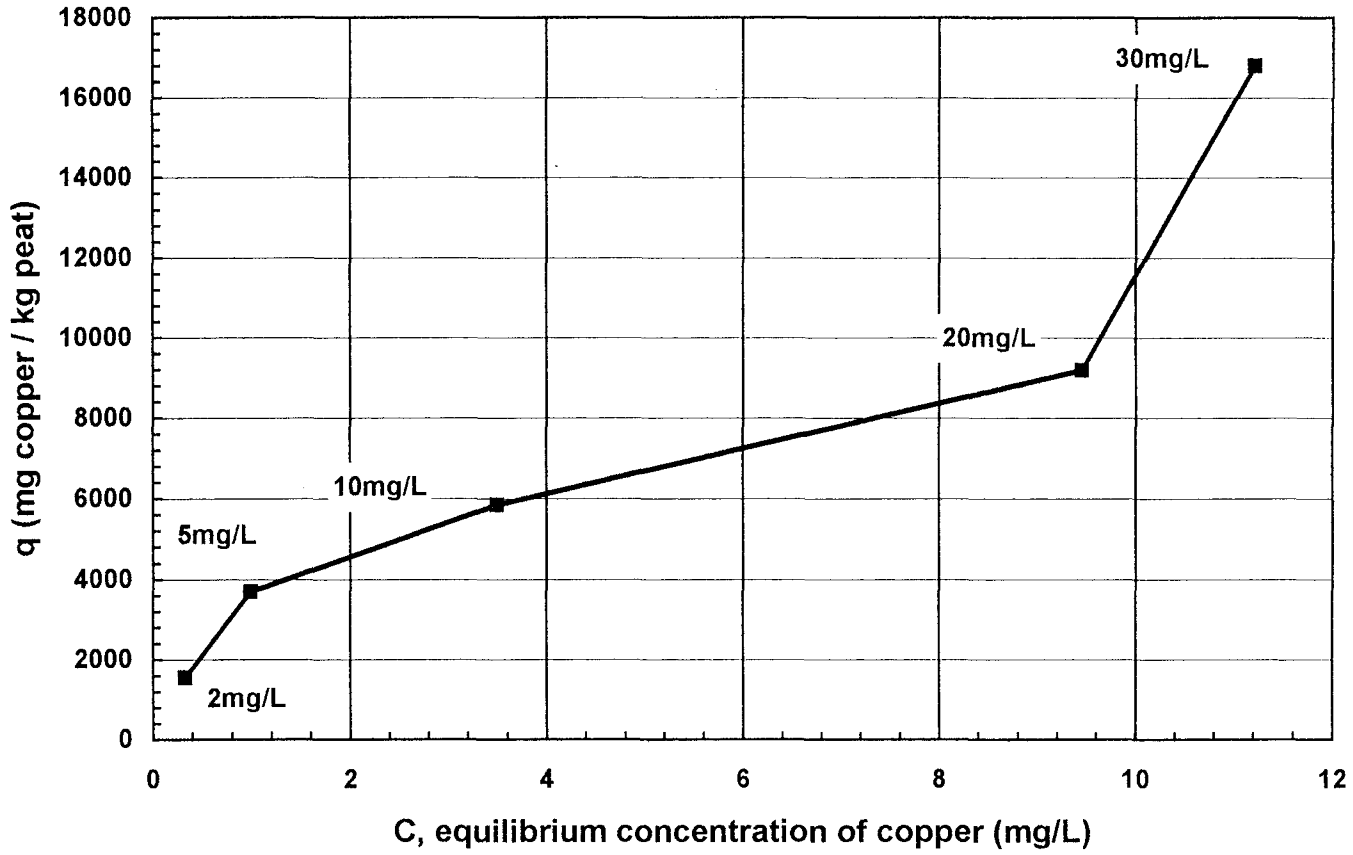

Figure 4.10 Batch Experiment #5 - Copper / Peat (pH = 5 - 6)

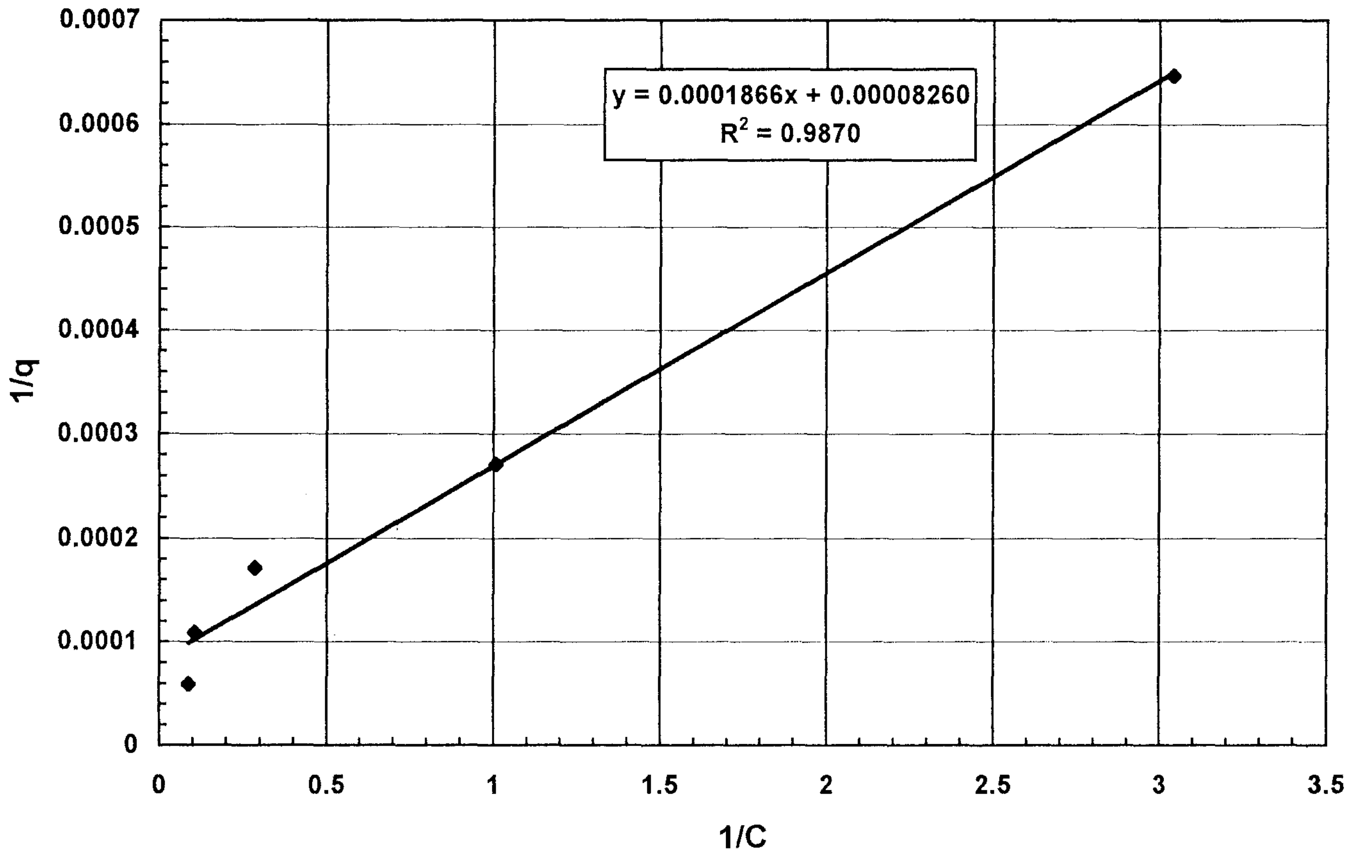

Figure 4.11 Batch Experiment #5 - Langmuir Isotherm

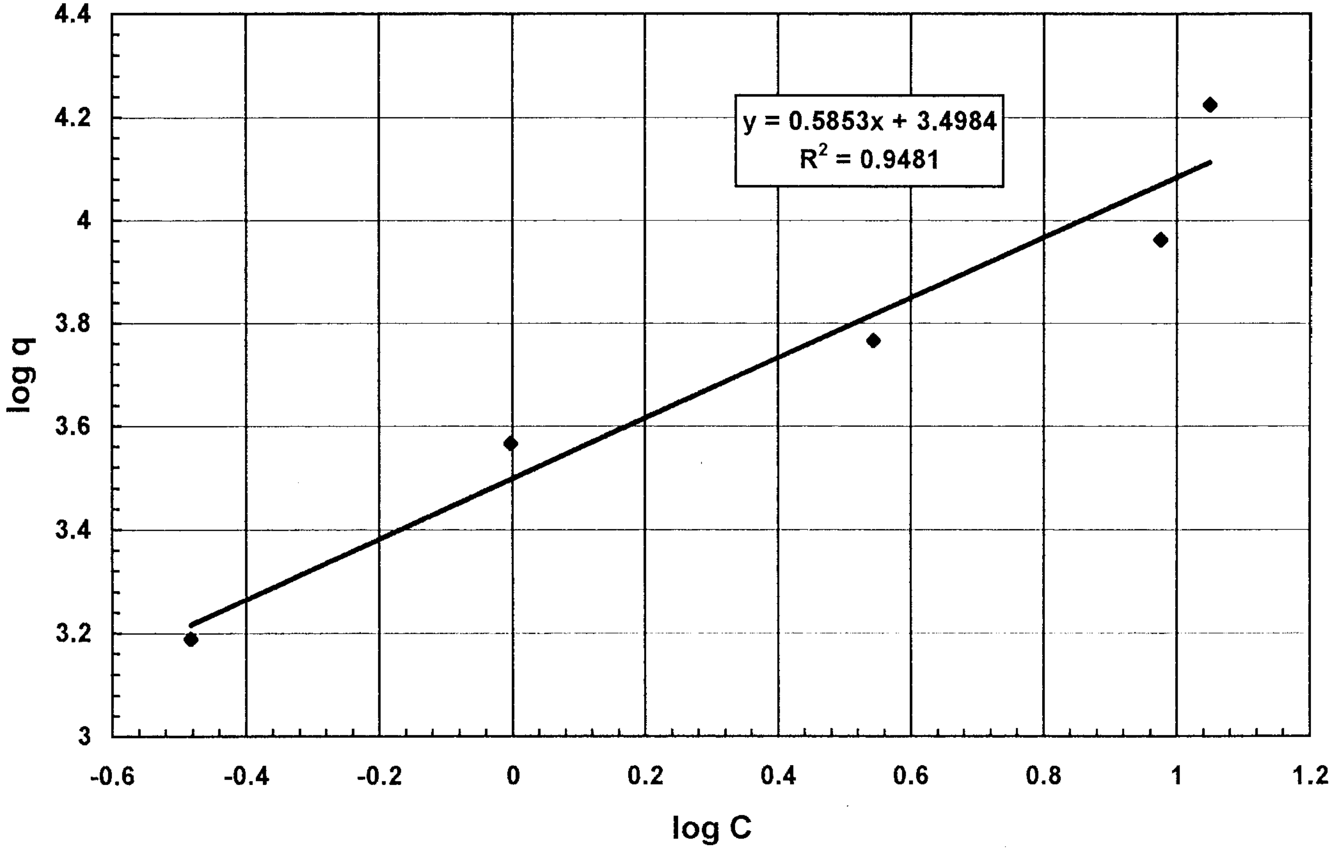

Figure 4.12 Batch Experiment #5 - Freundlich Isotherm

The theoretical maximum peat adsorption capacity was found to be 12107 mg copper per kg peat in this experiment. This number was lower compared to what Patterson (1996) was found (27710 mg copper/kg peat) because the initial pH was around 5 in this experiment, while pH was above 8 in Patterson's (1996) experiment.

4.1.6 Batch Experiment #6

4.1.6.1 Procedure of Experiment #6

The first five batch experiments were performed to detect the peat adsorption of copper, nickel and zinc individually. Batch experiment #6 was performed to detect peat adsorption of a mixture of the three metals. The mixture of copper, nickel and zinc was used as the adsorbate in this experiment. The stock solution of each metal used in batch experiment #6 was the same as in batch experiments #2 to #5. The 100 mL initial solutions containing each of the three metals at concentrations of 1 mg/L, 2 mg/L, 5 mg/L, 9 mg/L, 15 mg/L, and 20 mg/L were prepared by diluting the stock solutions into 0.1 M KH_2PO_4. The initial solutions were poured into clean 125 mL plastic bottles. The initial pH was measured on each sample, and 1.0 N NaOH was used to adjust the initial pH at about 5. Approximately 0.1 g dried peat was added to each flask to give a soil : solution ratio of 1 : 1000. One control sample containing 10 mg/L of each three metal without any peat was prepared to test the container (plastic) adsorption of heavy metals under the same experimental conditions. The samples were shaken for about 24 hours at a speed of 200 rpm. Final solution were filtered through Whatman GF/C glass fiber filters to filter out the peat. The equilibrium pH was measured on all the samples. Subsamples were saved in 50 mL glass vials for TOC measurements. Filtrates were acidified with approximately 1 mL concentrated nitric acid and stored in 125 mL plastic bottles. Concentrations of copper, nickel, and zinc in the filtrates were measured and recorded individually.

4.1.6.2 Results and Analysis of Experiment #6

A summary of results from batch experiment #6 is presented in Table 4.6.

Table 4.6 Summary of Batch Experiment #6 - Copper, Nickel and Zinc / Peat

Nominal initial metal concentration, (mg/L)	1	2	5	9	15	20
Measured initial copper concentration, C_0,cu (mg/L)	0.94	1.88	4.70	8.46	14.10	18.80
Measured initial nickel concentration, C_0,ni (mg/L)	0.96	1.92	4.80	8.64	14.40	19.20
Measured initial zinc concentration, C_0,zn (mg/L)	0.95	1.90	4.75	8.55	14.25	19.00
Initial pH	3.50	3.16	2.75	2.37	3.47	3.30
Adjusted pH	5.15	5.32	5.45	5.14	5.66	5.61
Peat weight, m (g)	0.1	0.1	0.1	0.1	0.1	0.1
Volume of Solution,V(mL)	100	100	100	100	100	100
Soil : Solution ratio	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000	1 : 1000
Equilibrium pH	4.81	4.98	4.86	4.21	5.19	5.16
Equilibrium copper concentration, Ccu (mg/L)	0.121	0.322	1.945	4.397	6.155	7.442
Equilibrium nickel concentration, Cni (mg/L)	0.521	1.174	3.466	7.365	11.215	15.315
Equilibrium zinc concentration, Czn (mg/L)	0.523	1.158	3.920	7.660	12.010	16.330
Container adsorbed, $C_{c,cu}$ (mg/L)	0.003	0.008	0.048	0.109	0.153	0.185
Container adsorbed, $C_{c,ni}$ (mg/L)	0.001	0.002	0.007	0.014	0.022	0.029
Container adsorbed, $C_{c,zn}$ (mg/L)	0.001	0.002	0.007	0.015	0.023	0.031
Amount of adsorbed, Ca,cu (mg/L)	0.817	1.550	2.707	3.954	7.792	11.174
Amount of adsorbed, Ca,ni (mg/L)	0.439	0.744	1.327	1.260	3.162	3.854
Amount of adsorbed, Ca,zn (mg/L)	0.427	0.740	0.823	0.875	2.217	2.639
Percent of copper adsorbed (%)	86.86	82.45	57.60	46.74	55.26	59.43
Percent of nickel adsorbed (%)	45.68	38.78	27.65	14.58	21.96	20.07
Percent of zinc adsorbed (%)	44.89	38.95	17.33	10.23	15.56	13.89
Amount of copper adsorbed, q (mg copper / kg peat)	816.5	1550	2707	3954	7792	11174
Amount of nickel adsorbed, q (mg nickel / kg peat)	438.5	744.5	1327	1260	3162	3854
Amount of zinc adsorbed, q (mg zinc / kg peat)	426.5	740	823	875	2217	2639
TOC (mg/L)	18	21	17	15	16	17

A plot of copper concentration at equilibrium versus the amount of copper adsorbed by peat is shown in Figure 4.13. A plot of data in the linearized form of the Langmuir equation is shown in Figure 4.14. The best fit line is described by equation 4-15:

$$1/q = 0.0001287/C + 0.0001849 \qquad (R^2 = 0.9578) \qquad (4\text{-}15)$$

The slope (1/Qb) and the intercept (1/Q) were 0.0001287 and 0.0001849, respectively, which give Q of 5408 mg copper / kg peat and constant b of 1.437. So, the theoretical maximum peat adsorption capacity for copper was 5408 mg copper per kg peat. R^2 was 0.9578 indicating the good fit to the data.

A plot of data in the linearized form of the Freundlich isotherm is shown in Figure 4.15. The best fit line is described by equation 4-16:

$$\log q = 0.5518 \log C + 3.4033 \qquad (R^2 = 0.9161) \qquad (4\text{-}16)$$

The slope (1/n) and the intercept (log K) were 0.5518 and 3.4033 respectively. So, it was found that the K was 2531 and n was 1.8122. R^2 was 0.9161 indicating the good fit to the data. The Freundlich isotherm can be rewritten as follows:

$$q = 2531\ C^{0.5518} \qquad (4\text{-}17)$$

A plot of nickel concentration at equilibrium versus the amount of nickel adsorbed by peat is shown in Figure 4.16. A plot of data in the linearized form of the Langmuir equation is shown in Figure 4.17. The Langmuir isotherm fit for this data can be described by equation 4-18:

$$1/q = 0.001010/C + 0.0003933 \qquad (R^2 = 0.9467) \qquad (4\text{-}18)$$

The slope (1/Qb) and the intercept (1/Q) were 0.001010 and 0.0003933, respectively, which give Q of 2543 mg nickel / kg peat and constant b of 0.3899. So, the theoretical

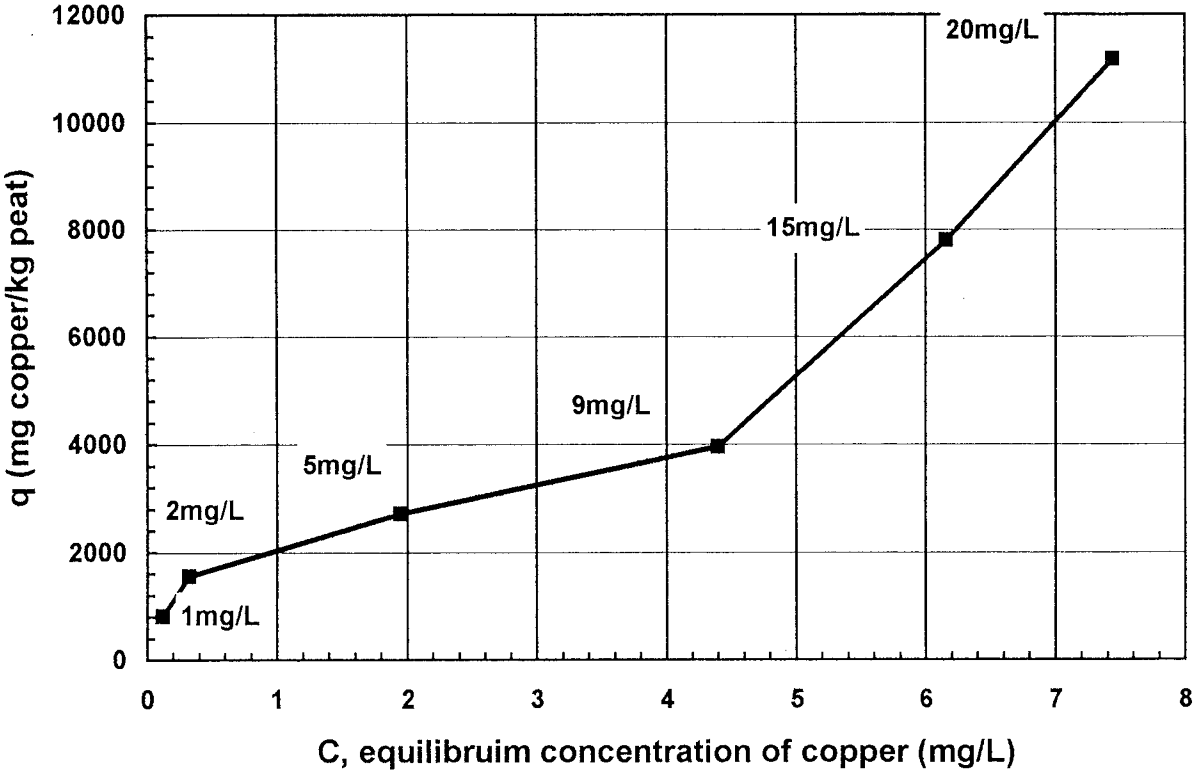

Figure 4.13 Batch Experiment #6 (Copper) - Copper, Nickel and Zinc / Peat

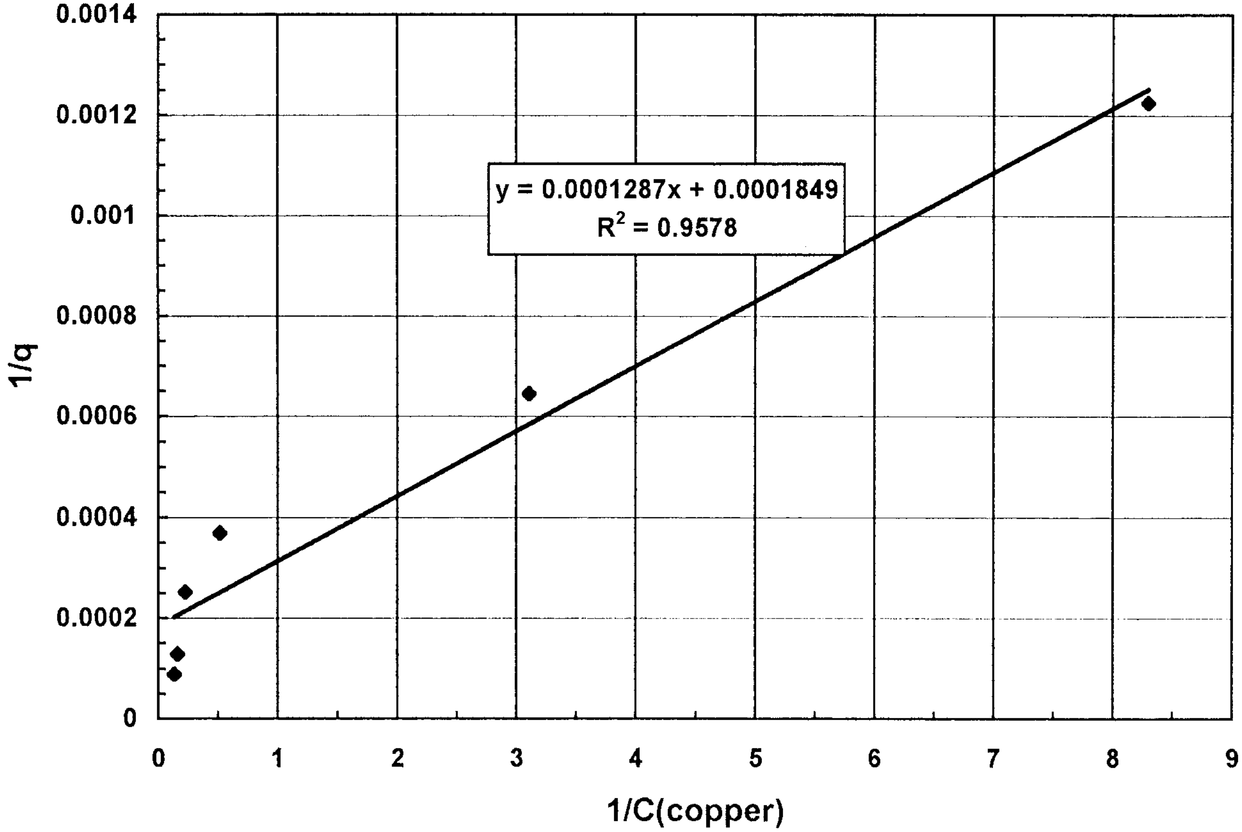

Figure 4.14 Batch Experiment #6 - Langmuir Isotherm for Copper

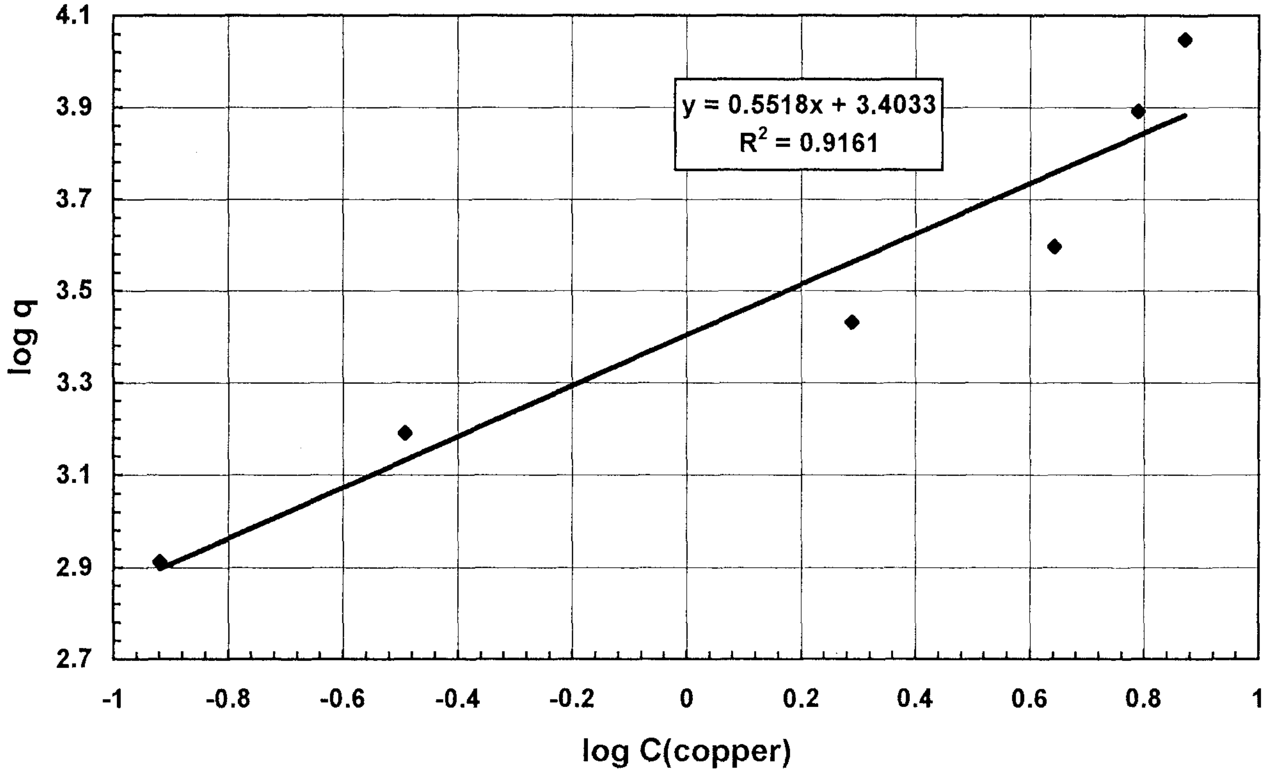

Figure 4.15 Batch Experiment #6 - Freundlich Isotherm for Copper

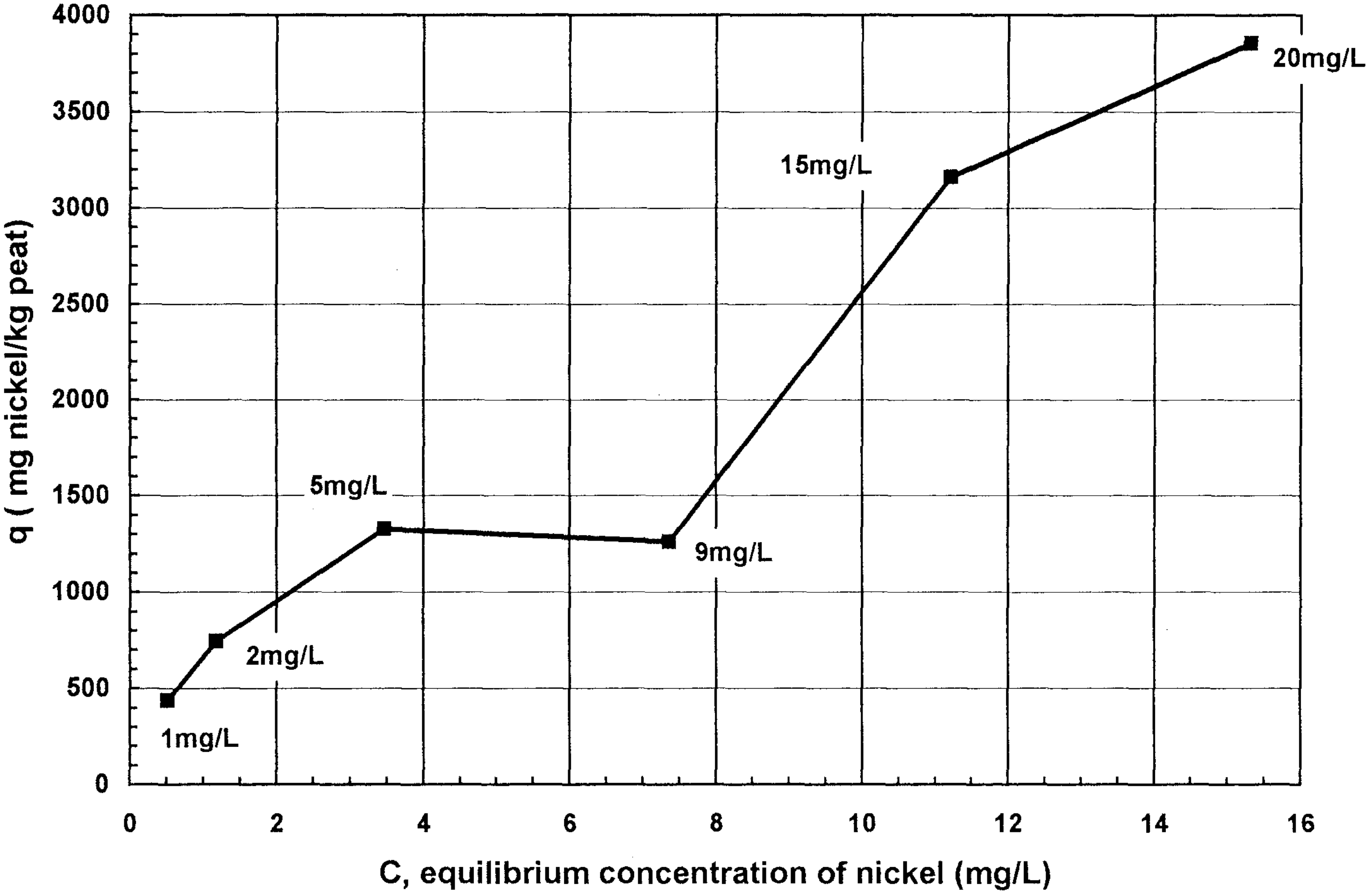

Figure 4.16 Batch Experiment #6 (Nickel)- Copper, Nickel and Zinc / Peat

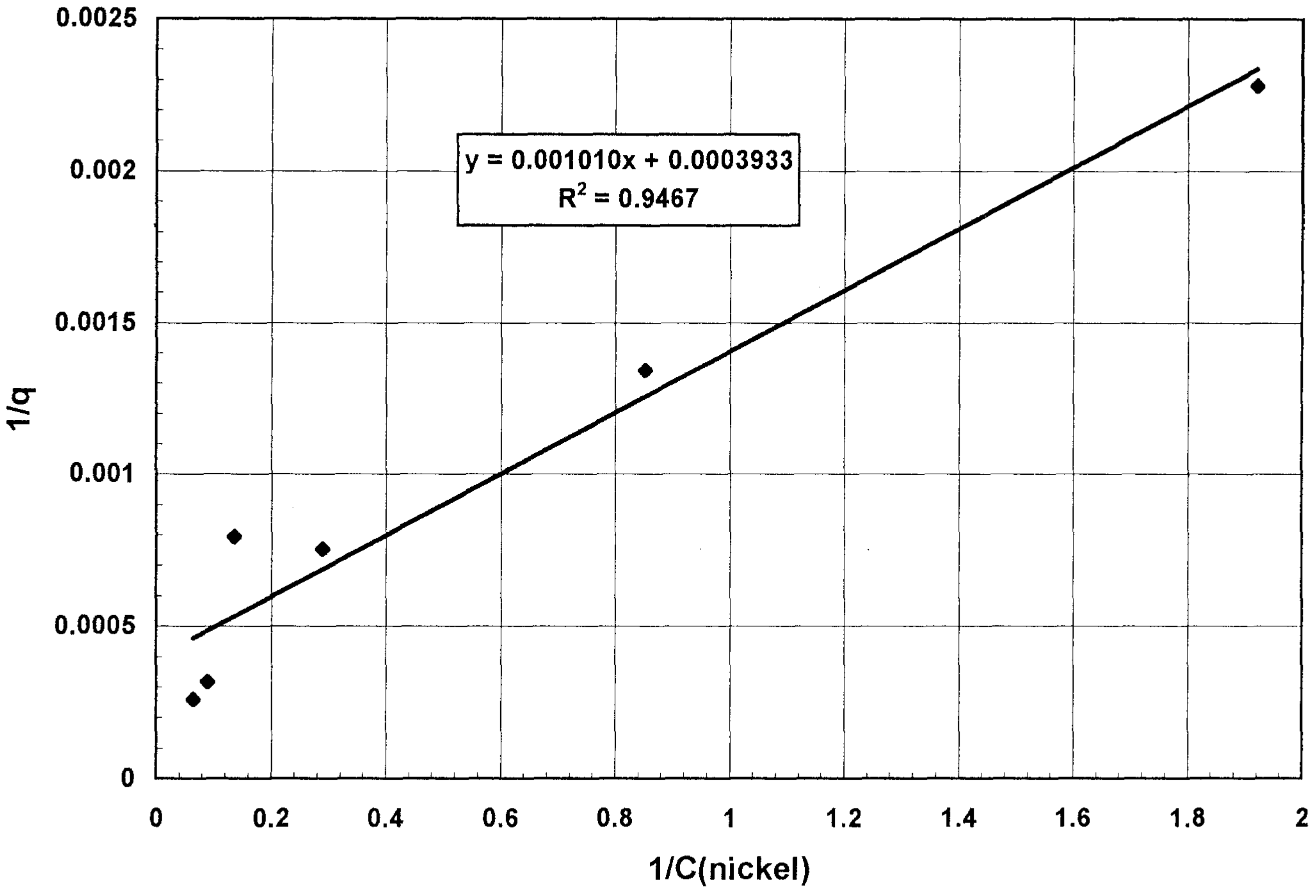

Figure 4.17 Batch Experiment #6 - Langmuir Isotherm for Nickel

maximum peat adsorption capacity for copper was 2542.6 mg nickel per kg peat. R^2 was 0.9733 indicating the good fit of the data.

A plot of data in the linearized form of the Freundlich isotherm is shown in Figure 4.18. The Freundlich isotherm fit is described by equation 4-19:

$$\log q = 0.5934 \log C + 2.7981 \qquad (R^2 = 0.9082) \qquad (4\text{-}19)$$

The slope (1/n) and the intercept (log K) were 0.5934 and 2.7981, respectively. So, it was found that the K was 628.2 and n was 1.685. R^2 was 0.9082 indicating a good fit to the data. The Freundlich isotherm can be rewritten as follows:

$$q = 628.2\ C^{0.5934} \qquad (4\text{-}20)$$

A plot of zinc concentration at equilibrium versus the amount of zinc adsorbed by peat was shown in Figure 4.19. A plot of data in the linearized form of the Langmuir equation is shown in Figure 4.20. The Langmuir isotherm fit is described by equation 4-21:

$$1/q = 0.0008885/C + 0.0006575 \qquad (R^2 = 0.8274) \qquad (4\text{-}21)$$

The slope (1/Qb) and the intercept (1/Q) are 0.0008885 and 0.0006575, respectively, which give the Q of 1521 mg zinc / kg peat and constant b of 0.74. So, the theoretical maximum peat adsorption capacity was 1520.9 mg zinc per kg peat. R^2 was 0.8274 indicating not very well fit to the data.

A plot of data in the linearized form of the Freundlich isotherm is shown in Figure 4.21. The Freundlich isotherm fit is described by equation 4-22:

$$\log q = 0.4600 \log C + 2.7483 \qquad (R^2 = 0.8072) \qquad (4\text{-}22)$$

where the slope (1/n) and the intercept (log K) were 0.4600 and 2.7483, respectively. So, it was found that the K was 560.1 and n was 2.174. R^2 was 0.8072

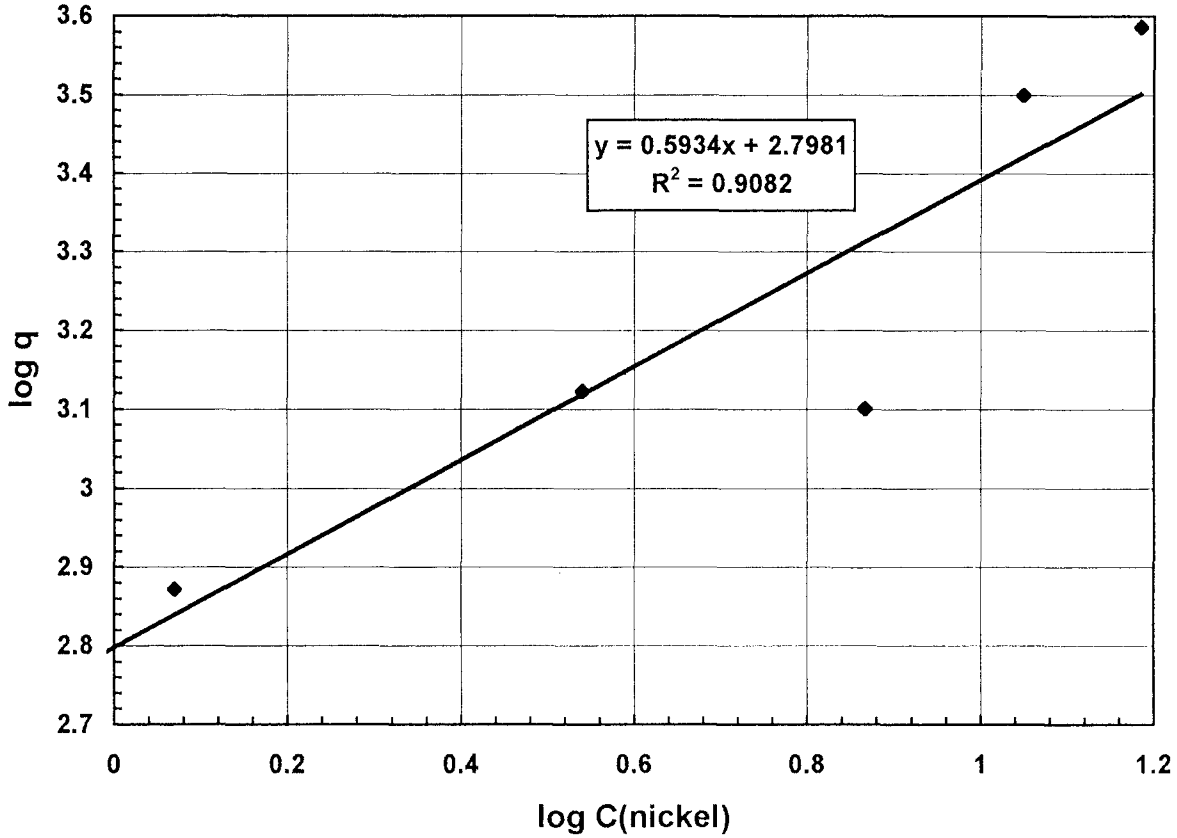

Figure 4.18 Batch Experiment #6 - Freundlich Isotherm for Nickel

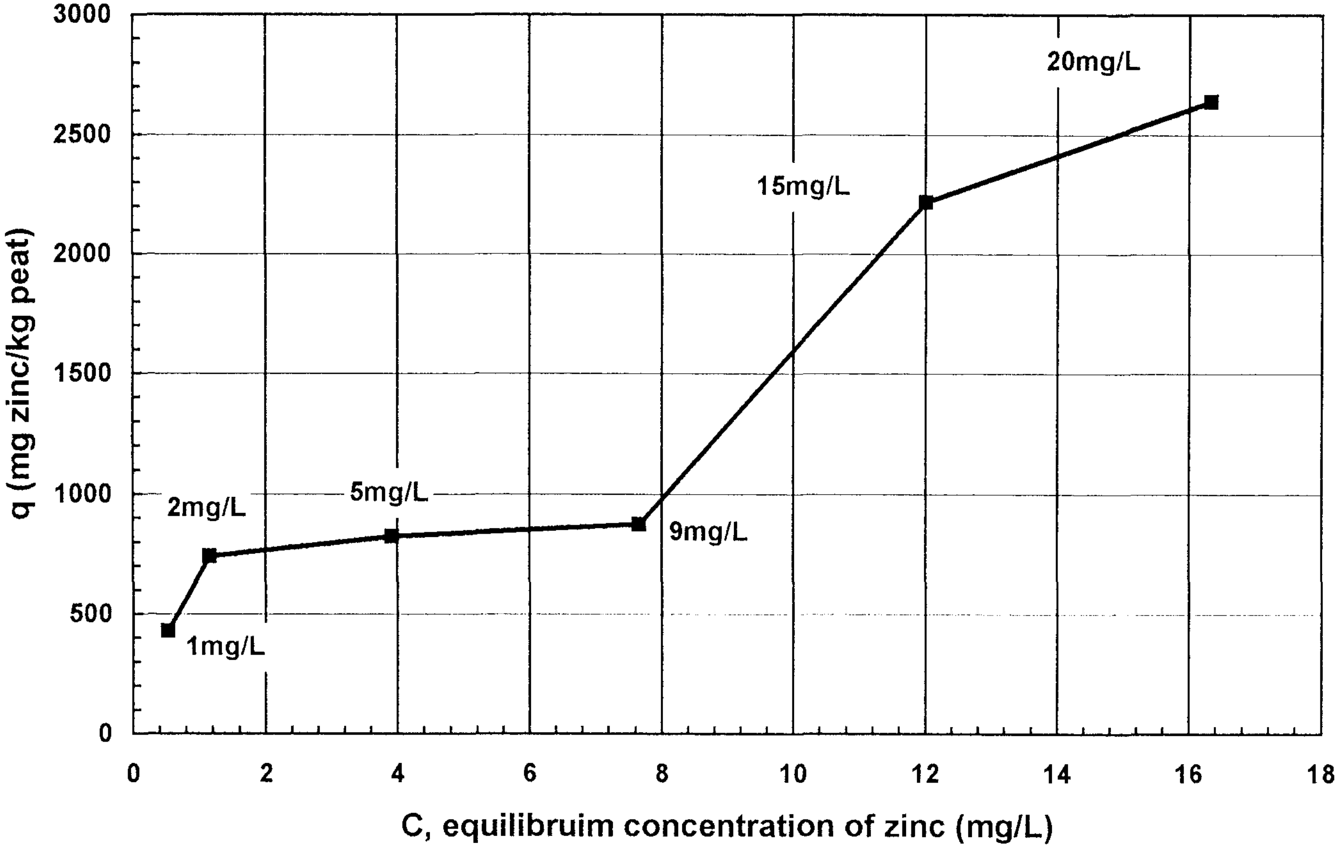

Figure 4.19 Batch Experiment #6 (Zinc) - Copper, Nickel and Zinc / Peat

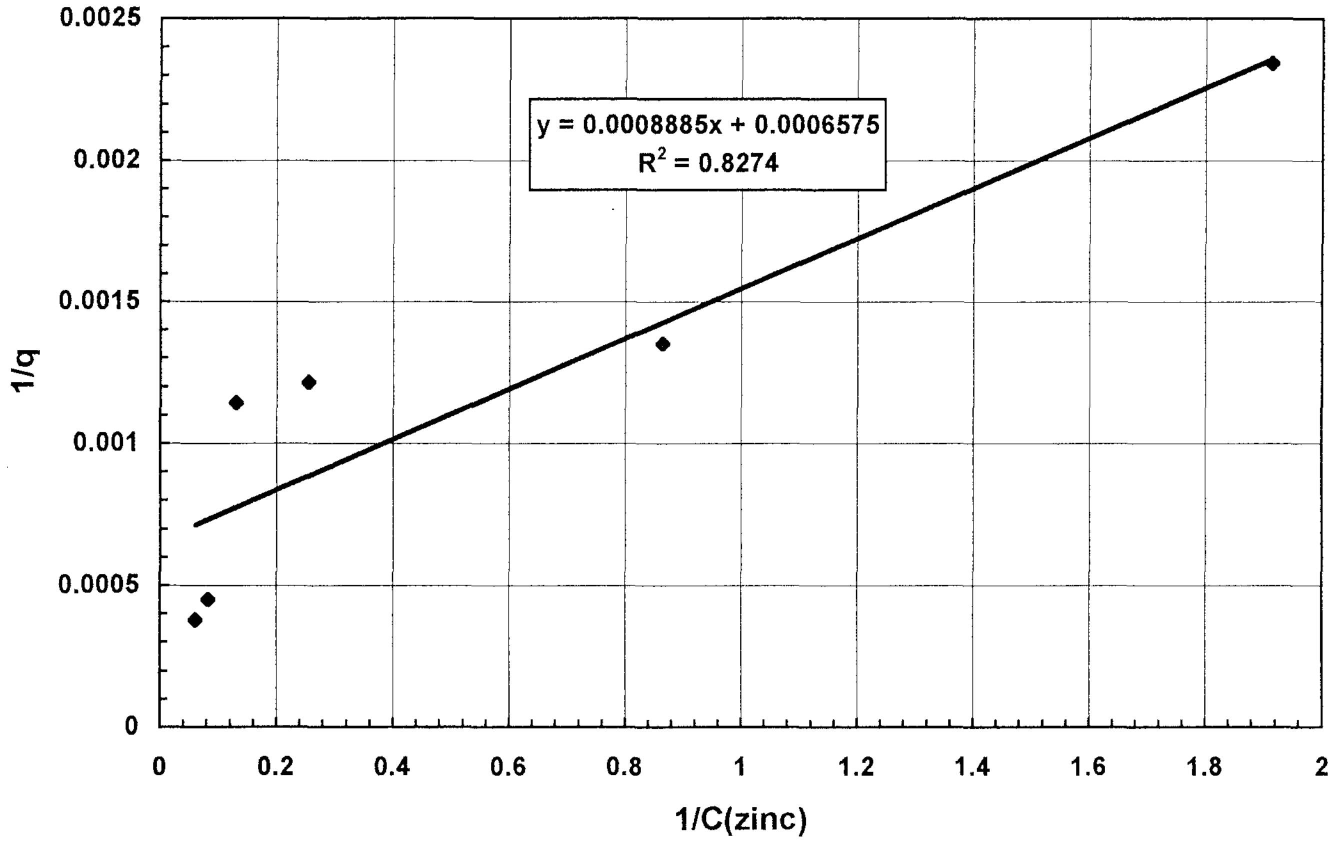

Figure 4.20 Batch Experiment #6 - Langmuir Isotherm for Zinc

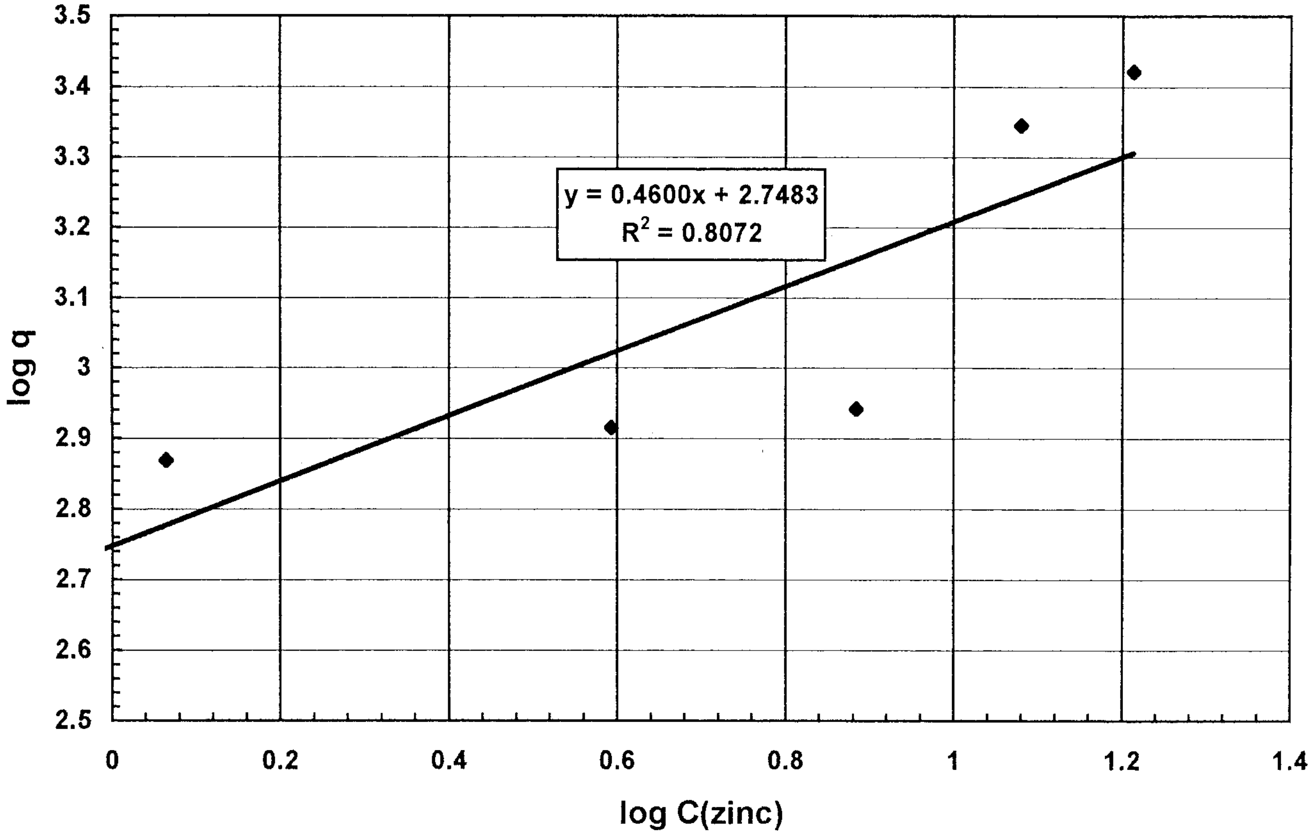

Figure 4.21 Batch Experiment #6 - Freundlich Isotherm for Zinc

indicating not very well fit to the data either. The Freundlich isotherm can be rewritten as follows:

$$q = 560.1\ C^{0.460} \tag{4-23}$$

Comparing the peat adsorption of the three metals under the same experimental conditions, the adsorption capacity decreased in the order of copper > nickel > zinc. At 1 : 1000 soil : solution ratio and pH around 5, according to the results of the Langmuir isotherm, the theoretical maximum adsorption capacity was 5408 mg copper per kg peat, 2543 mg nickel per kg peat and 1521 mg zinc per kg peat. The color of the filtrates were extremely light, with very little difference from the initial solution. The concentrations of TOC were about half compared to the TOC which was measured in batch experiments #1 and #3.

4.1.7 Summary of Batch Experiments

A summary of the Langmuir and Freundlich isotherm constants to each batch experiment is presented is Table 4.7.

Table 4.7 Summary of isotherm constants of Batch Experiments #1 - #6

#	the Langmuir Isotherm Equation	Q (mg metal/kg peat)	b	R^2	the Freundlich Isotherm Equation	K	n	R^2	Better fit
#1	$1/q = 0.0008921/C - 0.001124$	N/A	N/A	0.7757	$q = 3342\ C^{1.101}$	3342	0.908	0.8166	Freundlich
#2	$1/q = 0.002116/C + 0.00002260$	44248	0.01068	0.9807	$q = 502.5\ C^{0.9030}$	502.5	1.107	0.9807	Both
#3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
#4	$1/q = 0.002051/C + 0.0002755$	3639.8	0.1343	0.8816	$q = 391.4\ C^{0.7298}$	391.4	1.370	0.9709	Freundlich
#5	$1/q = 0.0001866/C + 0.00008260$	12107	0.4427	0.9870	$q = 3151\ C^{0.5853}$	3151	1.709	0.9742	Both
#6	Cu: $1/q = 0.0001287/C + 0.0001849$ Ni: $1/q = 0.001010/C + 0.0003933$ Zn: $1/q = 0.0008885/C + 0.0006575$	5408 2543 1521	1.437 0.3899 0.7400	0.9578 0.9467 0.8274	$q = 2531C^{0.5518}$ $q = 628.2\ C^{0.5934}$ $q = 560.1\ C^{0.460}$	2531 628.2 560.1	1.812 1.685 0.4600	0.9161 0.9082 0.8072	Langmuir Langmuir neither

From the Table 4.7, the theoretical maximum adsorption capacity (Q) for each heavy metals individually (batch experiment #1 - #5) was greater than those for the mixture of the three metals (batch experiment #6). This maybe due to competition between metals for adsorption sites. Under the same soil : solution ratio and initial copper concentrations, Q was found to be 27710 mg copper/kg peat when initial adjusted pH was around 8.5 - 9.0 by Patterson (1996) which was greater than the Q (12107 mg copper/kg peat) in batch experiment #5 with initial adjusted pH around 5.0 - 5.5 possibly because copper precipitate occurred at higher pH.

Since values of Q (maximum adsorption capacity of adsorbent) are highly sensitive to the y intercept of linear isotherm plots, estimates of this parameter are highly variable. Several batch experiments would be required to obtain a reliable average value for Q.

The adsorption isotherm equation from batch experiments with lower initial pH has better fit to the best fit straight line compared those from batch experiments with higher pH. The reason for this is possibly because metal precipitation in system at higher pH. TOC was higher in the high pH batch experiment which means more organic acids leached into the solution which could cause complexation between heavy metals and organic acids and reduced the adsorption.

4.2 Column Experiment

4.2.1 General Overview of the Column Experiment and Results

A long-term column experiment was performed in order to simulate adsorption of heavy metals by peat in a dynamic system. Procedures of the column experiments were discussed in Section 3.3. Three metals - copper, nickel and zinc - were contained in the synthetic column feed solution. The target metal concentration in the feed solution was 5 mg/L for each of the three metals, while the measured concentrations were slightly lower than this. The measured metal concentrations from the column outflow were near the AA analytical detection limits. The peat column adsorption experiment was divided into three phases based on different feed rates. In Phase I, the average feed rate was approximately 3 mL/min (slightly lower than the target feed rate 4 mL/min), and 240 L of the feed solution passed through the column in about 1351 hours (56 days). In Phase II, the average feed rate was approximately 8 mL/min, and 80 L of the feed solution passed through the column in about 161 hours (7 days). In Phase III, the average feed rate was 14 mL/min, and 60 L of the feed solution passed through the column in the last 72 hours (3 days). Table 4.8 gives a general overview of the entire column experiment, and results including operating conditions, and average measured values of pH, metals concentrations and TOC.

Figure 4.22 shows the inflow and outflow pH as a function of the total volume run through the column, while Figures 4.23, 4.24, 4.25 show the inflow and outflow metals concentrations versus the total volume treated.

Table 4.8 General Overview of Column Experiment and Results

Description	Phase I	Phase II	Phase III
# of Carboy	1 - 12	13 - 16	16 - 19
Total Volume of Feed Solution (L)	240	80	60
Total Time of Column Run (hr)	1351	161	72
Ave. Feed Rate (mL/min)	2.96	8.28	13.9
Ave. Inflow pH	6.43	4.93	4.93
Ave. Outflow pH	4.91	6.27	5.03
Ave. Inflow Cu^{2+} conc. (mg/L)	4.27	4.55	4.54
Ave. Inflow Ni^{2+} conc. (mg/L)	4.46	4.55	4.55
Ave. Inflow Zn^{2+} conc. (mg/L)	4.38	4.42	4.44
Ave. Outflow Cu^{2+} conc. (mg/L)	0.05	0.04	0.04
Ave. Outflow Ni^{2+} conc. (mg/L)	0.01	0.00	0.01
Ave. Outflow Zn^{2+} conc. (mg/L)	0.05	0.02	0.02
Ave. outflow TOC conc. (mg/L)	96	23	14

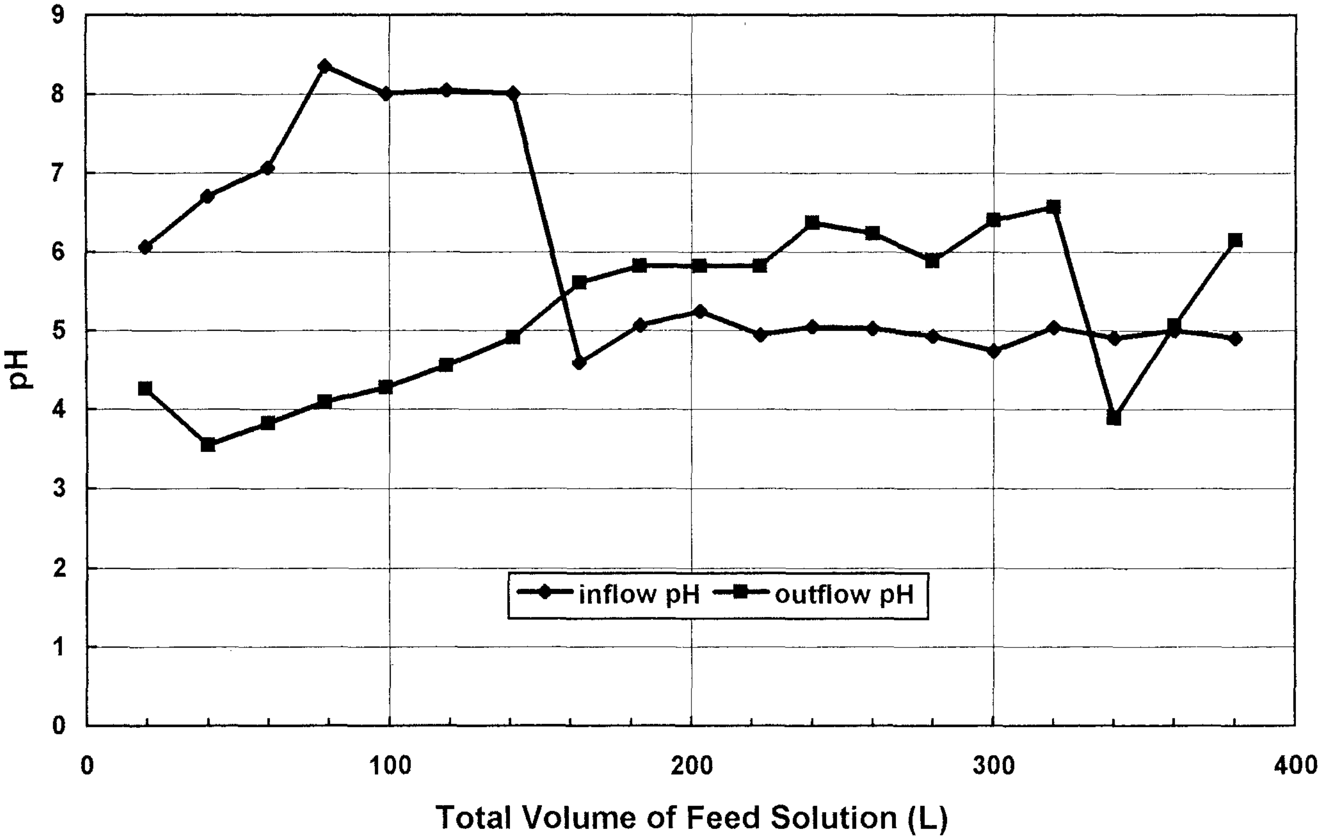

Figure 4.22 Column Experiment - Inflow and Outflow pH

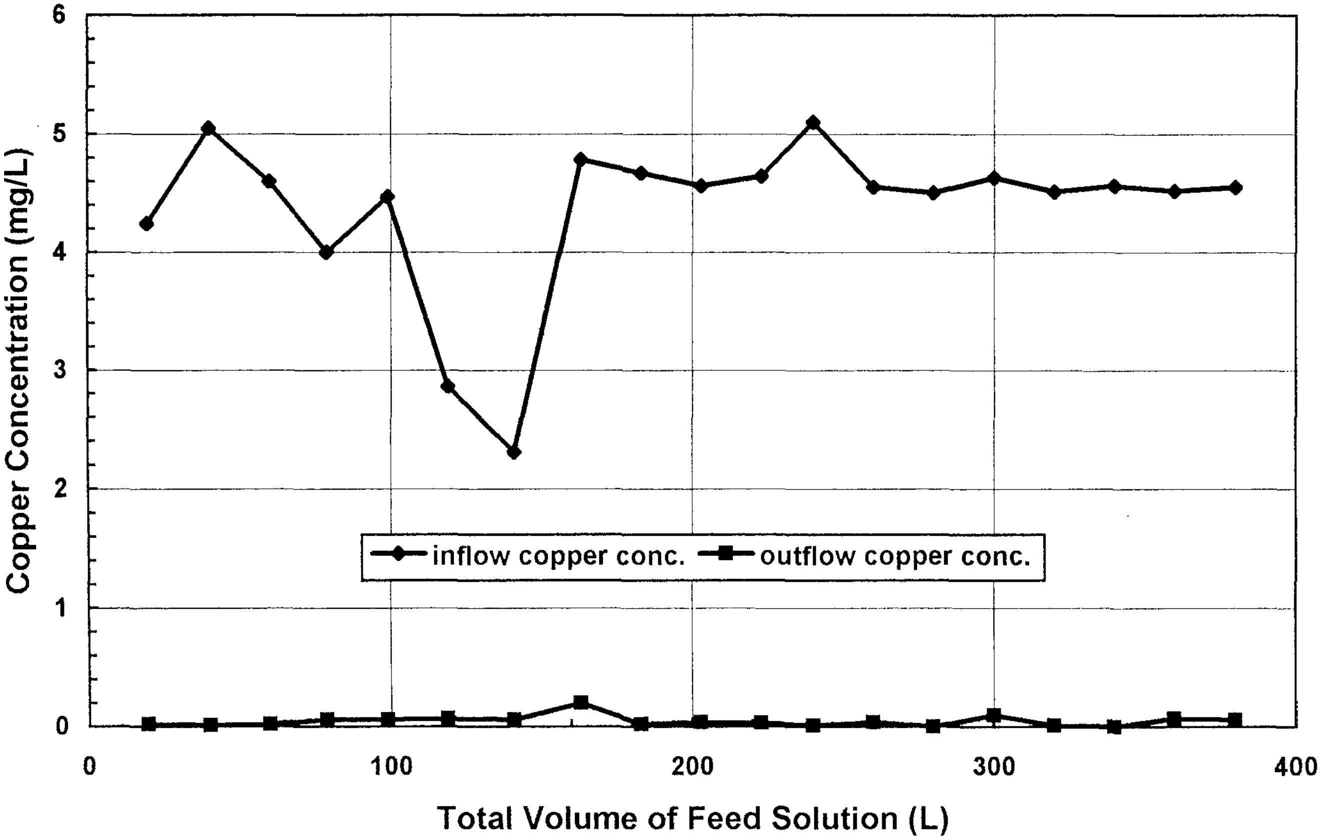

Figure 4.23 Column Experiment - Inflow and Outflow Copper Concentration

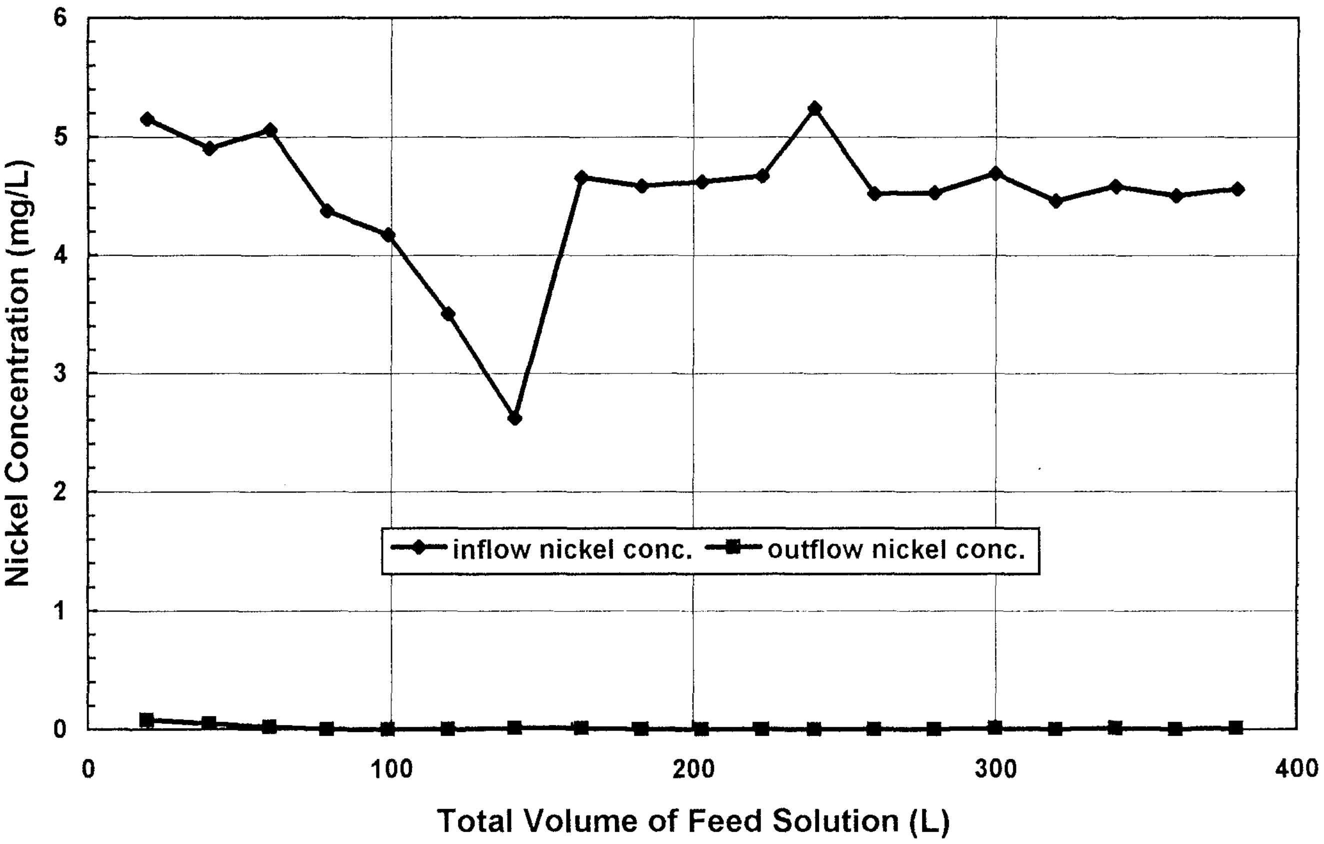

Figure 4.24 Column Experiment - Inflow and Outflow Nickel Concentration

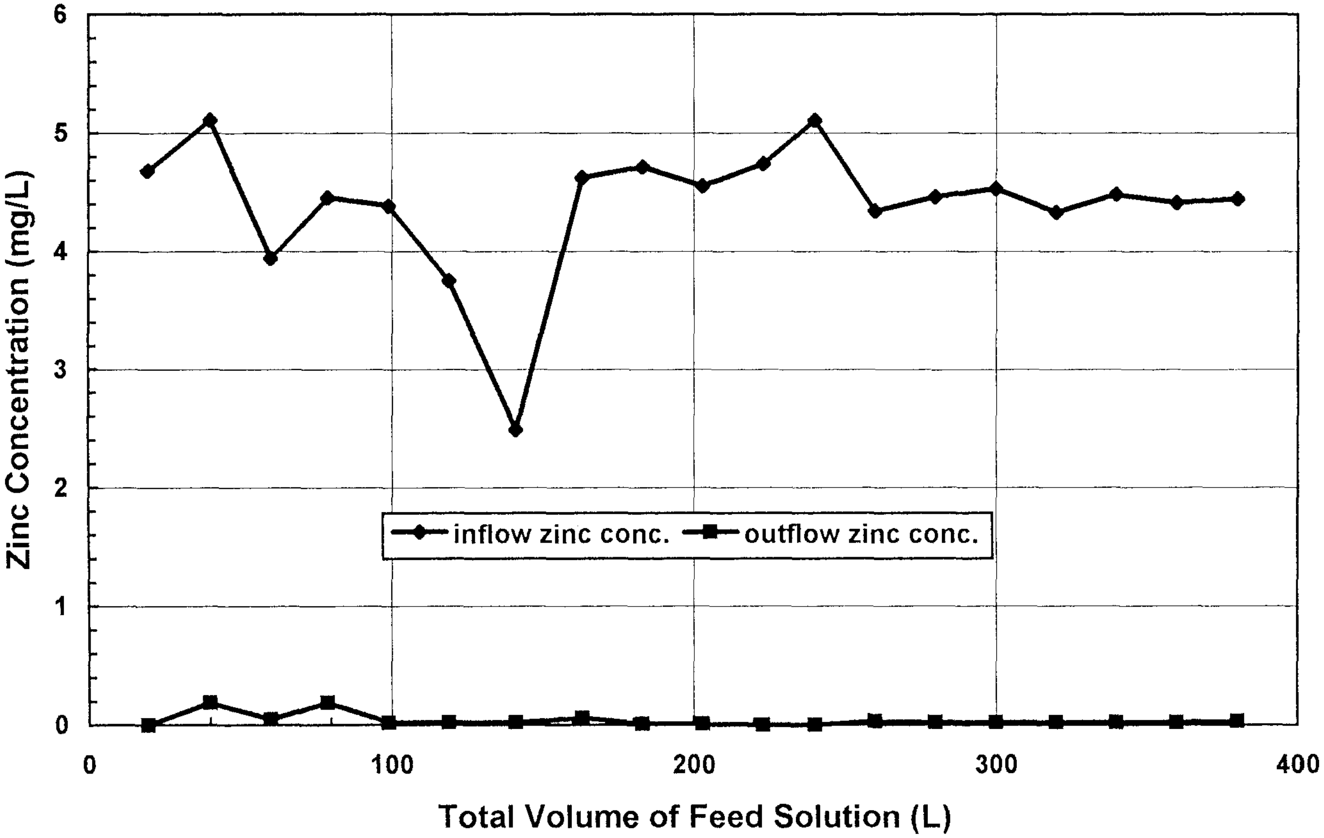

Figure 4.25 Column Experiment - Inflow and Outflow Zinc Concentration

4.2.2 Discussion of the Column Experiment Results - Phase I

During Phase I of the column experiment, a total of twelve 20L carboys (#1 - #12) of feed solution passed through the column within 1351 hours (56 days). The average feed rate was 2.96 mL/min. Table 4.9 lists the average feed rate, pH, inflow and outflow metal concentrations, and outflow TOC measured in Phase I.

The feed solutions in carboys #1 to #3 were made by diluting the 1000 mg/L commercial reference solutions, while the feed solutions in carboys #4 to #12 were prepared by dissolving chemicals in the deionized water with different types of buffer solutions. Mixed buffer of 0.01M KH_2PO_4 + 0.01 M K_2HPO_4 and 0.01 M K_2HPO_4 + NaOH (1.8g) was used in carboys #1 and #2 respectively. A light blue color indicated that copper precipitation was formed in carboy #2. A magnetic stirring bar was used inside the reservoir to break up the precipitate and keep it suspended. The measured concentrations of copper, nickel and zinc were around 5 mg/L in the #1 to #2 carboy. The buffer solution was decreased to 0.02 M K_2HPO_4, 0.01 M Na_2HPO_4 and 0.005 M Na_2HPO_4 in carboys #3, #4, and #5 - #7, respectively. However a noticeable light green precipitate was found as well at the bottom of carboys #6 and #7,possibly indicating a mixture of copper, nickel and zinc precipitate. The stirring bar did not perform very well in breaking up or suspending the precipitate as indicated by measured inflow metal concentrations below 3 mg/L. To avoid precipitation inside the reservoir, no buffer was added to carboys #8 to #12. After that, the measured metal concentrations in the feed solution in #8 to #12 were reasonably close to 5 mg/L for each of the three metals.

The pH was between 6 and 8 for the buffered feed solutions, and between 4 and 5 for the unbuffered feed solutions. The outflow pH was between 3.5 and 5.0 for carboys #1 to #7 (buffered feed solutions) and 5.6 to 6.4 for carboys #8 to #12 (unbuffered). The drop in pH values between the inflow and outflow for the buffered inflow is most likely due to released of organic acids into the column outflow. The outflow samples were dark brown in color and sediments could be found at the bottom of the plastic bottles some time after the samples were taken. This indicates that there were significant amounts of colloidal organic matter (e.g. organic acids) leached from the peat column into the outflow. The TOC measurements were begun on outflow samples for carboy #5, and the concentrations ranged from 136 mg/L to 196 mg/L in the carboy #5 to #7.

The outflow pH increased between the inflow and outflow for carboys #8 to #12 (unbuffered feed solution). The color of the outflow was much lighter than the previous samples which indicates that much less organic acids was released from the peat column. The TOC measurements were between 22 mg/L to 77 mg/L for carboys #8 to #12. The heavy metal concentrations in the outflow was between 0.01 mg/L to 0.20 mg/L for copper, 0 to 0.08 mg/L for nickel and 0 to 0.19 mg/L for zinc in Phase I of the column experiment. The percentage removals of all three metals were above 95% in Phase I. Since high concentrations of organic acids leached from peat into the outflow solution, the peat adsorption to heavy metals could be reduced by the metal - organic acids complexation in solution.

Humic acid is a organic acid which is soluble in base but insoluble in acid. From the experiment results, the concentration of TOC were higher at high pH than those at lower pH. It could be possibly assumed that most organic acids were humic acids.

Table 4.9 Results of Column Experiment - Phase I

#of Carboy	Total Volume (L)	Time (hr)	Ave. Feed Rate (mL/min)	TOC (mg/L)	Inflow				Outflow			
					pH	Cu2+ (mg/L)	Ni2+ (mg/L)	Zn2+ (mg/L)	pH	Cu2+ (mg/L)	Ni2+ (mg/L)	Zn2+ (mg/L)
1	19.5	115	2.83	N/A	6.06	4.24	5.15	4.68	4.26	0.02	0.08	0.00
2	40	233	2.90	N/A	6.70	5.05	4.90	5.11	3.55	0.01	0.05	0.19
3	60	352	2.80	N/A	7.07	4.60	5.06	3.94	3.82	0.02	0.02	0.05
4	79	414	5.11	N/A	8.35	4.00	4.37	4.45	4.09	0.06	0.00	0.19
5	99	548	2.49	136	8.01	4.47	4.17	4.38	4.28	0.06	0.00	0.02
6	119	591	7.75	196	8.05	2.86	3.50	3.75	4.55	0.07	0.00	0.02
7	141	799	1.76	173	8.01	2.31	2.62	2.49	4.91	0.06	0.01	0.02
8	163	891	3.99	77	4.59	4.78	4.66	4.62	5.61	0.20	0.01	0.06
9	183	986	3.51	47	5.06	4.67	4.58	4.71	5.82	0.02	0.00	0.01
10	203	1161	1.90	75	5.24	4.56	4.62	4.55	5.82	0.04	0.00	0.01
11	223	1252	3.66	39	4.94	4.64	4.67	4.74	5.82	0.03	0.00	0.00
12	240	1351	2.86	22	5.05	5.10	5.24	5.11	6.37	0.01	0.00	0.00
Ave.	N/A	N/A	3.46	96	6.43	4.27	4.46	4.38	4.91	0.05	0.01	0.05

4.2.3 Discussion of Column Experiment Results - Phase II

The feed rate was increased during Phase II of the column experiment. A total of four carboys (#13 - #16) of feed solution was passed through the peat column within 161 hours (7 days). The average feed rate was 8.28 mL/min. Table 4.10 lists the average feed rate, pH, inflow and outflow metal concentrations and outflow TOC for Phase II. All the feed solutions were prepared by dissolving chemicals into deionized water. No buffer was used in the feed solutions and no precipitation was observed inside the reservoir. The measured inflow metal concentrations were around 5 mg/L for each of the three metal. The pH was around 5 for the feed solution and between 6 and 6.5 for the outflow samples. The increase of pH was possibly because of the reversal of hydrolysis reactions in the column following metal adsorption. The color of the outflow was light brown. The TOC was from 18 mg/L to 42 mg/L. The heavy metal concentrations in the outflow were 0 - 0.04 mg/L for copper, 0 - 0.01 mg/L for nickel and 0.02 - 0.03 mg/L for zinc. So, the percentages of heavy metals adsorbed by peat were above 99% at the higher flow rate. Adsorption can be considered as the primary metal removal process in Phase II, since the pH levels were low enough to eliminate chemical precipitation.

Table 4.10 Results of Column Experiment - Phase II

#of Carboy	Total Volume (L)	Time (hr)	Ave. Feed Rate (mL/min)	TOC (mg/L)	Inflow				Outflow			
					pH	Cu2+ (mg/L)	Ni2+ (mg/L)	Zn2+ (mg/L)	pH	Cu2+ (mg/L)	Ni2+ (mg/L)	Zn2+ (mg/L)
13	260	1374	14.49	22	5.02	4.55	4.52	4.34	6.23	0.04	0.00	0.03
14	280	1445	4.69	18	4.93	4.50	4.53	4.46	5.88	0.00	0.00	0.02
15	300	1488	7.75	42	4.74	4.63	4.69	4.53	6.40	0.10	0.01	0.02
16	320	1512	13.89	10	5.04	4.51	4.46	4.33	6.57	0.01	0.00	0.02
Ave.	N/A	N/A	10.20	23	4.93	4.55	4.55	4.42	6.27	0.04	0.00	0.02

4.2.4 Discussion of Column Experiment Results - Phase III

Phase III was the last three days of the column experiment. Three carboys (#17 - #19) of feed solution were passed through the peat column within 72 hours (3 days). The average feed rate was 13.90 mL/min. The purpose of Phase III in the column experiment was to test the peat adsorption at a high feed rate and to investigate the possibility of breakthrough of the peat column at this high feed rate. Table 4.11 lists the average feed rate, pH, inflow and outflow metal concentrations, and outflow TOC measured in Phase III. All the feed solutions were prepared by dissolving chemicals into deionized water. No buffer was used in the feed solutions and no precipitation was found inside the reservoir. The measured inflow concentrations were around 5 mg/L for each of the three metals. The pH was around 5 for the feed solution and between 3.89 to 6.15 for the outflow samples. The color of the outflow was light brown. The TOC was from 10 mg/L to 18 mg/L. The heavy metal concentrations in the outflow were 0.06 - 0.07 mg/L for copper, 0 - 0.01 mg/L for nickel and 0.02 - 0.03 mg/L for zinc. So, in Phase III, heavy metal adsorbed by peat was still high and no breakthrough occurred in the peat column. Again, in Phase III, adsorption was considered to be the main metal removal process.

Table 4.11 Results of Column Experiment - Phase III

#of Carboy	Total Volume (L)	Time (hr)	Ave. Feed Rate (mL/min)	TOC (mg/L)	Inflow				Outflow			
					pH	Cu2+ (mg/L)	Ni2+ (mg/L)	Zn2+ (mg/L)	pH	Cu2+ (mg/L)	Ni2+ (mg/L)	Zn2+ (mg/L)
17	340	1536	13.90	18	4.90	4.56	4.58	4.48	3.89	0	0.01	0.02
18	360	1560	13.90	15	5.00	4.52	4.50	4.41	5.06	0.07	0.00	0.02
19	380	1584	13.90	10	4.90	4.55	4.56	4.44	6.15	0.06	0.01	0.03
Ave.	N/A	N/A	13.90	14	4.93	4.54	4.55	4.44	5.03	0.04	0.01	0.02

4.3 Modeling Study using MINTEQA2

4.3.1 MINTEQA2 Model of the Column Feed Solution

MINTEQA2 was used to model the chemical species at equilibrium in the feed solution. In carboys #1 to #7, the feed solution contained about 5mg/L each of three heavy metals (copper, nickel and zinc) and different buffer solutions, while the feed solution of carboys #8 - #19 was contained only the heavy metals. The measured metal concentrations were used as the input concentrations in MINTEQA2 to model the feed solutions for all carboys (#1 to #19) and buffer. A total of eight different runs of the MINTEQA2 model were performed for the column feed solutions. The input information (column 2 and 3) and results (column 4 to 8) were summarized in Table 4.12. One example of the MINTEQA2 output for the column experiment is attached in the Appendix I. The MINTEQA2 results showed that considerable potential for precipitation existed in the buffered column feed solutions (carboys #1 to #7), while no precipitation would be expected in the unbuffered feed solutions (carboys #8 to #19). The equilibrium pH from MINTEQA2 output was close to the measured average pH in the experiment.

Table 4.12 MINTEQA2 Results of Column Feed Solution

# of Carboy	Concentration of Chemical Component in Feed Solution (mg/L)	Buffer	Equ. pH	Equilibrium Dissolved Species Concentration (mg/L)	% (Dis.)	Equilibrium Precipitated Species Concentration (mg/L)	% (Ppt.)
1	$[Cu^{2+}]$ = 4.24 $[Ni^{2+}]$ = 5.15 $[Zn^{2+}]$ = 4.68	0.01M KH_2PO_4 + 0.01M K_2HPO_4	6.3	$[Cu^{2+}]$ = 0.02 $[Ni^{2+}]$ = 0.71 $[Zn^{2+}]$ = 0.43	0.4 13.8 9.1	$[Cu^{2+}]$ = 4.22 $[Ni^{2+}]$ = 4.25 $[Zn^{2+}]$ =4.44	99.6 86.2 90.9
2	$[Cu^{2+}]$ = 5.05 $[Ni^{2+}]$ = 4.90 $[Zn^{2+}]$ = 5.11	0.01M K_2HPO_4 + 1.8 g NaOH	8.53	$[Cu^{2+}]$ = 0.06 $[Ni^{2+}]$ = 4.90 $[Zn^{2+}]$ = 0.26	1.2 100 5.0	$[Cu^{2+}]$ = 4.99 $[Ni^{2+}]$ = 0.00 $[Zn^{2+}]$ = 4.85	98.8 0 95.0
3	$[Cu^{2+}]$ = 4.60 $[Ni^{2+}]$ = 5.06 $[Zn^{2+}]$ = 3.94	0.02M K_2HPO_4	8.14	$[Cu^{2+}]$ = 0.06 $[Ni^{2+}]$ = 1.24 $[Zn^{2+}]$ = 3.90	1.3 24.4 2.1	$[Cu^{2+}]$ = 4.54 $[Ni^{2+}]$ = 3.82 $[Zn^{2+}]$ = 0.04	98.7 75.6 97.9
4	$[Cu^{2+}]$ = 4.00 $[Ni^{2+}]$ = 4.37 $[Zn^{2+}]$ = 4.45	0.01M Na_2HPO_4	8.00	$[Cu^{2+}]$ = 0.05 $[Ni^{2+}]$ = 1.21 $[Zn^{2+}]$ = 0.11	1.3 27.6 2.4	$[Cu^{2+}]$ = 3.95 $[Ni^{2+}]$ = 3.16 $[Zn^{2+}]$ = 4.34	98.7 72.4 97.6
5	$[Cu^{2+}]$ = 4.47 $[Ni^{2+}]$ = 4.17 $[Zn^{2+}]$ = 4.38	0.005M Na2HPO$_4$	7.85	$[Cu^{2+}]$ = 0.02 $[Ni^{2+}]$ = 1.20 $[Zn^{2+}]$ = 0.15	1.3 28.7 3.4	$[Cu^{2+}]$ = 1.28 $[Ni^{2+}]$ = 2.97 $[Zn^{2+}]$ = 4.23	98.7 71.3 96.6
6	$[Cu^{2+}]$ = 2.86 $[Ni^{2+}]$ = 3.50 $[Zn^{2+}]$ = 3.75	0.005M Na_2HPO_4	7.88	$[Cu^{2+}]$ = 0.06 $[Ni^{2+}]$ = 1.27 $[Zn^{2+}]$ = 0.15	2.1 36.3 3.9	$[Cu^{2+}]$ = 2.80 $[Ni^{2+}]$ = 2.23 $[Zn^{2+}]$ = 3.60	97.9 63.7 96.1
7	$[Cu^{2+}]$ = 2.31 $[Ni^{2+}]$ = 2.62 $[Zn^{2+}]$ = 2.49	0.005M Na_2HPO_4	7.89	$[Cu^{2+}]$ = 0.06 $[Ni^{2+}]$ = 1.33 $[Zn^{2+}]$ = 0.16	2.6 50.9 6.3	$[Cu^{2+}]$ = 2.25 $[Ni^{2+}]$ = 1.29 $[Zn^{2+}]$ = 2.33	97.4 49.1 93.7
8-19	$[Cu^{2+}]$ = 4.63 $[Ni^{2+}]$ = 4.63 $[Zn^{2+}]$ = 4.56	NONE	5.57	$[Cu^{2+}]$ = 4.63 $[Ni^{2+}]$ = 4.63 $[Zn^{2+}]$ = 4.56	100 100 100	$[Cu^{2+}]$ = 0.00 $[Ni^{2+}]$ = 0.00 $[Zn^{2+}]$ =0.00	0.0 0.0 0.0

4.3.2 MINTEQA2 Model of the Batch Experiment

In order to quantify the amount of heavy metals bound (or complexed) to colloidal particles, MINTEQA2 was used to model the batch study containing the heavy metals and the dissolved organic matter (DOM). To test the direct relationship between the metal concentration and the amount bound to DOM, it was assumed that the heavy metal and DOM were the only components in the solution. Four concentrations (0.1 mg/L, 1 mg/L, 5 mg/L, and 20 mg/L) were selected to represent the concentrations of each of the three metals, and 10^{-5} moles/L (M) of DOM was assumed. The final pH was fixed at 4 and 7 to test the complexation of metals at different pH. Table 4.13, 4.14, and 4.15 list the MINTEQA2 output results for copper, nickel and zinc, respectively. The results are shown graphically in Figure 4.26, 4.27, and 4.28.

MINTEQA2 results showed that the percentage of metal bound to DOM increased with increasing pH (See Figures 4.26, 4.27 and 4.28). At the same pH, the affinity for bonding to the DOM decreased in the order of copper > zinc > nickel, as shown by Figures 4.29 and 4.30. One example of MINTEQA2 output with DOM included is listed in Appendix I.

At metal concentration greater than 5 mg/L, fraction bound to DOM was low (less than 10%). This may be because adequate DOM is not available for complex formation. Complexation of metals to DOM may hinder heavy metals removal at low concentrations and high pH, since the metals effectively are held in solution.

Table 4.13 MINTEQA2 output - Equilibrium Species of Copper

	pH = 4		pH = 7					
Cu (mg/L)	% bound to DOM	% Free	% bound to DOM	% Free	$Cu(OH)_2$ AQ	$CuCO_3$ AQ	$CuOH^+$	$Cu_2(OH)_2^{2+}$
0.1	30.1	69.9	77.7	6.8	13.8	0	1.7	0
1.0	19.2	80.8	23.9	23.1	46.6	2.8	2.3	0
5.0	7.3	92.7	6.8	27.3	54.5	3.3	2.6	4.9
20.0	2.3	97.7	2.1	25.6	49.6	3.0	2.4	16.8

Table 4.14 MINTEQA2 output - Equilibrium Species of Nickel

	pH = 4		pH = 7		
Ni (mg/L)	% bound to DOM	% Free	% bound to DOM	% Free	$NiCO_3$ AQ
0.1	1.2	98.8	33.7	56.3	9.5
1.0	1.1	98.9	10.9	75.8	12.7
5.0	0.9	99.1	3.6	82.3	13.5
20.0	0.6	99.4	1.2	84.9	13.2

Table 4.15 MINTEQA2 output - Equilibrium Species of Zinc

	pH = 4		pH = 7		
Zn (mg/L)	% bound to DOM	% Free	% bound to DOM	% Free	ZnHCO3, ZnOH, ZnCO3,AQ, Zn(OH)2, AQ
0.1	1.8	98.2	44.9	53.9	1.2
1.0	1.7	98.3	14.2	84.0	1.8
5.0	1.4	98.6	4.5	93.4	2.1
20.0	0.9	99.1	1.5	96.5	2.0

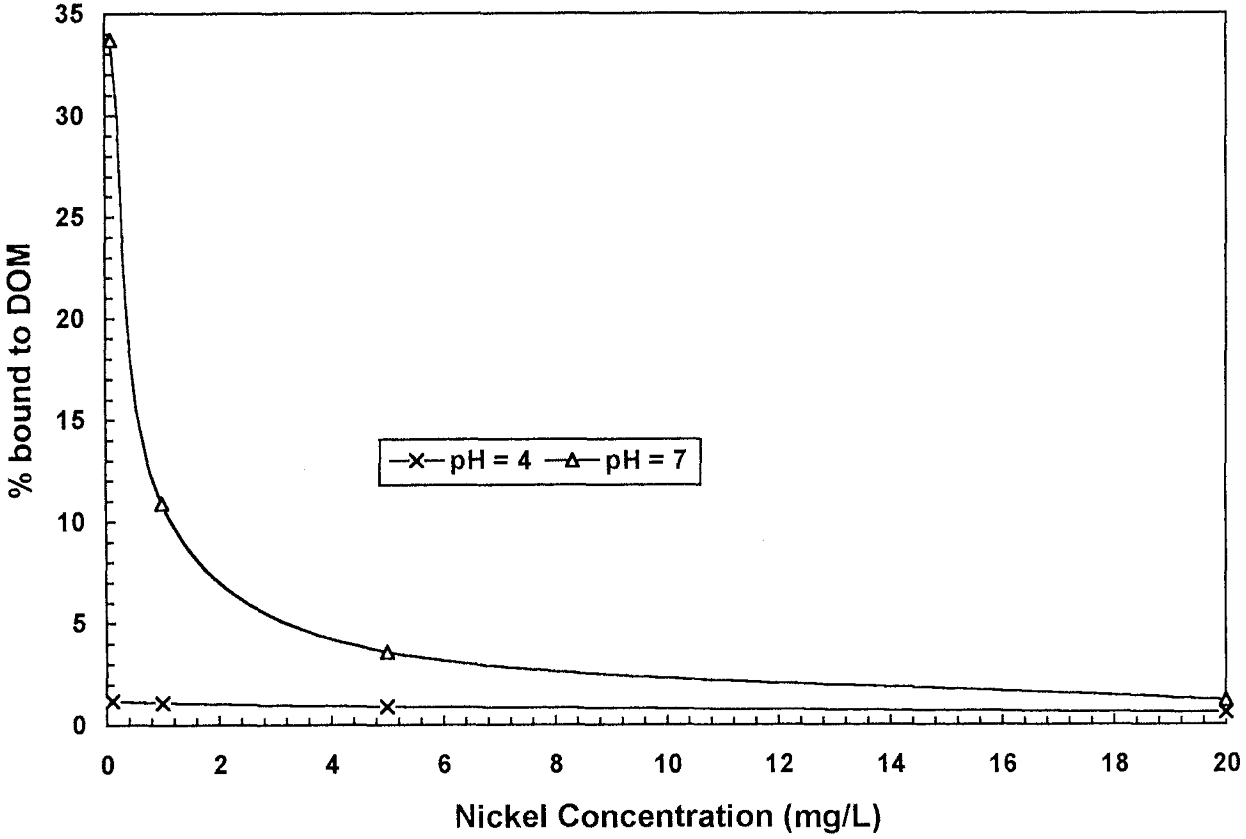

Figure 4.27 MINTEQA2 Output - Nickel / DOM

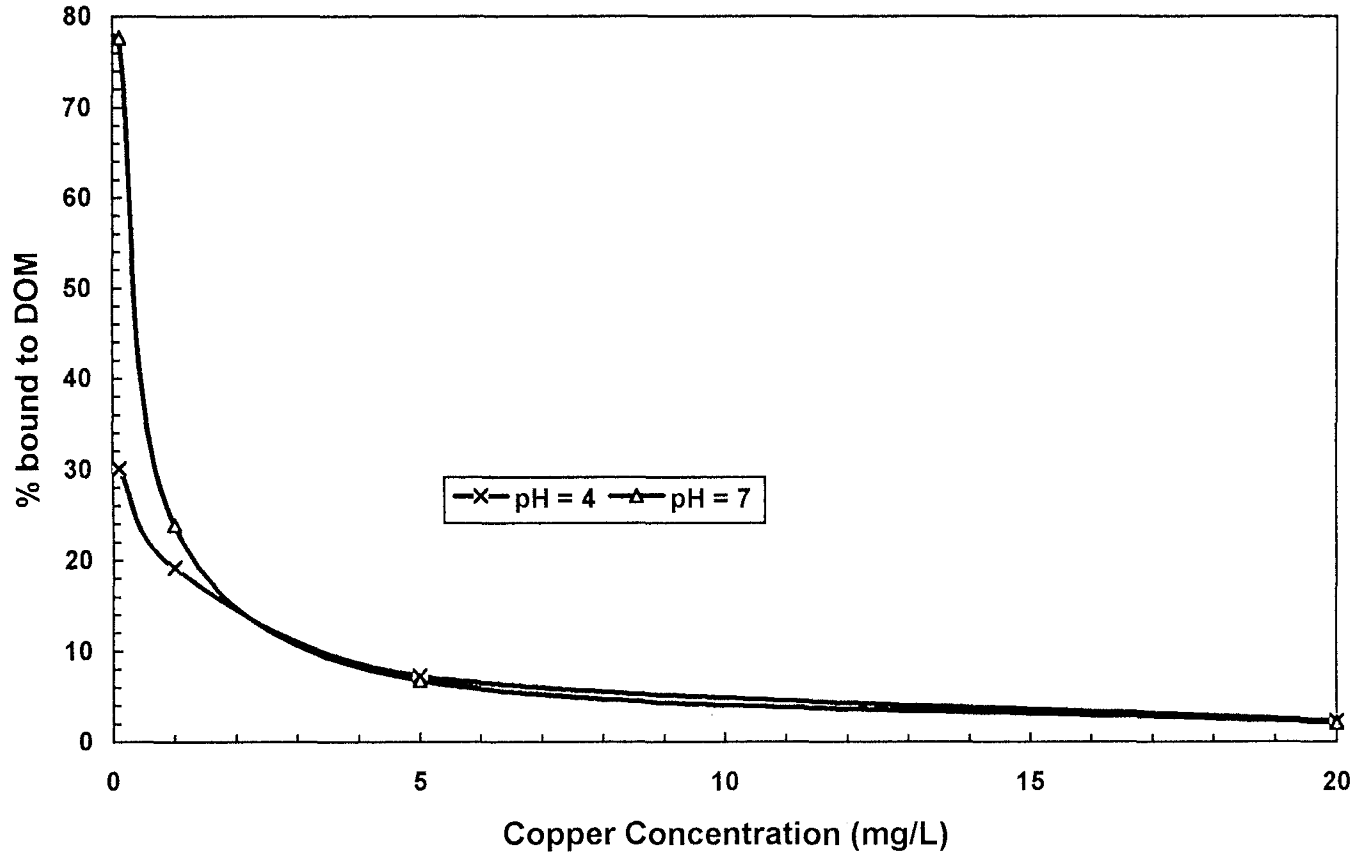

Figure 4.26 MINTEQA2 Output - Copper / DOM

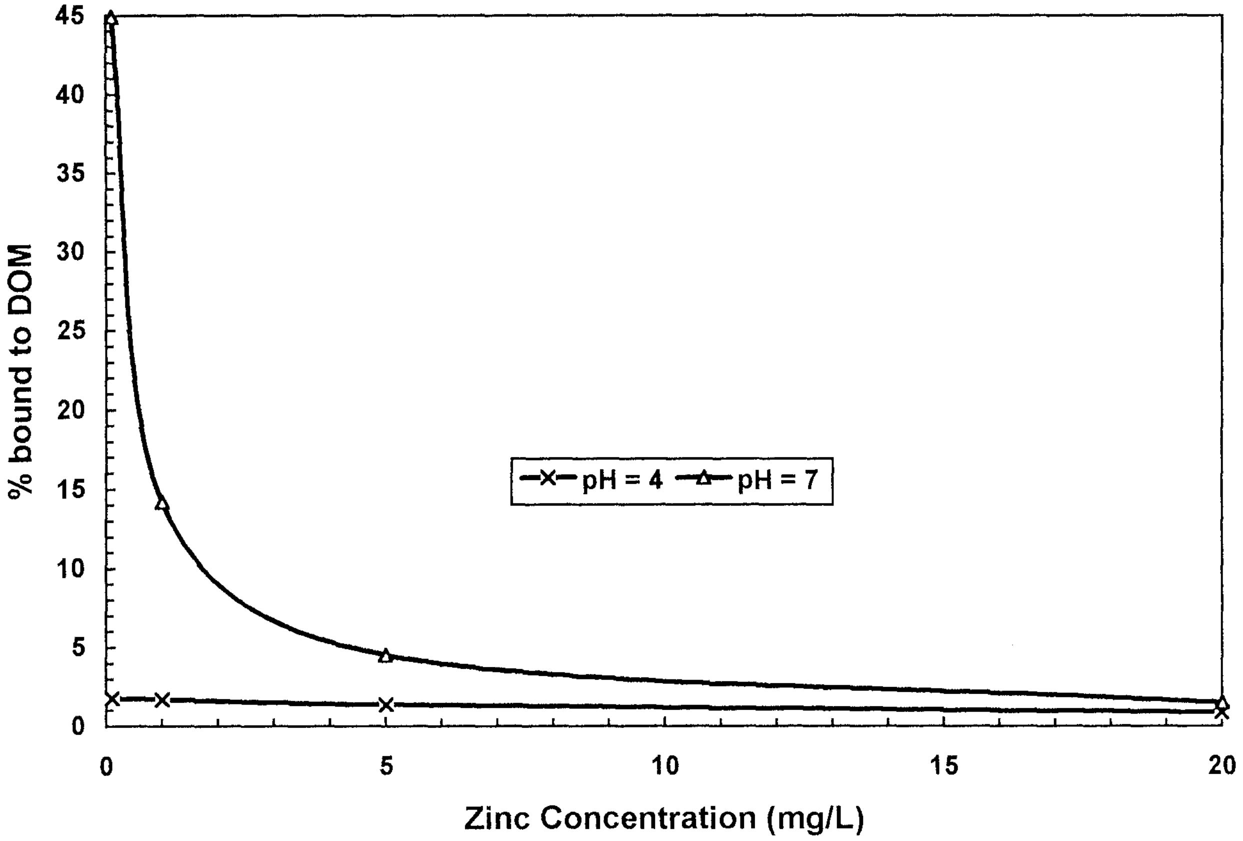

Figure 4.28 MINTEQA2 Output - Zinc / DOM

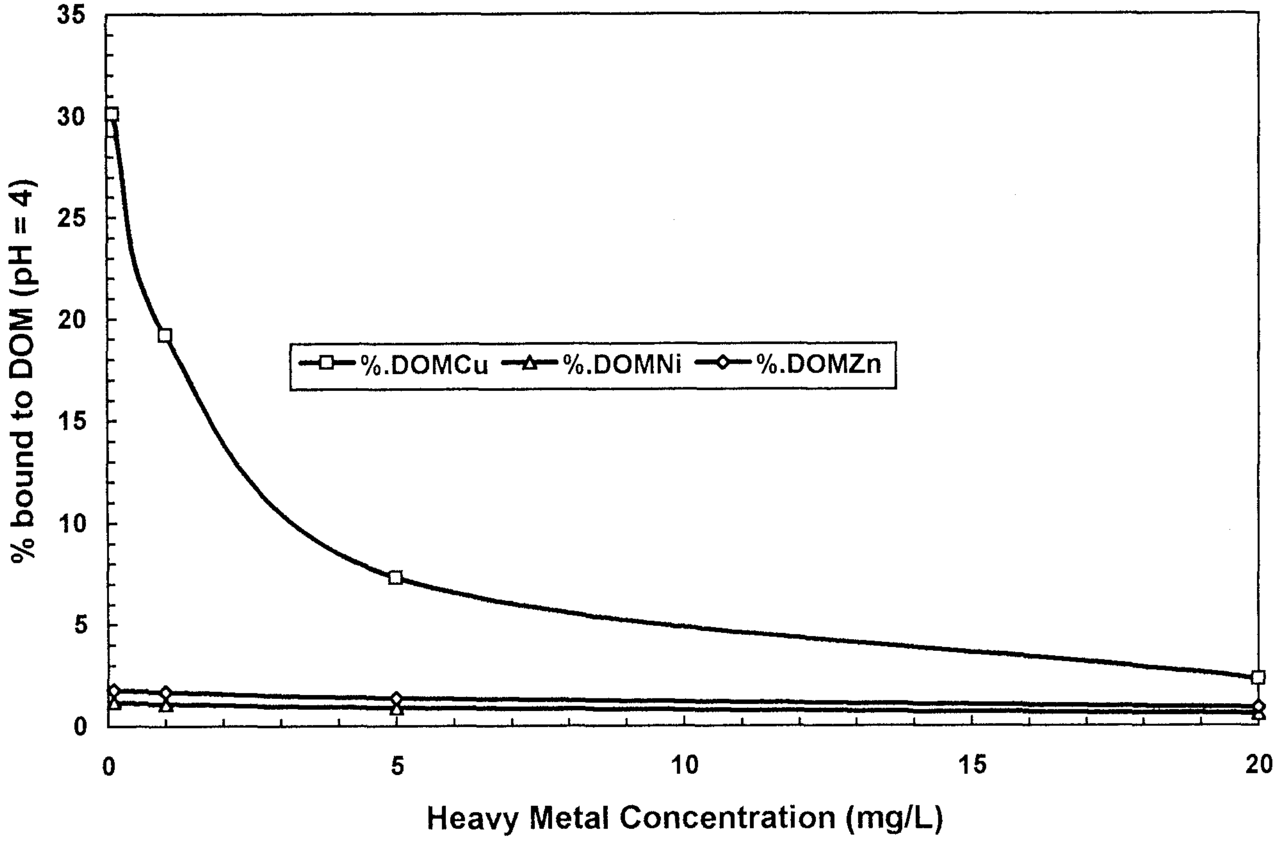

Figure 4.29 MINTEQA2 Output - Metal / DOM at pH = 4

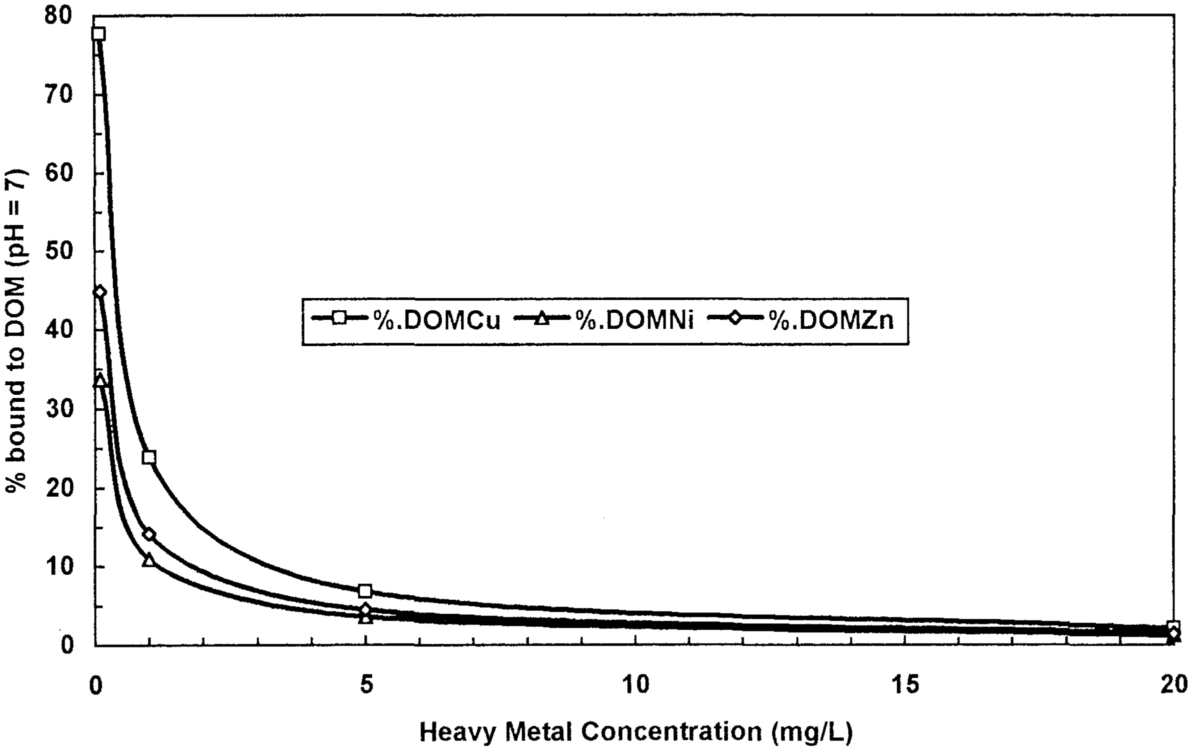

Figure 4.30 MINTEQA2 Output - Metal / DOM at pH = 7

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary of the Project

5.1.1 Summary of Batch Experiments

Six batch experiments showed the effective removal of copper, nickel and zinc by peat. The experimental conditions and several conclusions are summarized below:

1. peat was used as adsorbent used in all batch experiments;
2. soil : solution ratio was 1 : 200 in batch experiment #1, while 1 : 1000 in batch experiments #2 to #6.
3. Batch experiments #1 and #2 were performed with nickel using initial adjusted pH of around 4 and 7, respectively; batch experiments #3 and #4 were performed with zinc using initial adjusted pH of around 4 and 7, respectively; batch experiment #5 was performed to copper with copper at initial pH of around 5; batch experiment #6 was perform with a mixture of copper, nickel and zinc at initial adjusted pH around 5;
4. Better isotherms were obtained from experiments #2, #4 and #5 (lower initial adjusted pH) than from experiments #1 and #3 (higher initial adjusted pH);
5. Good isotherms were obtained from experiment #6 for all three metals;
6. Adsorption isotherms for copper followed both the Langmuir and the Freundlich isotherm, while adsorption isotherms for nickel and zinc followed the Freundlich isotherm more closely;

7. Adsorption isotherms for the mixture of the three metals all followed the Langmuir isotherm better than the Freundlich isotherm, although copper and nickel followed both isotherms, while zinc fit neither of them very well;
8. The theoretical maximum adsorption capacity of the peat was found to be 12107 mg/kg for copper, 44248 mg/kg for nickel and 3639.8 mg/kg for zinc individually (experiment #5, #2 and #4 respectively), while the values obtained for the mixture of three metals (experiment #6) were 5408 mg/kg for copper, 2543 mg/kg for nickel and 1521 mg/kg for zinc. This suggests that the peat has a higher adsorption capacity for each metal individually than for the metals in a mixture;
9. pH plays an important role in the leaching of organic acids from peat. Concentrations of TOC were measured in experiment #1, #3 and #6. More organic acids leached into solution at higher initial pH than at lower initial pH.

5.1.2 Summary of the Column Experiment

Consistent removal of above 95% of copper, nickel and zinc was obtained during the entire 66 days operation of the peat column. Several observations were listed below:

1. Effluent with dark brown color was obtained during the column run; the color became lighter during the course of the column experiment;
2. TOC measured in the column effluent ranged from 10 mg/L to 196 mg/L; TOC was greater at high effluent pH than at low effluent pH, which means more organic acids leached into solution when pH was high;
3. Porosity of peat in the column was obtained to be 93%.

5.1.3 Summary of MINTEQA2 Model Output

5.1.3.1 MINTEQA2 Analysis of Column Feed Solution

MINTEQA2 was used to model the column feed solution; the results showed:

1. Considerable potential for precipitation existed in the buffered feed solution, the model indicated that copper phosphate, nickel phosphate and zinc phosphate precipitate should form;
2. No potential for precipitation existed in the unbuffered feed solution.

5.1.3.2 MINTEQA2 Analysis of Batch Experiments

MINTEQA2 model was also used to model the batch experiments; the results showed:

1. The possibility of metal - organic acids complexation was stronger at higher pH than at lower pH based on the same metal concentrations and same organic matter concentration;
2. The affinity of metal binding to organic matter decreased in the order of copper > zinc > nickel based at same metal concentration and organic matter concentration.

5.2 Scope of Further Work

The understanding of heavy metal adsorption by peat could benefit from further work, including the following:

1. Additional bench scale experiments would be useful, including batch studies with different soil : solution ratio, no buffer in solution, and using different types of adsorbents other than the peat.
2. More rapid feed rate and longer run times should be used in a column study

to determine the time to reach breakthrough.

3. Analysis of the organic acids should be done to determine the type of organic acids leached into the solution.
4. MINTEQA2 model should be used to predict the feed solution with a solid phase added.
5. To avoid the limitation of using synthetic wastewater, real landfill leachate or acid mine drainage should be used to run the bench-scale experiments.
6. Different substrate systems, and larger scale systems, should be used to better simulate real engineered systems.

While much work needs to be done to further research in this area, the results obtained here certainly support the use of engineered natural system for wastewater treatment.

REFERENCE

Allison Geoscience Consultants, Inc., "MINTEQA2 Geochemical Speciation Workshop", September 12-14, 1995.

Bastian R.K., and Hammer D.A., "the Use of Constructed Wetlands for Wastewater Treatment and Recycling" in Constructed Wetlands for Water Quality Improvement, Moshiri G.A., ed., CRC Press, Inc., 1993, pp. 59-69.

Benefield L.D., Judkins J.F. and Weand B.L., Process Chemistry for Water and Wastewater Treatment, Prentice-Hall, Inc., 1982.

Brix H., "Wastewater Treatment in Constructed Wetlands: System Design, Removal Processed, and Treatment Performance" in Constructed Wetlands for Water Quality Improvement, Moshiri G.A., ed., CRC Press, Inc., 1993, pp. 9-23.

Couillard D., "Review, the Use of Peat in Wastewater Treatment", Water Resources, Vol. 28, No. 6, pp.1261-1274, 1994.

Crum H., A Focus on Peatlands and Peat Mosses, The University of Michigan, 1988.

Dissanayake C.B., Weerasooriya, S.V.R., "Peat as Metal Trapping Material in the Purification of Industrial Effluents" in International Journal of Environmental Studies, 17 (3-4), 1981, pp. 233-238.

Eger P., Melchert G., Antouson D., and Wagner J., "The Use of Wetland Treatment to Remove Trace Metals from Mine Drainage" in Constructed Wetlands for Water Quality Improvement, Moshiri G.A., ed., CRC Press, Inc., 1993, pp. 171-178.

Freeman R.J.Jr., "Constructed Wetlands Experience in the Southeast" in Constructed Wetlands for Water Quality Improvement, Moshiri G.A., ed., CRC Press, Inc., 1993, pp. 69-77.

Fuchsman C.H., PEAT Industrial Chemistry and Technology, Academic Press, Inc., 1980.

Gosset T., Trancart J.L., and Thevenot K.R., "Batch Metal Removal By Peat Kinetics and Thermodynamics", Water Resource, Vol. 20, No. 1, pp. 21-26, 1986.

Hammer D.A. and Bastian R.K., "Wetlands Ecosystems: Natural Water Purifiers?" in Constructed Wetlands for Wastewater Treatment Municipal, Industrial and Agricultural, Hammer D.A., ed., Lewis Publishers, Inc., 1989, pp. 5-21.

James M. Montgomery, Consulting Engineers, Inc., Water Treatment Principles and Design, John Wiley & Sons, Inc., 1985.

Lehocine M.B., "Zinc Removal Using Peat Adsorption", Environmental Technology Letters, Vol. 10, pp. 101-108, Sepler Ltd., 1989.

Litchfield D.K., Schatz D.D., "Constructed Wetlands for Wastewater Treatment at Amoco Oil Company's Mandan, North Dakota Refinery" in Constructed Wetlands for Wastewater Treatment Municipal, Industrial and Agricultural, Hammer D.A., ed., Lewis Publishers, Inc., 1989, pp. 233-238.

Maddox J.J. and Kingslay J.B., "Waste Treatment for Confined Swine with an Integrated Artificial Wetland and Aquaculture System" in Constructed Wetlands for Wastewater Treatment Municipal, Industrial and Agricultural, Hammer D.A., ed., Lewis Publishers, Inc., 1989, pp.191-201.

Mckay B. and Allen S.J., "Pore Diffusion Model for Dye Adsorption onto Peat in Batch Adsorbers", The Canadian Journal of Chemical Engineering, Vol. 62, June, 1994 pp. 340-345.

Patterson, R.C.Jr., "Heavy Metal Removal Mechanisms in Constructed Wetland Wastewater Treatment", Master's Thesis, unpublished, 1996, pp.43.

Reed S.C., "Natural Systems for Wastewater Treatment", Manuals of Practice for Water Pollution Control, Water Pollution Control Federation, 1990, pp. 211-261.

Rock C.A., Fiola J.W., Greer T.F. and Woodward F.E., "Pollution of Sphagnum Peat to Removal Metals for Landfill Leachate", Journal of the New England Water Pollution Control Association, 19(1): pp. 32-47, 1985.

Smith E.F., MacCarthy P., Yu T.C., and Mark H.B.Jr., "Sulfuric Acid Treatment of Peat for Cation Exchange", Journal of Water Pollution Control Federation, 49(4), 1977, pp.633-638.

Snoeying V.L and Jenkins D., Water Chemistry, John Wiley & Sons, Inc., 1980.

Tchobanoglous G., "Constructed Wetlands and Aquatic Plant Systems: Research, Design, Operational, and Monitoring Issues" in Constructed Wetlands for Water Quality Improvement, Moshiri G.A., ed., CRC Press, Inc., 1993, pp. 23-35.

United States Environmental Protection Agency (US EPA), Design Manual: Constructed Wetlands and Aquatic Plant Systems for Municipal Wastewater Treatment, EPA 625/1-88/022, September, 1988.

United States Environmental Protection Agency (US EPA), Report on the Use of Wetlands for Municipal Wastewater Treatment and Disposal, EPA 430/09-88-005 October, 1987.

Viraraghavan T. and Mathavan G.N., “Use of Peat in the Treatment of Oily Waters”, Water, Air, and Soil Pollution, 45, Kluwer Academic Publishers, 1989, pp. 17-26.

Viraraghavan T. and Ayyaswami A., “Use of Peat in Water Pollution Control: a review” Canadian Journal of Civil Engineering, Vol. 14,1987, pp. 230-233.

Weber W.J.Jr., Physicochemical Processes for Water Quality Control, John Wiley & Sons, Inc., 1972.

Witthar S.R., “Wetland Water Treatment Systems” in Constructed Wetlands for Water Quality Improvement, Moshiri G.A., ed., CRC Press, Inc., 1993, pp. 147-157.

APPENDIX

Two of MINTEQA2 output files

```
______________________________ PART 1 of OUTPUT FILE ___________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 28-MAY-96  TIME:  9:41:33


column run for carboy #1
contain 0.01m KH2PO4 + 0.01m K2HPO4 as buffer

--------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed for all solids in the thermodynamic database and
   the print option for solids is set to: 1
 The maximum number of iterations is: 100
 The method used to compute activity coefficients is: Davies equation
 Abbreviated output file

-------------------------------------------------------------------------------
    330  3.000E-02   -3.70 y
    231  6.673E-05   -4.10 y
    950  7.159E-05   -4.11 y
    540  8.772E-05   -4.07 y
    410  3.000E-02   -1.70 y
    140  0.000E-01  -16.00 y
    580  2.000E-02   -1.70

 H2O has been inserted as a COMPONENT
  3   1
3301403    21.6285    -0.5300

     Charge Balance: UNSPECIATED

       Sum of CATIONS=  6.045E-02 Sum of ANIONS =  6.000E-02

       PERCENT DIFFERENCE =  3.753E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)


              ------------------------------------------------------
             | IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION: |
             |      Cu+2       Log activity guess:     -4.18       |
             |      CO3-2      Log activity guess:    -14.23       |
             |      PO4-3      Log activity guess:    -13.85       |
             |                                                     |
              ------------------------------------------------------
```

```
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 28-MAY-96  TIME:   9:41:33


PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

     ITER       NAME          TOTAL MOL    DIFF FXN    LOG ACTVTY     RESIDUAL
      0    PO4-3              2.000E-02   5.599E-04   -13.85211     5.579E-04
      1    PO4-3              2.000E-02  -1.397E-02   -12.37554     1.397E-02
      2    PO4-3              2.000E-02   6.298E-03    -9.82432     6.295E-03
      3    PO4-3              2.000E-02  -1.455E-02    -8.65259     1.455E-02
      4    PO4-3              2.000E-02  -1.832E-02    -7.75172     1.832E-02
      5    PO4-3              2.000E-02   5.349E-02    -7.60016     5.349E-02
      6    PO4-3              2.000E-02   5.781E-03    -7.93030     5.779E-03
      7    PO4-3              2.000E-02  -2.429E-03    -7.82034     2.427E-03
      8    PO4-3              2.000E-02  -1.869E-04    -7.72922     1.849E-04
      9    PO4-3              2.000E-02   2.372E-05    -7.73754     2.172E-05
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 28-MAY-96  TIME:   9:41:33

 ITERATIONS=  10:  SOLID CU3(PO4)2    PRECIPITATES
```

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 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 28-MAY-96  TIME:  9:41:33


PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

     ITER       NAME        TOTAL MOL     DIFF FXN    LOG ACTVTY    RESIDUAL
     10    K+1              3.000E-02  -5.270E-03    -1.60677     5.267E-03
     11    K+1              3.000E-02   3.931E-03    -1.52372     3.927E-03
     12    K+1              3.000E-02   3.782E-04    -1.57819     3.752E-04
     13    K+1              3.000E-02  -4.619E-04    -1.58392     4.589E-04
     14    K+1              3.000E-02   7.301E-03    -1.57724     7.297E-03
     15    K+1              3.000E-02   1.005E-04    -1.67325     9.750E-05
     16    K+1              3.000E-02  -3.934E-04    -1.67461     3.904E-04
     17    K+1              3.000E-02  -1.694E-03    -1.66934     1.691E-03
     18    K+1              3.000E-02  -1.469E-03    -1.64550     1.466E-03
     19    K+1              3.000E-02  -7.054E-04    -1.62543     7.024E-04
     20    K+1              3.000E-02  -4.130E-04    -1.61664     4.100E-04
     21    K+1              3.000E-02  -3.131E-04    -1.61162     3.101E-04
     22    K+1              3.000E-02  -1.564E-04    -1.60743     1.534E-04
     23    K+1              3.000E-02   7.722E-05    -1.60551     7.422E-05
     25    K+1              3.000E-02   4.171E-06    -1.60661     1.171E-06
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 28-MAY-96  TIME:  9:41:33


 ITERATIONS=  26:  SOLID ZN3(PO4),4W  PRECIPITATES
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________________________________ PART 3 of OUTPUT FILE ___________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 28-MAY-96  TIME:  9:41:33


PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

     ITER       NAME        TOTAL MOL    DIFF FXN   LOG ACTVTY    RESIDUAL
     26   Ni+2              8.772E-05  -4.279E-05    -4.40504    4.278E-05
     27   Ni+2              8.772E-05   3.085E-04    -4.15942    3.085E-04
     28   Ni+2              8.772E-05   1.524E-04    -4.23634    1.524E-04
     29   Ni+2              8.772E-05   4.004E-05    -4.38601    4.002E-05
     30   Ni+2              8.772E-05   8.599E-07    -4.45748    8.511E-07
     31   Ni+2              8.772E-05  -4.406E-06    -4.43905    4.397E-06
     32   Ni+2              8.772E-05  -1.929E-06    -4.41331    1.921E-06
     33   Ni+2              8.772E-05  -1.241E-07    -4.40422    1.153E-07
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 28-MAY-96  TIME:  9:41:33


  ITERATIONS=  34:  SOLID NI3(PO4)2    PRECIPITATES
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PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

     ITER       NAME          TOTAL MOL    DIFF FXN    LOG ACTVTY     RESIDUAL
     34    K+1                3.000E-02  -5.029E-03     -1.60643     5.026E-03
     35    K+1                3.000E-02   9.655E-03     -1.52999     9.652E-03
     36    K+1                3.000E-02   1.940E-03     -1.62409     1.937E-03
     37    K+1                3.000E-02  -3.682E-04     -1.63933     3.652E-04
     38    K+1                3.000E-02  -7.105E-04     -1.62867     7.075E-04
     39    K+1                3.000E-02  -4.861E-04     -1.61631     4.831E-04
     40    K+1                3.000E-02  -1.766E-04     -1.60885     1.736E-04
     41    K+1                3.000E-02  -1.163E-05     -1.60634     8.631E-06

 ID        NAME          ANAL MOL   CALC MOL   LOG ACTVTY      GAMMA      DIFF FXN
  330  H+1              3.000E-02  1.398E-07    -6.93381     0.832836  -5.748E-07
  231  Cu+2             6.673E-05  1.605E-07    -7.11228     0.481104   7.141E-07
  410  K+1              3.000E-02  2.973E-02    -1.60617     0.832836  -3.141E-07
  140  CO3-2            0.000E-01  3.600E-08    -7.76147     0.481104   0.000E-01
  950  Zn+2             7.159E-05  6.451E-06    -5.50815     0.481104   0.000E-01
  540  Ni+2             8.772E-05  1.136E-05    -5.26228     0.481104   0.000E-01
    2  H2O              0.000E-01 -1.509E-04    -0.00059     1.000000   0.000E-01
  580  PO4-3            2.000E-02  9.086E-08    -7.75659     0.192769   0.000E-01
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                  PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
               TYPE I and TYPE II (dissolved and adsorbed) species

H+1                        31.2     PERCENT BOUND IN SPECIES #3305800   HPO4 -2
                67.7    PERCENT BOUND IN SPECIES #3305801   H2PO4 -

Cu+2                       54.4     PERCENT BOUND IN SPECIES #    231   Cu+2
                 2.4    PERCENT BOUND IN SPECIES #2311400   CuCO3 AQ
                 2.7    PERCENT BOUND IN SPECIES #2313300   CuOH +
                39.8    PERCENT BOUND IN SPECIES #2313301   Cu(OH)2 AQ

K+1                        99.1     PERCENT BOUND IN SPECIES #    410   K+1

CO3-2                       1.1     PERCENT BOUND IN SPECIES #5401401   NiCO3 A
                81.2    PERCENT BOUND IN SPECIES #3301400   HCO3 -
                17.5    PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ

Zn+2                       99.0     PERCENT BOUND IN SPECIES #    950   Zn+2

Ni+2                       93.9     PERCENT BOUND IN SPECIES #    540   Ni+2
                 5.7    PERCENT BOUND IN SPECIES #5401401   NiCO3 AQ

H2O                        26.2     PERCENT BOUND IN SPECIES #3300020   OH-
                 2.0    PERCENT BOUND IN SPECIES #2313300   CuOH +
                59.5    PERCENT BOUND IN SPECIES #2313301   Cu(OH)2 AQ
                 8.9    PERCENT BOUND IN SPECIES #9503300   ZnOH +
                 1.4    PERCENT BOUND IN SPECIES #9503301   Zn(OH)2 AQ
                 2.0    PERCENT BOUND IN SPECIES #5403300   NiOH +

PO4-3                       1.3     PERCENT BOUND IN SPECIES #4105800   KHPO4 -
                47.4    PERCENT BOUND IN SPECIES #3305800   HPO4 -2
                51.3    PERCENT BOUND IN SPECIES #3305801   H2PO4 -
```

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______________________________ PART 5 of OUTPUT FILE __________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 28-MAY-96  TIME:  9:41:33


                  -------------------------------------------------------
                  ----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX      NAME           DISSOLVED            SORBED            PRECIPITATED
                     MOL/KG   PERCENT     MOL/KG   PERCENT     MOL/KG   PERCENT

330  H+1           3.013E-02   100.0    0.000E-01      0.0   0.000E-01      0.0
231  Cu+2          2.951E-07     0.4    0.000E-01      0.0   6.715E-05     99.6
410  K+1           3.000E-02   100.0    0.000E-01      0.0   0.000E-01      0.0
140  CO3-2         6.371E-05   100.0    0.000E-01      0.0   0.000E-01      0.0
950  Zn+2          6.518E-06     9.1    0.000E-01      0.0   6.507E-05     90.9
540  Ni+2          1.211E-05    13.8    0.000E-01      0.0   7.561E-05     86.2
  2  H2O           3.952E-07   100.0    0.000E-01      0.0   0.000E-01      0.0
580  PO4-3         1.986E-02    99.3    0.000E-01      0.0   1.386E-04      0.7

     Charge Balance: SPECIATED

       Sum of CATIONS =  2.977E-02 Sum of ANIONS    2.932E-02

       PERCENT DIFFERENCE =   7.660E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)

     EQUILIBRIUM IONIC STRENGTH (m) =   3.897E-02

     EQUILIBRIUM pH                 =   6.934

     DATE ID NUMBER:          960528
     TIME ID NUMBER:         9413389
```

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________________________________________________________________________________
______________________________ PART 1 of OUTPUT FILE ___________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAY-96  TIME: 11:34:45


batch study for copper and DOM
Cu 0.1 mg/L, DOM 1e-5 molar, pH = 4

--------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 The maximum number of iterations is:  40
 The method used to compute activity coefficients is: Davies equation
 Abbreviated output file

-------------------------------------------------------------------------------
    330  0.000E-01   -4.00 y
    231  1.574E-06   -5.80 y
    145  1.000E-05   -5.00 y
    140  0.000E-01  -16.00 y

 H2O has been inserted as a COMPONENT
  3   2
3301403    21.6285    -0.5300
    330     4.0000     0.0000


     Charge Balance: UNSPECIATED

       Sum of CATIONS=  3.148E-06 Sum of ANIONS =  2.800E-05

       PERCENT DIFFERENCE =  7.979E+01  (ANIONS - CATIONS)/(ANIONS + CATIONS)



              ------------------------------------------------------
             |  IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION: |
             |       Cu+2         Log activity guess:     -5.80     |
             |       CO3-2        Log activity guess:    -13.63     |
             |                                                      |
              ------------------------------------------------------
```

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_______________________________ PART 3 of OUTPUT FILE _____________________________
  PC MINTEQA2 v3.10    DATE OF CALCULATIONS: 11-MAY-96   TIME: 11:34:45


PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

     ITER       NAME         TOTAL MOL    DIFF FXN    LOG ACTVTY    RESIDUAL
      0    Cu+2              1.574E-06   7.024E-07    -5.80304    7.023E-07
      1    Cu+2              1.574E-06   1.824E-08    -5.96329    1.808E-08
      2    Cu+2              1.574E-06   2.945E-08    -5.96829    2.929E-08
      3    Cu+2              1.574E-06   8.385E-10    -5.97635    6.811E-10

 ID        NAME          ANAL MOL    CALC MOL   LOG ACTVTY      GAMMA      DIFF FXN
  145   DOM             1.000E-05  5.224E-06    -5.31748     0.921502  -9.842E-12
  231   Cu+2            1.574E-06  1.100E-06    -5.97658     0.959148   2.322E-11
  140   CO3-2           0.000E-01  2.453E-14   -13.62850     0.959148   0.000E-01
  330   H+1             0.000E-01  1.010E-04    -4.00000     0.989627   0.000E-01
    2   H2O             0.000E-01 -1.134E-05     0.00000     1.000000   0.000E-01
```

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________________________________ PART 4 of OUTPUT FILE __________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAY-96  TIME: 11:34:45


                PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
             TYPE I and TYPE II (dissolved and adsorbed) species

DOM               52.2     PERCENT BOUND IN SPECIES #     145   DOM
                  43.0     PERCENT BOUND IN SPECIES #1453300   H DOM
                   4.7     PERCENT BOUND IN SPECIES #1452310   Cu DOM

Cu+2              69.9     PERCENT BOUND IN SPECIES #     231   Cu+2
                  30.1     PERCENT BOUND IN SPECIES #1452310   Cu DOM

CO3-2             99.6     PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ

H+1               79.0     PERCENT BOUND IN SPECIES #     330   H+1
                  17.6     PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ
                   3.4     PERCENT BOUND IN SPECIES #1453300   H DOM

H2O               47.8     PERCENT BOUND IN SPECIES #3300020   OH-
                  50.2     PERCENT BOUND IN SPECIES #2313300   CuOH +
                   2.1     PERCENT BOUND IN SPECIES #2313301   Cu(OH)2 AQ
```

```
_______________________________ PART 5 of OUTPUT FILE _________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAY-96  TIME: 11:34:45


               ------------------------------------------------------
               ----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX     NAME            DISSOLVED            SORBED            PRECIPITATED
                      MOL/KG   PERCENT    MOL/KG   PERCENT    MOL/KG   PERCENT

145  DOM            1.000E-05   100.0   0.000E-01     0.0   0.000E-01     0.0
231  Cu+2           1.574E-06   100.0   0.000E-01     0.0   0.000E-01     0.0
140  CO3-2          1.134E-05   100.0   0.000E-01     0.0   0.000E-01     0.0
330  H+1            1.280E-04   100.0   0.000E-01     0.0   0.000E-01     0.0
  2  H2O            2.126E-10   100.0   0.000E-01     0.0   0.000E-01     0.0

     Charge Balance: SPECIATED

       Sum of CATIONS =  1.032E-04 Sum of ANIONS   2.280E-05

       PERCENT DIFFERENCE =   6.382E+01  (ANIONS - CATIONS)/(ANIONS + CATIONS)

     EQUILIBRIUM IONIC STRENGTH (m) =   8.035E-05

     EQUILIBRIUM pH                 =   4.000

     DATE ID NUMBER:          960511
     TIME ID NUMBER:        11344542
```