HEAVY METAL REMOVAL MECHANISMS IN CONSTRUCTED WETLAND WASTEWATER TREATMENT

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Robert C. Patterson, Jr.

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Signature:

Robert C Patterson Jr 2/5/96
Student Date

Approvals:

Scott C. Martin 2/16/96
Thesis Advisor Date

Laurie S. Garton 2/16/96
Committee Member Date

2/16/96
Committee Member Date

Peter J Kasvinsky 2/19/96
Dean of Graduate Studies Date

ABSTRACT

The detrimental effects of the untreated release of compounds containing heavy metals to the environment has been well documented. Numerous energy-intensive and/or labor intensive technologies have been developed to remove metals from various types of wastewater. However, constructed wetland (CW) treatment of wastewater has been shown to be an effective method for reducing or removing biochemical oxygen demand (BOD), nitrogen, phosphorus, and solids (both settleable and colloidal) through passive means which are much less resource-intensive. A limited amount of research has been conducted which indicates the removal of metals may be possible using CW systems.

The primary objectives of this study were to confirm the mechanisms responsible for the removal of metallic compounds in the substrates (soils) of constructed wetlands, and to examine the effect different types of substrate materials have on the removal of metals from wastewaters such as acid mine drainage and landfill leachate - wastewaters which typically contain high levels of various metals. Mechanisms identified in the literature as being responsible for the removal of metals in the wetland environment include filtration, oxidation, precipitation, adsorption, complexation, and plant uptake.

A series of static Batch Adsorption Experiments were conducted using the following pairs of adsorbates and adsorbents: copper/peat, copper/yard waste compost, copper/sand, iron/sand and iron/peat. Copper was observed to be readily adsorbed by the organic soils (peat and yard waste compost), and generally followed the Freundlich Adsorption Isotherm. The adsorption of both copper and iron by sand was minimal, indicating the presence of organic material was important to the adsorption process.

A dynamic Column Experiment was conducted utilizing copper as the adsorbate and peat as the adsorbent. The removal of 95% of the applied copper was consistently achieved through the combination of adsorption, complexation, and the filtration of precipitate.

DEDICATION

To my parents, Bob and Maxine -

without your love and support this work would never have materialized.

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Look to this day,
For it is life,
The very life of life.
In its brief course lie all
The realities and verities of existence,
The bliss of growth,
The splendor of action,
The glory of power ---

For yesterday is but a dream,
And tomorrow is only a vision,
But today, well lived,
Makes every yesterday a dream of happiness
And every tomorrow a vision of hope.

Look well, therefore, to this day.

Sanskrit Proverb

TABLE OF CONTENTS

PAGE

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF TABLES

INTRODUCTION

1.1 Constructed Wetland Overview

1.1.1 Background

As the human species has progressed through many stages of development ranging from prehistoric man to today's civilization dependent upon high tech gadgetry, man's relationship and interaction with the physical environment has grown and deepened in complexity. Understanding and awareness of mankind's impact, as well as dependence, on the environment have increased in the twentieth century.

As civilization developed, scientists and engineers devised many methods of treating the increased wastes and pollution resulting from population growth and industrialization. However, the earth's self-cleansing capabilities were also noted. Natural biological, chemical, and geophysical processes can, in effect, treat and minimize the effects of certain levels of pollution. Natural wetland systems - those which develop naturally - are known to support complex ecosystems composed of diverse populations of plants, animals, and microorganisms. Careful study has also shown that wetlands are capable of cleansing polluted water through various chemical, physical, and biological processes.

1.1.2 Wetland Research

Since wetlands were observed to efficiently assimilate a variety of contaminants, they were the focus of early research to understand the biochemical cycling of nutrients, metals, micronutrients and trace elements, and the flux of materials in the earth's biosphere. Studies conducted during the 1950s in Germany focused on wastewater treatment and contaminant removal through the use of wetland plants. Research continued using natural systems for wastewater treatment in Europe and the United States through the 1960s and 1970s. Soon researchers were directing their efforts toward creating and building wetland systems emulating those which occurred naturally [Bastian & Hammer, 1993].

In the United States, discharge of water into existing wetlands generally requires a US Army Corps of Engineers permit, since they are considered "waters of the US" as specified under Section 404 of the Clean Water Act. Constructed wetlands (CW) usually aren't subject to these requirements. This reason, combined with the fact that more efficient use of treatment processes could be obtained with CW systems, led researchers to focus on these man-made systems [US EPA, 1990; 1987]. Constructed wetlands have been shown to be less energy-intensive and less dependent on mechanized equipment than conventional man-made treatment facilities. Thus, they require less operation and maintenance once established.

1.1.3 Constructed Wetlands Definition

Constructed wetlands may be defined as man-made, engineered systems designed, constructed, and operated to optimize the physical, chemical, and biological processes of wetland ecosystems to treat wastewater in a more controlled environment, and more consistent manner, than that occurring in the natural wetland environment [US EPA, 1987; Steiner & Watson, 1993].

1.1.4 Constructed Wetlands Uses and Objectives

Constructed wetland systems have been used to treat a variety of wastewaters, including municipal and residential sewage, industrial discharges, acid mine drainage, stormwater discharges, livestock wastewaters, and leachates from landfills and composting facilities. Treatment objectives are dependent upon the type of wastewater being processed, but include the removal of biochemical oxygen demand (BOD), nutrients such as phosphorus and ammonia, suspended solids (SS), and metals.

1.2 Goals of Project

The primary objectives of this project were to confirm the mechanisms responsible for the removal of metallic contaminants in constructed wetlands, and to examine the effect of the type of substrate material used in the system on the removal of metals. Metal removal efficiency in constructed wetlands has varied among existing systems. These systems have been designed with different treatment objectives, and installed using different substrates, vegetation, configurations, and design parameters. The ultimate goal of the project was to isolate and better understand the metal removal processes occurring in constructed wetlands, concentrating on the effect different substrate materials have upon the metal removal efficiency.

The focus of this study was the application of constructed wetland systems to the treatment of acid-mine drainage and landfill leachate. Both of these types of wastewater may contain high concentrations of metal contaminants. Untreated discharges of metal-containing wastewaters to the environment result in negative consequences to the surrounding ecosystems. A greater understanding of metal removal mechanisms could lead to more effective design and implementation of constructed wetland systems to prevent potential pollution problems.

Copper (Cu) and iron (Fe) were selected as representative metals for the study. Both of these metallic elements are typical constituents of acid-mine drainage and landfill leachate [Eger, *et al.*, 1993; LaGrega, *et al.*, 1994]. Both pose environmental risks if left untreated at sufficiently high concentrations. The substrate materials selected for the study were peat, sand, and yard waste compost. These materials are typical of substances utilized as substrates in constructed wetlands [Steiner & Freeman, 1989; Frostman, 1993].

All tests were run on the bench-scale. Batch studies were conducted to analyze the potential metallic cation adsorptive capacity of each of the substrate materials. Adsorption isotherms were developed from the static batch study results. In order to test a dynamic system, a solution containing varying concentrations of copper was fed into a column containing peat. Influent and effluent pH and copper concentrations were monitored for a seven week period.

LITERATURE REVIEW

2.1 Constructed Wetland Design Considerations

2.1.1 Types of Constructed Wetlands

Constructed wetlands are generally divided into two types. The classification is based upon the intended water flow pattern in the system. Free water surface (FWS) systems allow for flow through one or more shallow basins or channels called cells or beds. Flow is usually at low velocity and shallow depth over a relatively impermeable substrate. The water surface is exposed to the atmosphere. Wetland plants are rooted in the substrate, and extend, or emerge, above the water surface. Subsurface flow (SF) systems consist of one or more cells with emergent vegetation, but water flows at a low velocity below the surface through a permeable substrate. SF systems are also called vegetated submerged bed (VSB) systems, reed bed systems, and gravel bed treatment wetlands [US EPA, 1988; Steiner & Freeman, 1989; Witthar, 1993].

2.1.2 Treatment Objectives

Constructed wetlands (CW) may be designed with a number of treatment objectives, or focus on the removal of a specific contaminant. Typically, CW systems have been used to remove BOD, SS, nutrients such as nitrogen and phosphorus, trace organics, and heavy metals such as iron, copper, nickel, manganese, and zinc. They have been shown to raise the pH of acidic waters such as mine drainage, industrial wastewater, and leachate from landfills and composting facilities. Constructed wetlands have also been utilized to treat point and non-point source flows of agricultural and stormwater discharges [US EPA, 1988,1987].

2.1.3 Substrate Types and Characteristics

The substrate of a constructed wetland is essentially the soil, or soil-like material, that supports the growth of wetland plants and microorganisms. The substrate also plays a key role in pollutant removal -- directly by uptake or adsorption, and indirectly through other processes associated with the substrate-water and substrate-root interfaces.

Interacting factors which influence the growth of plants and microorganisms include the organic and mineral composition of the soil, media depth, permeability or hydraulic conductivity, and oxygen transfer rate.

Substrate requirements depend on which type of constructed wetland is to be utilized. FWS systems require a base composed of a natural or constructed impermeable layer of clay, compacted *in situ* soil, geotechnical material, or asphalt. The desired permeability of this layer ranges from 10^{-6} to 10^{-7} m/s (0.14 to 0.014 in/hr) [US EPA, 1988]. A shallow layer of native or imported soil is placed over the impermeable layer to support vegetation.

Subsurface flow systems consist of a layer of media over an impermeable clay layer or synthetic liner. 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.

In both FWS and SF systems, the type of substrate utilized influences metal removal through ion exchange and adsorption onto clay particles and organic substances. Coarse substances with a high mineral content, like sands and gravels, have lower exchange capacities than clay and organic soils. The high humic content of organic soils, such as peat, promotes the removal of metallic ions through cation exchange [Steiner & Freeman, 1989]. In subsurface flow systems the wastewater is exposed to a much greater substrate surface area, increasing the potential for metal removal via cation exchange or adsorption.

Peat is a type of soil having an organic content of greater than twenty percent and an ash content of less than fifty percent which forms through the anaerobic decay of accumulated layers of plant litter under water-soaked conditions [Crum, 1988]. Peat is formed in wetland areas, but not all wetlands produce peat. Only those in which plant remains accumulate under oxygen-poor conditions faster than they decompose can be classified as peat storing. The principal peatlands are bogs and fens [Crum, 1988].

The composition of peat is highly variable based on its origin and its formation, but the primary components of peat are lignin and cellulose. Colloidal humic substances formed from the incomplete decay of the lignin and cellulose also are a major constituent [Couillard, 1994; Crum, 1988]. Cellulose is a complex polysaccharide which forms the cell walls in plant tissue. Lignin is the substance that gives plant stems and roots a hard, woody nature [Fuchsman, 1980], and is defined only as any residual material left after a substance is treated with strong sulfuric acid [Crum, 1988].

The moisture content of peat soil *in situ* typically reaches 80-90%, but is considerably less for material which has been removed from its natural state, processed, and allowed to air dry. Porosity can range as high as 95% [Couillard, 1994].

Humic substances include a group of diverse organic substances whose origin and primary constituents are well known, but whose chemical structure is not well understood. Humic substances constitute a major portion of the organic matter in natural soils and waters, and give a characteristic brown, yellow-brown, or black color to natural waters, as well as sewage. They originate as decomposition products and by-products of plant and animal matter [Snoeyink & Jenkins, 1980].

The major components of humic substances have been arbitrarily divided into three groups based on their solubility in dilute acids and dilute bases. Humic acid (HA) is not soluble in dilute acids, but is soluble in dilute base. Fulvic acid (FA) is soluble in both dilute acid and dilute base. Humin precipitates in both dilute acid and dilute base [James M. Montgomery, Inc., 1985; Snoeyink & Jenkins, 1980]. The term "humic acid" is typically used to refer to all three components, however.

The chemical structures of HA and FA have not been precisely determined, but are thought to be a pattern of various aromatic carbon rings with attached functional groups. The functional groups which have been identified include carboxyl, carbonyl, methoxyl, phenols, ethers, esters, and alcohols [Snoeyink & Jenkins, 1980]. Table 2-1 lists some physical and chemical properties of humic and fulvic acids.

Table 2-1 Chemical and Physical Properties of Humic and Fulvic Acids

Property	Humic Acids	Fulvic Acids
Elemental composition	*(% by weight)*	*(% by weight)*
Carbon	50 - 60	40 - 50
Hydrogen	4 - 6	4 - 6
Oxygen	30 - 35	44 - 50
Nitrogen	2 - 4	<1 - 3
Sulfur	1 - 2	0 - 2
Solubility in strong acid (pH 1)	Not Soluble	Soluble
Molecular weight range	low 100s - 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

2.1.4 Vegetation

Soils in wetland areas often are saturated and subject to anaerobic conditions. Plants that can thrive in these conditions are necessary for effective treatment of polluted waters. Fortunately, nature has provided a number of wetland plants which fulfill at least three important purposes [Hammer & Bastian, 1989]:

(1) Plants have the ability to transfer oxygen and other atmospheric gases through their stalks, roots, and rhizomes to the oxygen depleted substrate;

(2) Plant tissues, particularly the roots and rhizomes, greatly increase the available surface area for the attachment of microbial populations in the water column and the substrate; and

(3) Though less significant to pollutant removal, plants utilize nutrients and trace elements found in the wastewater to carry out life processes.

Oxygen transported below the water surface can oxidize substrate material, supporting aerobic microbial populations. Microbes, including protozoa, algae, fungi, and bacteria, convert contaminants into nutrients and energy for their metabolism, and also oxidize metals such as iron and manganese [Guntenspergen, *et al.*, 1989; Hammer & Bastian, 1989].

Wetland vegetation plays an important role in water purification through the plants' interaction with the microorganisms, substrate, water, and atmosphere. Plants get nutrients from the soil and subsurface water, acting as key components in the cycling of many chemical elements important to the environment, including nitrogen, phosphorus, and carbon [Faulkner & Richardson, 1989]. Root systems work with the substrate to act as a filter for larger suspended solids particles, and also slow water flow to allow for sedimentation of particles. Decaying plant biomass contributes to the pool of organic material in wetland soils, enhancing its adsorptive capacity for metals and other pollutants.

Emergent vegetation typically is rooted in the substrate with part of its stalk submerged and part exposed to the atmosphere. The predominant types of emergent vegetation used in constructed wetlands are cattails (*Typha* spp.), bulrushes (*Scirpus* spp.), rushes (*Juncus* spp.), reeds (*Phragmites* spp.), sedges (*Carex* spp.), and various grasses [US EPA, 1988; Hammer & Bastian, 1989]. For CW systems it is suggested to use plants commonly found in nearby natural wetlands. Table 2-2 lists plants commonly considered for use in CW systems.

2.1.5 BOD Removal

The removal of biochemical oxygen demand (BOD) in both FWS and SF constructed wetlands is generally accepted to follow first-order, plug-flow kinetics, much like an attached-growth biological reactor. In practice, constructed wetlands do not strictly follow either the plug-flow scheme or the completely-mixed (continuously stirred) model. Alternative schemes are under study, but the US EPA recommends use of the plug-flow model for design purposes until sufficient data is collected to validate alternate models [US EPA, 1993]. The first-order model has been described as follows [US EPA, 1993; Watson & Hobson, 1989]:

$$C_e/C_o = \exp[-K_T\, t] \qquad \{\text{Eqn. 2-1}\}$$

where, C_e = effluent BOD_5 concentration, mg/L

Table 2-2 CW Treatment Systems Candidate Emergent Plants

Common Name	Scientific Name
Arrowheads	*Sagittari spp.*
Bald Cypress	*Taxodium distichum*
Bladderworts	*Ultricularia spp.*
Bulrush	*Scirpus spp.*
Burreeds	*Sparganium spp.*
Cattails	*Typha spp.*
Maidencane	*Panacium spp.*
Manna Grass	*Glyceria spp.*
Mosses	*Sphagnum spp.*
Pickerelweed	*Pontederia cordata*
Pondweeds	*Potamogeton spp.*
Reed	*Phragmites spp.*
Rush	*Juncus spp.*
Sawgrass	*Cladium jamaicense*
Sedges	*Carex spp.*
Spikerushes	*Eleocharis spp.*
Tupelo	*Nyssa spp.*
Waterweeds	*Elodea spp.*

Source: Corbitt & Bowen, 1994

C_o = influent BOD_5 concentration, mg/L

K_T = temperature-dependent rate constant, d^{-1}

t = hydraulic residence time, d

The rate constant, K_T, is dependent on temperature as defined below:

$$K_T = K_{20}\,\theta^{(T-20°)} \qquad \{\text{Eqn. 2-2}\}$$

where, K_T = rate constant at temperature T, d^{-1}

K_{20} = 1.104 d^{-1} = rate constant at 20°C

θ = 1.106

T = water temperature, °C

2.1.6 Hydraulic Residence Time

Hydraulic residence time (HRT) is an important design and operational parameter for CW systems. Equation 2-1 implies that the effluent BOD_5 concentration will decrease as residence time increases. Typical HRT design values range from 4 to 15 days for both free water surface systems and subsurface flow systems [Tchobanoglous & Burton, 1991]. HRT can be found by the following equation [US EPA, 1988 & 1993, Watson & Hobson, 1989]:

$$HRT = LWnd / Q \qquad \{\text{Eqn. 2-3}\}$$

where, L = length (parallel to flow), ft or m

W = width(perpendicular to flow), ft or m

n = effective media porosity as a decimal

d = depth, ft or m

Q = average flow through bed, ft^3/d or m^3/d

2.1.7 System Area Requirements

The required surface area of a CW equals the length times the width (LW), and can be determined by substituting Equation 2-3 into Equation 2-1 and rearranging terms:

$$A_S = [Q(\ln C_e - \ln C_o)] / (K_T d\, n) \qquad \{\text{Eqn. 2-4}\}$$

where, A_S = system surface area, ft^2 or m^2

The required CW cross-sectional bed area is equal to the width times the depth, and is based on Darcy's Law for flow through porous media as follows [Holtz & Kovacs, 1981; US EPA, 1993]:

$$A_C = Q / (k_s\ S) \qquad \{\text{Eqn. 2-5}\}$$

where, A_C = total cross-sectional area perpendicular to the flow, ft^2 or m^2

Q = flow rate, ft^3/d or m^3/d

k_s = hydraulic conductivity (permeability) of the substrate, ft/d or m/d

S = hydraulic gradient, ft/ft or m/m

Table 2-3 gives typical values of media size, porosity, and unadjusted hydraulic conductivity for various substrate materials. The value of k_s used in the design process should be conservatively adjusted to provide for solids accumulation and clogging potential in the substrate over the life of the system. A design value of 850 ft/d (260 m/s) for clean, "small" gravel has been suggested in the literature [Steiner & Watson, 1993]. To provide an adequate hydraulic safety factor, the US EPA [1993] suggests using a value of ≤ 33% of the "effective" hydraulic conductivity, to utilize no more than 10% of the potential hydraulic gradient, and to install adequate inlet and outlet control structures.

Table 2-3 SF Wetlands Substrate Characteristics

Substrate Type	D10, Effective Size (mm)	n, Porosity (%)	ks, Hydraulic Conductivity (ft/d)	ks, Hydraulic Conductivity (m/d)
Coarse Sand	2	32	3,280	1,000
Gravelly Sand	8	35	16,400	5,000
Fine Gravel	16	38	24,600	7,500
Medium Gravel	32	40	32,800	10,000
Coarse Rock	128	45	328,000	100,000

Source: US EPA, 1993

2.1.7.1 Limitations of Darcy's Law

Several limitations to the applicability of Darcy's Law exist, but it remains the accepted design method for constructed wetland systems. The use of Darcy's Law assumes laminar flow which is constant and uniform into and out of the system. If the system is designed with a large hydraulic gradient, and very coarse gravel or large rock is employed as media, turbulent flow may occur. Short circuiting of flow, infiltration, exfiltration, evapotranspiration, and precipitation all contribute to differences in uniformity and magnitude between influent and effluent flows.

However, Darcy's Law can be used as a reasonable model of subsurface flow if the systems are properly designed and constructed to minimize turbulent flow and short circuiting. Also, the flow used in Equation 2-5 should be an average of the inflow and outflow of the system (i.e., $\{Q_{in}+Q_{out}\}/2$) to account for the possible losses or gains listed above [US EPA, 1993; Watson, *et al.*,1989].

2.1.8 Aspect Ratio

The ratio of cell length to width (L:W), or aspect ratio, is an important factor of constructed wetland design. In FWS systems the aspect ratios used have generally been greater than 10:1 with the intent of minimizing short circuiting [Knight, *et al.*, 1993; Steiner & Freeman, 1989]. However, either ratios approaching 1:1 [Tchobanoglous, 1993], or a wrap-around serpentine channel with step feed of the wastewater [Tchobanoglous & Burton, 1992] have been suggested to prevent pollutant overload in the inlet region.

The recommended aspect ratio for subsurface flow systems is less than 1:1 in order to initially distribute flow over a larger media surface area preventing premature water surfacing and bed clogging due to organic overloading. If the recommended design limits on k_s values (see Section 2.1.7) are followed, the aspect ratio will be limited to about 0.75:1 for 1 ft (0.3 m) cell depths and to less than 3:1 for 2 ft (0.6 m) bed depths [US EPA, 1993].

2.1.9 Configuration

The configuration of the constructed wetland system is dependent upon many factors, including the required surface area, and the size, shape, and topography of the land available at the proposed site. The required surface area should be divided into two, or more, cells which may be in parallel or in series. The system may be homogeneous (i.e., entirely FWS cells or completely SF beds), or a combination of FWS and SF cells.

Both types of wetland cells have disadvantages. FWS cells are subject to freezing in cold climates and are an excellent breeding area for both disease-carrying and nuisance organisms such as mosquitoes and rodents during warmer months. However, FWS systems have been found to be an excellent method of treatment for BOD and suspended solids removal. Mosquitoes have been controlled through the introduction of certain species of fish. SF systems are not suitable for treating waters with high levels of suspended solids because the solids can accumulate, prematurely filling the voids in the substrate and causing short-circuiting or surfacing of the flow through the cell. However, SF systems provide considerable potential for adsorption and exchange of ions from solution as the water passes through the substrate, creating an environment suitable for the removal of metals from the wastewater.

A parallel arrangement is preferred to provide flexibility of operation and maintenance procedures. The utilization of both FWS and SF cells with different substrate materials would improve pollutant removal by introducing a greater variety of treatment mechanisms [Steiner & Freeman, 1989].

Bed depths should be less than 2.5 ft (0.76 m), and should be coordinated with the type of vegetation used to allow adequate root penetration. Bed slope should be minimal (0-2%) to avoid premature flow surfacing. Flow control structures should be placed at inlets and outlets to all cells to aid operation. These control structures should be designed to permit variation of water depth and hydraulic gradient, providing maximum flexibility of operation.

2.2 Wastewater Characterization

2.2.1 Acid Mine Drainage

The drainage from areas that have been mined for coal and metallic ores causes serious environmental problems. Surface and ground waters suffer severe degradation when exposed to mine drainage. Typically, this drainage has a low pH. Hence, it is referred to as acid mine drainage (AMD). At low pH values, metals tend to become soluble, so AMD also usually contains high levels of metals. Typical constituents of AMD include iron, manganese, copper, zinc, cadmium, lead, and other metals [Faulkner & Richardson, 1989]. Typical water quality ranges of acid mine drainage are given in Table 2-4.

2.2.2 Landfill Leachate

Leachate from landfills may be defined as the liquid which percolates through the solid waste in the landfill and extracts dissolved or suspended material. It is composed of the liquid produced by decomposition of the solid waste, plus any infiltration from surface or subsurface sources [Tchobanoglous, *et al.*, 1993].

Leachate composition is dependent upon the composition of the solid waste deposited in the landfill (municipal or hazardous wastes), the age of the landfill, and the phase of landfill gas production. Typically, leachate contains much higher levels of pollutants than domestic wastewater. Table 2-5 lists typical concentration ranges of pollutants in leachate from municipal solid waste landfills. Table 2-6 shows similar information for hazardous waste landfill leachate.

2.2.3 Domestic Wastewater

Wastewater is the liquid portion of wastes produced by a residence, development, or a community. Essentially, it is a blending of the water soluble or water-carried wastes from residential, institutional, commercial, and industrial sources. Untreated wastewater may contain pathogenic microorganisms, toxic substances, nutrients, and organic matter [Tchobanoglous, *et al.*, 1991]. Therefore, the efficient treatment and removal of pollutants from the wastewater flow before it is discharged to the environment is of paramount importance. For the comparison to acid mine drainage and landfill leachate, Table 2-7 lists the typical ranges in composition of untreated domestic wastewater.

Table 2-4 Typical Ranges in the Composition of Acid Mine Drainage

Constituent	*Precious Metal Mine*	*Coal Mine/ Processing Facilities*
Al	0.1 - 100	0.8 - 50
As	<0.001 - 97	
Ca	24 - 370	162 - 248
Cd	<0.01 - 3	
Cu	<0.01 - 60	0.04 - 0.19
Fe	0.1 - 700	10 - 300
K	1.4 - 46	
Mg	7 - 260	54 - 80
Mn	0.9 - 120	1.7 - 300
Na	3 - 61	6.6 - 13.5
Ni	4.8 - 200	1.65 - 1.98
Pb	<0.01 - 0.5	
SiO2	20 - 70	90
Sulfate	86 - 4000	20 - 2400
Zn	0.3 -400	0.06 - 1.13
pH	2.1 - 6.9	2.6 - 6.6

Sources (metal mine): Fyson, *et al.*, 1994; Wildeman & Laudon, 1989
(coal mine): Aljoe, 1994; Deitz, *et al.*, 1994; Eger, *et al.*, 1994; Stark, *et al.*, 1994; Brodie, 1993; Wildeman & Laudon, 1989

Table 2-5 Typical Composition Ranges of Municipal Solid Waste Landfill Leachate

Constituent	***Units***	***New Landfill < 2 years old***	***Mature Landfill >10 years old***	***General Landfill***
5 day BOD	mg/L	2,000-30,000	100-200	42-10,900
TOC	mg/L	1,500-20,000	80-160	11-8,700
COD	mg/L	3,000-60,000	100-500	
TSS	mg/L	200-2,000	100-400	
Specific Conductance	micromhos/cm			1,200-16,000
Organic Nitrogen	mg/L	10-800	80-120	
Ammonia Nitrogen	mg/L	10-800	20-40	0.01-1,000
Nitrate	mg/L	5-40	5-10	
Total Phosphorus	mg/L	5-100	5-10	
Ortho Phosphorus	mg/L	4-80	4-8	
Phosphates	mg/L			< 0.01-2.7
Total Alkalinity	mg/L as CaCO3	1,000-10,000	200-1,000	21-5,400
pH		4.5-7.5	6.6-7.5	3.0-7.9
Total Hardness	mg/L as CaCO3	300-10,000	200-1,000	
Calcium	mg/L	200-3,000	100-400	
Magnesium	mg/L	50-1,500	50-200	
Potassium	mg/L	200-1,000	50-400	
Sodium	mg/L	200-2,500	100-200	
Chloride	mg/L	200-3,000	100-400	4-9,920
Sulfate	mg/L	50-1,000	20-50	
Total Iron	mg/L	50-1,200	20-200	
Arsenic	mg/L			0.090-678
Barium	mg/L			0.011-10,000
Chromium	mg/L			0.1-2,000
Manganese	mg/L			0.001-208
Vinyl Chloride	mg/L			0.010-550
Lead	mg/L			0.140-32.5
Benzene	mg/L			0.001-19
Cadmium	mg/L			<0.0011-7.37
DDT	mg/L			0.0043-0.143
Dieldron	mg/L			<0.02-0.0045
Phenols	mg/L			<0.003-17
Selenium	mg/L			0.003-0.59
Tolulene	mg/L			<0.005-100

Source: Tchobanoglous, *et al.*, 1993; Staubitz, *et al.*, 1989

Table 2-6 Typical Composition Ranges of Hazardous Waste Landfill Leachate

Constituent		***Reported Concentration*** **mg/L**
Inorganics	Arsenic	0.011-10,000
	Barium	0.1-2,000
	Cadmium	0.005-8.2
	Chromium	0.001-208
	Copper	0.001-16
	Mercury	0.0005-0.007
	Nickel	0.020-48
	Lead	0.001-19
	Selenium	0.003-0.59
	Cyanide	0.005-14
Organics	Acetone	0.0001-62
	Aldrin	<0.0002-0.01
	Benzene	<0.0011-7.37
	Chlorobenzene	0.0046-4.62
	Chloroform	0.00002-4.55
	Dichlorobenzene	<0.01-0.517
	1,1-dichloroethane	<0.005-14.28
	1,2-dichloreethane	0.0021-4.5
	Trans-1,2-dichloroethane	0.025-8.15
	1,1-dichloroethylene	0.028-19.85
	Dichloromethane	0.0031-6.57
	Ethyl benzene	0.003-10.1
	Hexachlorobutadiene	<0.020-0.109
	Methlylene chloride	<0.3-184.0
	Methyl isobutyl ketone	2-10
	Perchloroethylene	ND-8.2
	Phenol	<0.003-17.0
	Tetrachloroethene	<0.001-89.2
	Tetrachloromethane	<0.001-25.0
	TOC	10.9-8,700
	Tolulene	<0.005-100.0
	1,1,1-Trichloroethane	0.0016-590
	Trichloroethene	<0.003-84.0
	Trichlorethylene	<0.003-260.0
	Vinyl chloride	0.014-32.5

Source: LaGrega, *et al.*, 1994

Table 2-7 Typical Composition of Untreated Domestic Wastewater

Constituent	*units*	Concentration		
		Weak	*Mediun*	*Strong*
Total Solids (TS)	mg/L	350	720	1200
Total Dissolved Solids (TDS)	mg/L	250	500	850
Fixed	mg/L	145	300	525
Volatile	mg/L	105	200	325
Suspended Solids (TSS)	mg/L	100	220	350
Fixed	mg/L	20	55	75
Volatile	mg/L	80	165	275
Settleable Solids	mL/L	5	10	20
5 Day BOD	mg/L	110	220	400
Total Organic Carbon (TOC)	mg/L	80	160	290
Nitrogen (total as N)	mg/L	20	40	85
Organic	mg/L	8	15	35
Free Ammonia	mg/L	12	25	50
Nitrites	mg/L	0	0	0
Nitrates	mg/L	0	0	0
Phosphorus (total as P)	mg/L	4	8	15
Organic	mg/L	1	3	5
Inorganic	mg/L	3	5	10
Chlorides	mg/L	30	50	100
Sulfate	mg/L	20	30	50
Alkalinity (as CaCO3)	mg/L	50	100	200
Grease	mg/L	50	100	150
Total Coliform	No. / 100 mL	1e06 - 1e07	1e07 - 1e08	1e08 - 1e09
Volatile Organic Compounds	mg/L	<0.001	0.001 - 0.004	> 0.004

Source: Tchobanoglous & Burton, 1991

2.3 Metal Removal Mechanisms in Constructed Wetlands

2.3.1 General Pollutant Removal Mechanisms

Pollutants are removed from wastewater treated in constructed wetlands through a variety of mechanisms. These include sedimentation, filtration, precipitation, adsorption, decomposition, biological activity, and plant uptake [US EPA, 1988]. Table 2-8 gives an overview of mechanisms responsible for the elimination of typical wastewater constituents. The removal of metals is typically achieved through chemical mechanisms such as precipitation, adsorption, and decomposition via oxidation-reduction reactions.

2.3.2 Constructed Wetland Metal Removal Mechanisms

Mechanisms identified as playing a role in the removal of metals in constructed wetlands include [Faulkner & Richardson, 1989]:

(1) Adsorption of metallic cations by the substrate;
(2) Complexation with organic matter in soil;
(3) Precipitation as sulfides, carbonates, or hydroxides;
(4) Oxidation or reduction through microbial processes;
(5) Plant uptake and utilization.

It is often difficult to differentiate which mechanisms are predominant in the wetland environment. Usually a combination of these processes are at work simultaneously within a given wetland. Active mechanisms also, will vary with substrate depth and distance from the point of introduction to the wetland site.

Microbial processes play a key role in wetland metal removal, but were not considered in this study. Under aerobic conditions, metals, such as iron and manganese, are oxidized to more insoluble states through bacterial action. In anaerobic zones, bacteria catalyze the reduction of sulfates to sulfides, producing insoluble precipitates. Hydroxide precipitation occurs throughout the wetland via increases in pH caused by the production of ammonia (NH_3) and bicarbonate (HCO_3^-) through the bacterial decay of organic matter [Wildeman & Laudon; 1989, Frostman, 1993].

Table 2-8 Wetland Pollutant Removal Mechanisms

	Contaminant								
Mechanisms	**Settleable Solids**	**Colloidal Solids**	**BOD**	**Nitro-gen**	**Phos-phorus**	**Heavy Metals**	**Refractory Organics**	**Bacteria & Virus**	**Description**
Physical Mechanisms									
Sedimentation	P	S	I	I	I	I	I	I	Solids & Constituent Contaminants settled by gravity in pond/marsh settings.
Filtration	S	S							Particulates filtered mechanically as water passes through substrate, root masses, or fish.
Adsorption		S							Interparticle attractive forces (van der Waals force).
Chemical Mechanisms									
Precipitation				P	P	P			Formation of or co-precipitation with insoluble compounds.
Adsorption				P		P			Adsorption on substrate and plant surfaces
Decomposition						P	P	P	Decomposition or alteration of less stable compounds by phenomena such as UV irradiation, oxidation, and reduction.
Biological Mechanisms									
Bacterial Metabolism		P	P	P		P	P		Removal of colloidal solids and soluble organics by suspended, benthic, and plant-supported bacteria. Bacterial nitrification/denitrification. Microbially mediated oxidation of metals.
Plant Metabolism							S	S	Uptake and metabolism of organics by plants. Root excretions may be toxic to organisms of enteric origin.
Plant Adsorption				S	S	S	S		Under proper conditions, significant quantities of these contaminants will be taken up by plants.
Natural Die-Off								P	Natural decay of organisms in an unfavorable environment.

P = primary effect; S = secondary effect; I = incremental effect (effect occurring incidental to removal of another contaminant).

Source: Watson, *et al.*, 1989; US EPA, 1988

2.3.3 Adsorption and Complexation

2.3.3.1 Definition of Terms

Adsorption is defined as the physical and/or chemical process which causes the accumulation of a material or substance at the interface between phases [James M. Montgomery, Inc., 1985; Tchobanoglous and Schroeder, 1985]. In a constructed wetland, pollutants accumulate at the solution-solid interface (i.e., the water-substrate interface), resulting in the adsorption of impurities from solution. The material being adsorbed (i.e., the pollutant) is known as the adsorbate. The adsorbent is the material on which adsorption is occurring (the substrate).

Adsorption is a process which is often portrayed as occurring in three steps: macrotransport, microtransport, and sorption. Macrotransport refers to the movement of the pollutant with the water, and is also called bulk transport. Microtransport involves the diffusion of the pollutant within the quiescent layer of water next to the substrate. Sorption is the generic term describing the attachment of the pollutant to the surface of the substrate and its later movement within the substrate. The term sorption does not differentiate whether chemical or physical processes are responsible for particle attachment [Tchobanoglous & Burton, 1991; Tchobanoglous and Schroeder, 1985].

Complex formation, or coordination, is defined by Stumm & Morgan (1981) as:

> ". . . any combination of cations with molecules or anions containing free pairs of electrons (bases) is called coordination (or complex formation) and can be electrostatic, covalent, or a mixture of both. The metal cation [is] called the *central atom*, and the anions or molecules with which it forms a coordination compound [are] referred to as *ligands*. If a ligand is composed of several atoms, the one responsible for the basic or nucleophilic nature of the ligand is called the ligand atom. If a base contains more than one ligand atom, and thus can occupy more than one coordination position in the complex, it is referred to as a *multidentate* complex former. Ligands occupying one, two, three, and so on, positions are referred to as unidentate, bidentate, tridentate, and so on . . . Complex formation with multidentate ligands is called *chelation*, and the complexes are called chelates."

2.3.3.2 Physiochemical Forces and Mechanisms of Adsorption from Solution

Adsorption from solution at the solution-solid interface is a complex process, involving physiochemical forces which have been categorized into a number of types [US EPA, 1992], including:

(1) London-van der Waals forces. These are weak attractive forces caused by short-lived dipoles about atoms or molecules, which result from instantaneous unsymmetrical electron distributions in molecules [Busch, *et al.*, 1978]. London-van der Waals forces are principally spherical in nature, with an energy of interaction of 10 to 40 kJ/mol. They are given credit for non-ideal behavior in gases, and also are of importance in the adsorption of organics [Stumm & Morgan, 1981].

(2) Coulombic-electrostatic-chemical forces. These forces are important in adsorption of inorganic ions and ionized organic molecules, and are principally physical in nature. Electrostatic forces result from materials that have a charged surface. The charged surface is caused by chemical reactions at the surface; either a pH-dependent charge (i.e., degree of proton transfer), or a permanent charge due to isomorphic substitution within the mineral lattice. This type of adsorption can occur in multiple layers. [US EPA, 1992; Stumm & Morgan, 1981].

(3) Ligand exchange-anion penetration-coordination. Coordinated complexes are formed through the interaction of many atoms and molecules with ligands. These complexes vary in complexity from simple linear molecules to chelates. These coordinated complexes may contain localized points of net charge that may bond to charged surfaces by polyvalent cation bridging, or by hydrogen bonding. This leads to a diverse range of possible geometrical arrangements. Bonded complexes may also be replaced by stronger complexing agents that better satisfy electroneutrality requirements. Typical reaction energies range from 8 to 60

kJ/mol for ligand exchange reactions with inorganic ions [US EPA, 1992; Stumm & Morgan, 1981].

(4) Hydrogen bonding. No distinct agreement exists on the best characterization of the hydrogen bond, but it is generally portrayed as an induced dipole phenomenon. Hydrogen bonding involves the bonding of two polar molecules at a preferred orientation. The energy range for hydrogen bonding is 10 to 40 kJ/mol [US EPA, 1992; Stumm & Morgan, 1981].

(5) Chemisorption. This process is similar to physical adsorption in that it is also based on electrostatic forces. Chemisorption, however, involves the formation of an actual chemical bond, usually covalent, between the surface atoms and the adsorbate molecule. This adsorption process is more selective with regard to which compounds or molecules adsorb at which sites, has shorter bond lengths and higher bond energies, and generally only occurs in one layer (i.e., monolayer adsorption). Nonetheless, the distinction between physical adsorption and chemisorption is often difficult, and some ligand exchange reactions are chemisorption processes [US EPA, 1992; James M. Montgomery, Inc.,1985].

2.3.3.3 Metal Removal by Peat

The removal of metals in peat appears to be principally performed though the mechanisms of ion exchange, complexation, and chelation [Coulliard, 1994; Crum, 1988]. Humic acids play a very important role in these processes. Since the surface layers of the organic material are negatively charged, cations are the major chemical species adsorbed. Cation exchange occurs between the metal ions in solution and hydrogen ions on the carboxylic, phenolic hydroxyl, and heterocyclic groups of humic colloids. Cations are selectively adsorbed by the peat in the order of affinity: $Pb^{+2} > Cu^{+2} > Zn^{+2} > Fe^{+3} > Ca^{+2}$ [Coulliard, 1994].

Peat contains a large number of polar groups, including alcohols and aldehydes, which act as chelating agents. The degree of chelation that occurs is dependent upon both the presence of these multidentate ligands and characteristics of the metallic ions. The affinity for cation chelation has been reported as $Fe^{+3} > Pb^{+2} > Ba^{+2} > Cu^{+2} > Ca^{+2}$. Also, hydrogen bonds are formed between polyvalent cations and the lignin, cellulose, hemicellulose, and hydroxyl groups of the humic acids [Coulliard, 1994].

The adsorption of copper on peat has been reported to be strongly dependent upon pH. At low pH (2.8 to 3.0), Cu^{+2} was readily adsorbed. At higher pH (6.5 to 7.0), precipitation of $Cu(OH)_2$ occurred [Coulliard, 1994]. At higher pH values, the removal of metals is enhanced through the precipitation of metallic oxides, hydroxides, sulfides, and carbonates. Subsequently, these precipitates can be effectively filtered by the peat.

2.3.4 Adsorption Isotherms

The capacity of an adsorbent to take up a given adsorbate is often determined through the development of an adsorption isotherm. This capacity is a function of the concentration and characteristics of the adsorbate, the characteristics of the adsorbent, and the temperature of the system. The adsorption isotherm is a graphical representation of the variability of adsorption capacity of an adsorbent with adsorbate concentration remaining in bulk solution at a constant temperature [Weber, 1972]. The isotherm is developed through a process often used in laboratory studies known as the static-equilibrium technique, or batch-adsorption technique [US EPA, 1992]. Refer to Section 3.1 for details on the procedures for developing isotherm data.

2.3.4.1 The Freundlich Isotherm

The Freundlich equation is an empirically derived equation for adsorption in solid-liquid systems. Since its formulation by H. Freundlich in 1909, it has become probably the most widely used expression for describing adsorption phenomena [US EPA, 1992]. It is commonly used in water and wastewater treatment to describe activated carbon adsorption, and is often useful in fitting experimental data [Weber, 1972]. It is defined as follows [US EPA, 1992; Tchobanoglous & Burton, 1991]:

$$q_e = x/m = K_f C_e^{1/n} \qquad \{\text{Eqn. 2-6}\}$$

where, $q_e = x/m$ = amount of adsorbate adsorbed per unit weight of adsorbent, mg/kg

x = amount of adsorbate adsorbed, mg

m = mass of adsorbent, kg

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

K_f, n = empirical constants

A typical Freundlich isotherm is shown in Figure 2-1. The empirical constants may be determined by plotting log q_e versus log C_e (Figure 2-2), and rewriting Equation 2-6 in the form of $y = a + bx$:

$$\log q_e = \log K_f + (1/n) \log C_e \qquad \{\text{Eqn. 2-7}\}$$

Taking the inverse of the slope of this straight-line plot gives the value of n, and the inverse log of the intercept gives the value of K_f.

It has been reported that the adsorption of copper by peat follows the Freundlich isotherm. This is attributed to the formation of complexes, chelation, and ion exchange reactions [Couillard, 1994].

2.3.4.2 The Langmuir Isotherm

The Langmuir equation was developed based on the assumptions that single-layer adsorption occurs at a fixed number of accessible adsorption sites on the surface of the adsorbent, with each of the sites having the same energy [Tchobanoglous & Burton 1991; Weber, 1972]. This model has been widely used in water and wastewater treatment applications. Advantages of the Langmuir isotherm include its relative simplicity, its ability to correspond to a broad range of experimental data, and its foundation in a model with some physical basis. Disadvantages include its allowance for only monolayer adsorption, and its assumption that energy of adsorption is independent of the degree of surface coverage [James M. Montgomery, Inc., 1985]

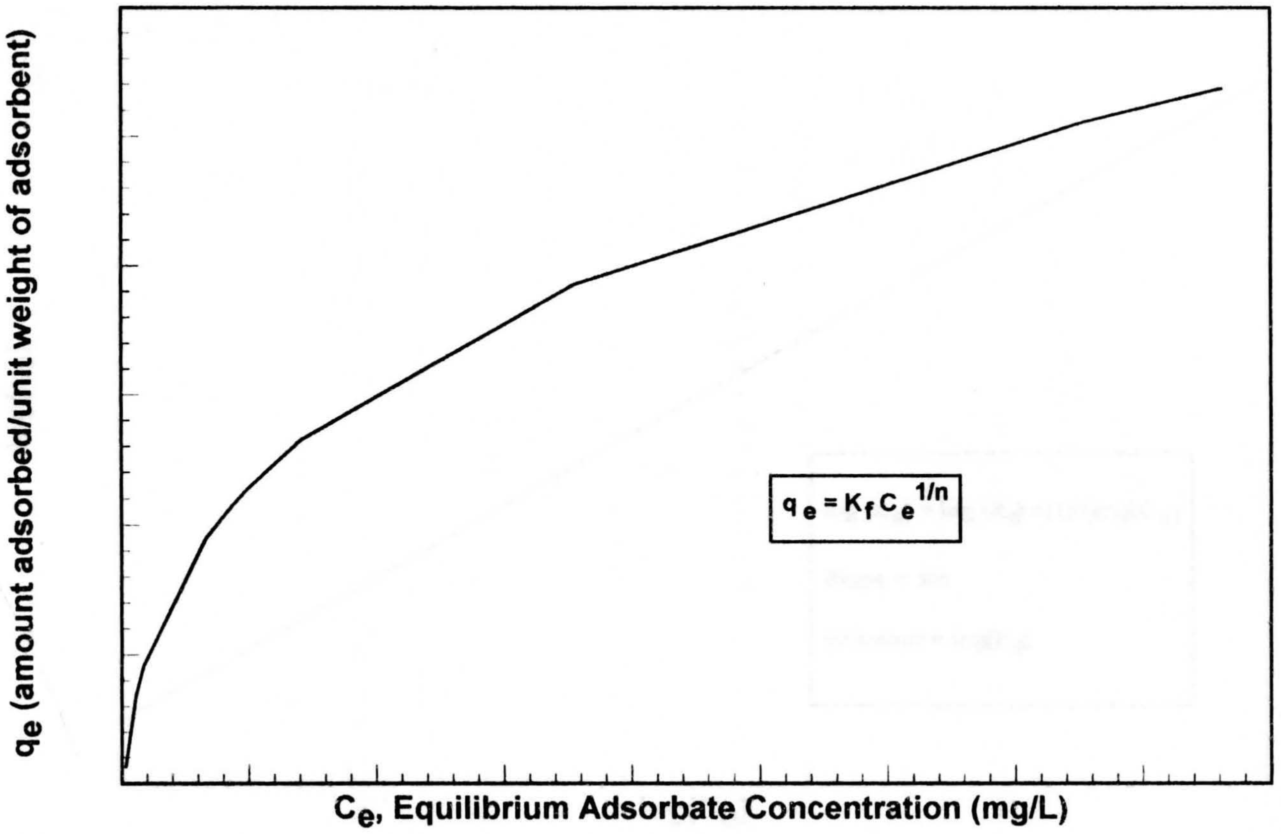


Figure 2-1. Typical Freundlich Isotherm (Source: James M. Montgomery, Inc., 1985)

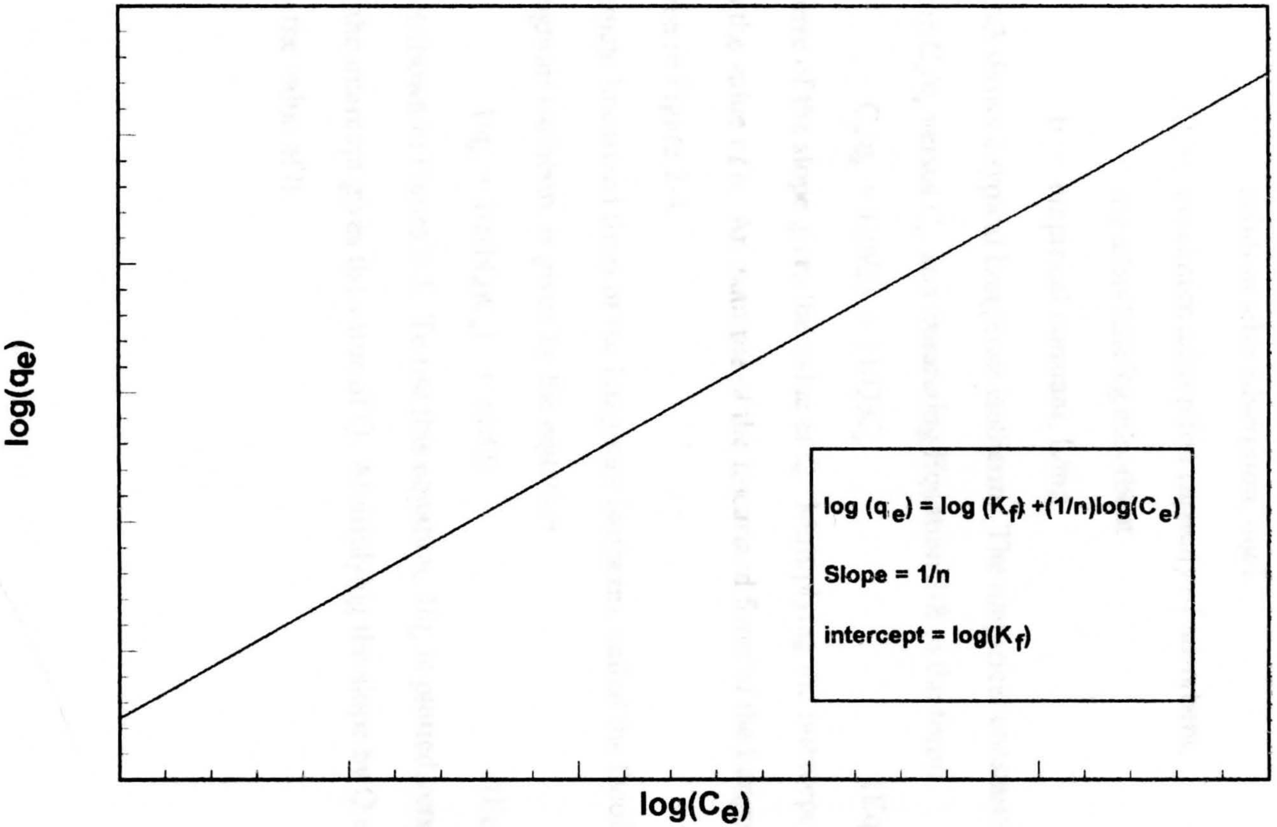


Figure 2-2. Typical Linearized Freundlich Isotherm (Source: James M. Montgomery, Inc., 1985)

The Langmuir equation is expressed as [Tchobanoglous & Burton 1991]:

$$q_e = x/m = (QbC_e)/[1 + (bC_e)] \qquad \{\text{Eqn. 2-8}\}$$

where $q_e = x/m$ = amount of adsorbate adsorbed per unit weight of adsorbent, mg/kg

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

Q = maximum adsorption capacity of adsorbent, mg adsorbate/kg adsorbent

b = empirical constant, L/mg

Figure 2-3 shows a typical Langmuir isotherm. The empirical constants may be found by plotting C_e/q_e versus C_e and linearizing Equation 2-8 to the form:

$$C_e/q_e = 1/(bQ) + (1/Q)C_e \qquad \{\text{Eqn. 2-9}\}$$

Taking the inverse of the slope gives the value of Q. Multiplying the intercept by Q and inverting gives the value of b. An example of the linearized form of the Langmuir isotherm is given in Figure 2-4.

An alternate linearized form of the Langmuir isotherm, called the Double Reciprocal Langmuir isotherm, is given by the equation:

$$1/q_e = 1/\{(bQ)C_e\} + (1/Q) \qquad \{\text{Eqn. 2-10}\}$$

This isotherm is shown in Figure 2-5. To use this equation, $1/q_e$ is plotted versus $1/C_e$. The inverse of the intercept gives the value of Q. Multiplying the slope by Q and inverting gives the value of b.

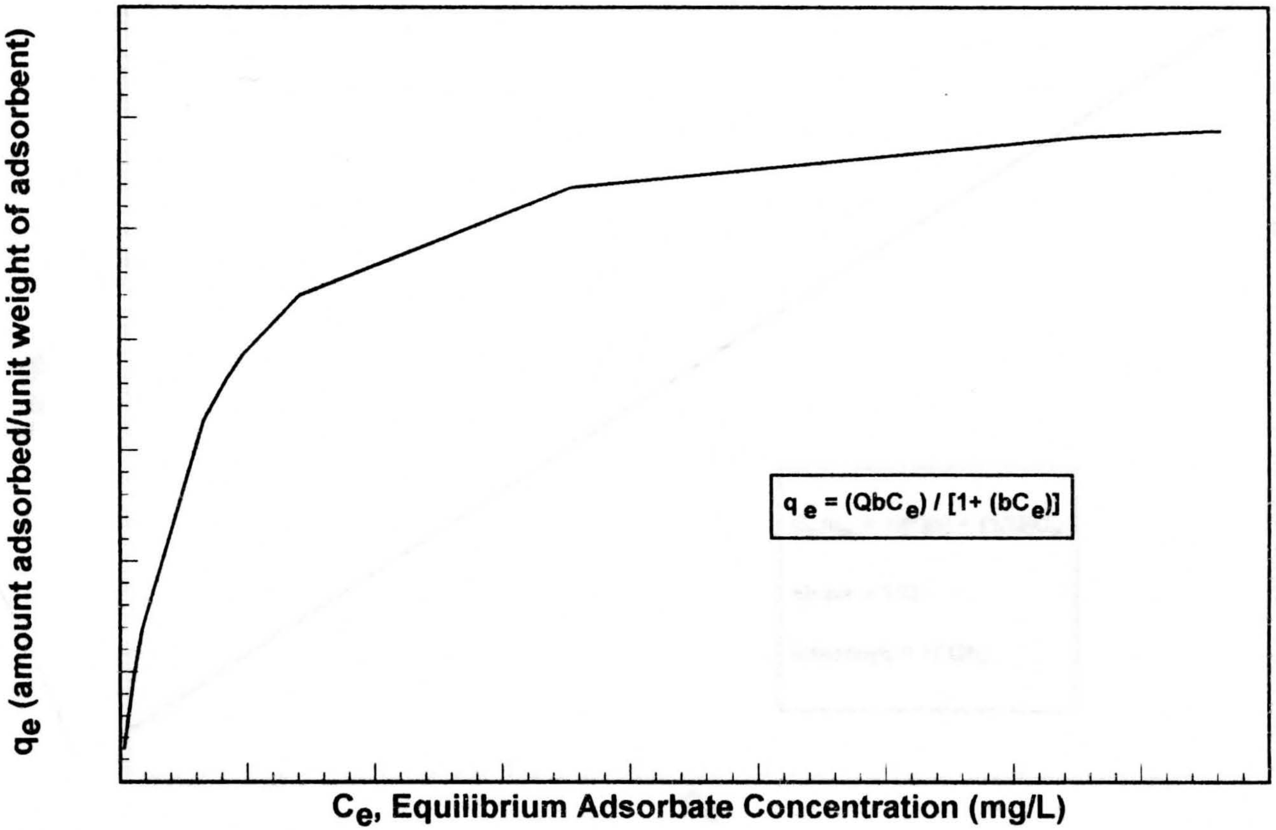


Figure 2-3. Typical Langmuir Isotherm (Source: James M. Montgomery, Inc., 1985)

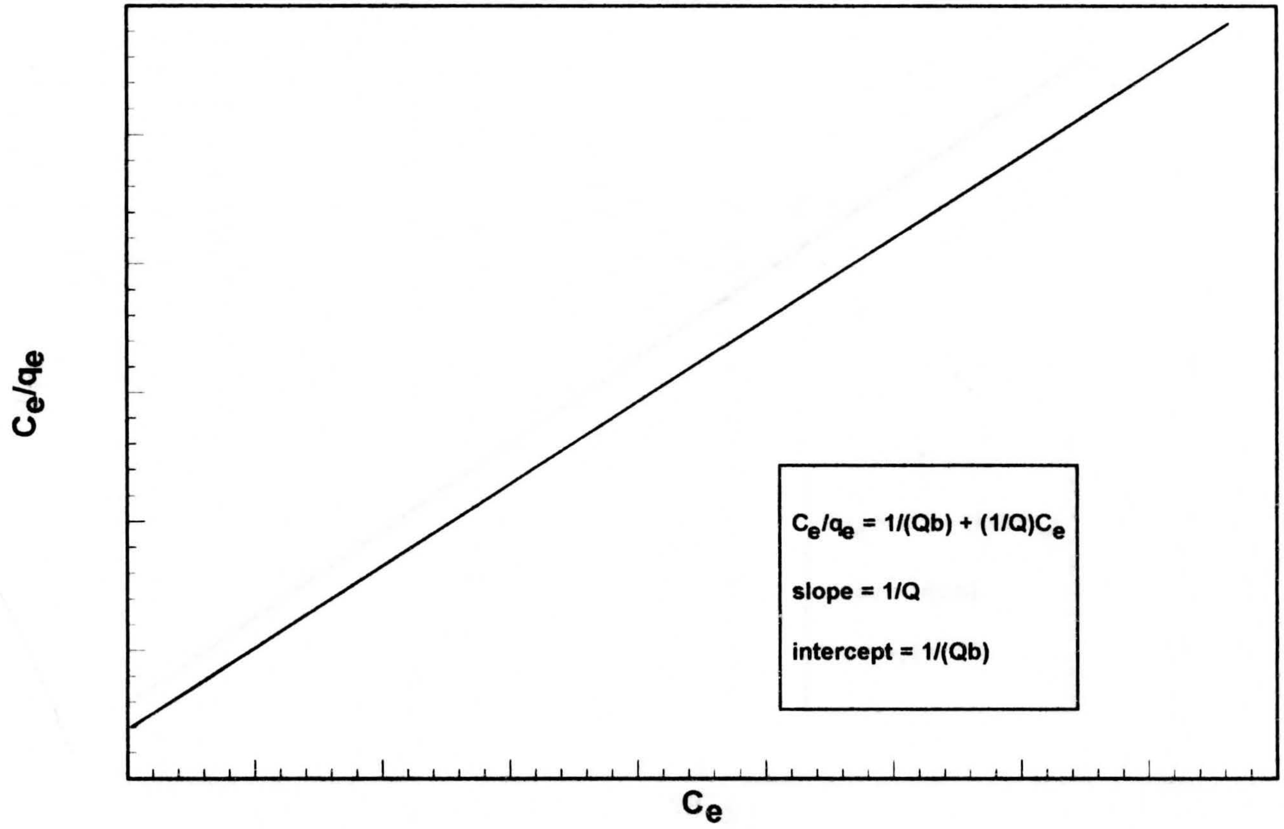


Figure 2-4. Typical Linearized Langmuir Isotherm (Source: James M. Montgomery, Inc., 1985)

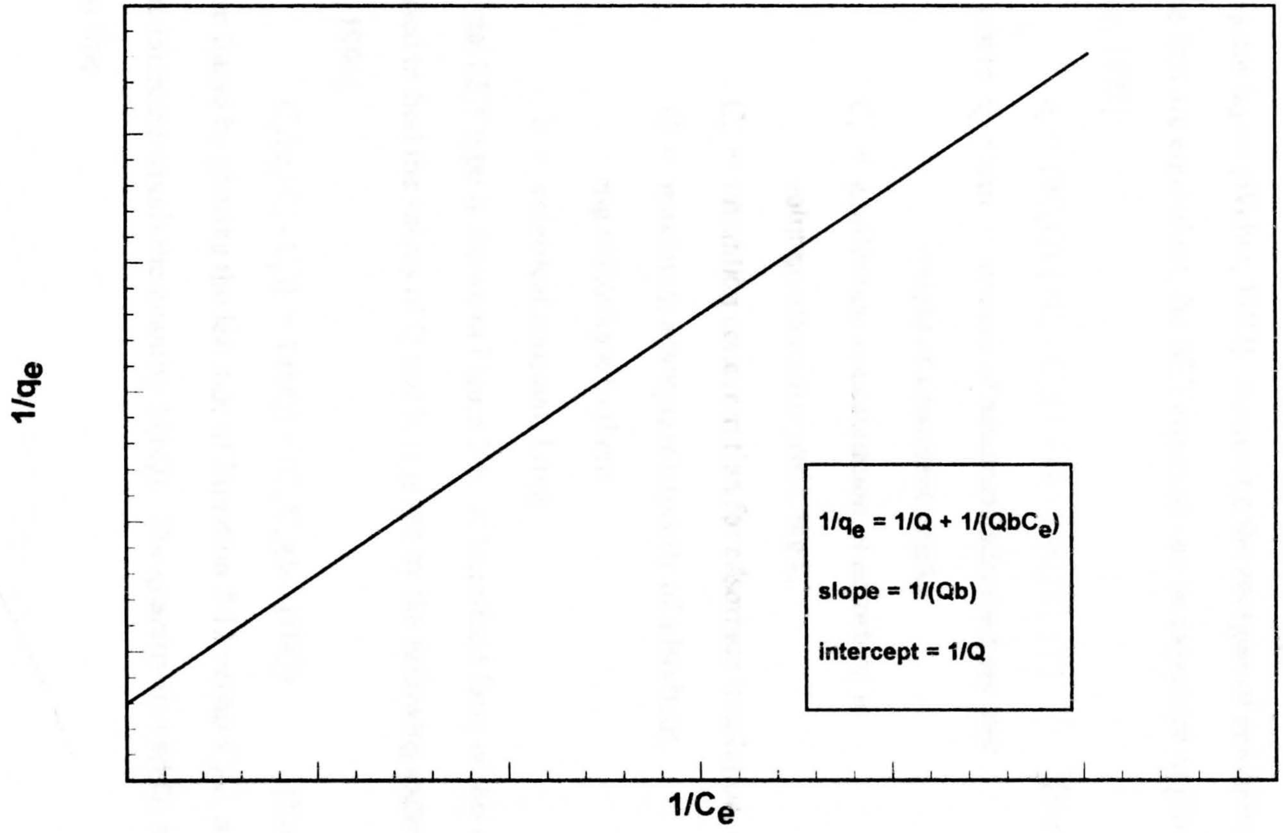


Figure 2-5. **Typical Linearized Double Reciprocal Langmuir Isotherm** (Source: US EPA, 1992; Weber, 1972)

2.3.4.3 The BET Isotherm

The BET equation was developed by Brunauer, Emmett, and Teller who assumed adsorption occurred in a multiple number of layers, with adsorption in each layer following the Langmuir equation. It was also assumed that adsorption on one layer need not be complete (i.e., all potential adsorption sites need not be filled) before adsorption occurs at subsequent layers [Weber, 1972]. Assuming the energies of adsorption for each layer beyond the first are equivalent, the BET equation can be expressed as [Sawyer, *et al.*, 1994, Weber, 1972]:

$$q_e = (bC_eQ)/\{ (C_s - C_e)[1 + (b - 1)(C_e/C_s)]\} \qquad \{\text{Eqn. 2-11}\}$$

where, $q_e = x/m$ = amount of adsorbate adsorbed per unit weight of adsorbent, mg/kg

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

C_s = saturation concentration for adsorbate in solution, mg/L

Q = maximum adsorption capacity of adsorbent, mg solute/kg adsorbent

b = empirical constant, L/mg

An isotherm of the BET type is shown in Figure 2-6. A linearized form of this equation, which can be used to find the values of Q and b, is given by the following expression [Sawyer, *et al.*, 1994]:

$$C_e/[q_e(C_s - C_e)] = 1/(bQ) + (C_e/C_s)(b-1)/(bQ) \qquad \{\text{Eqn. 2-12}\}$$

These values are found by plotting the left side of Equation 2-12 versus C_e/C_s as shown in Figure 2-7. The intercept equals the quantity 1/(bQ). The quantity (b-1)/(bQ) represents the slope of this line.

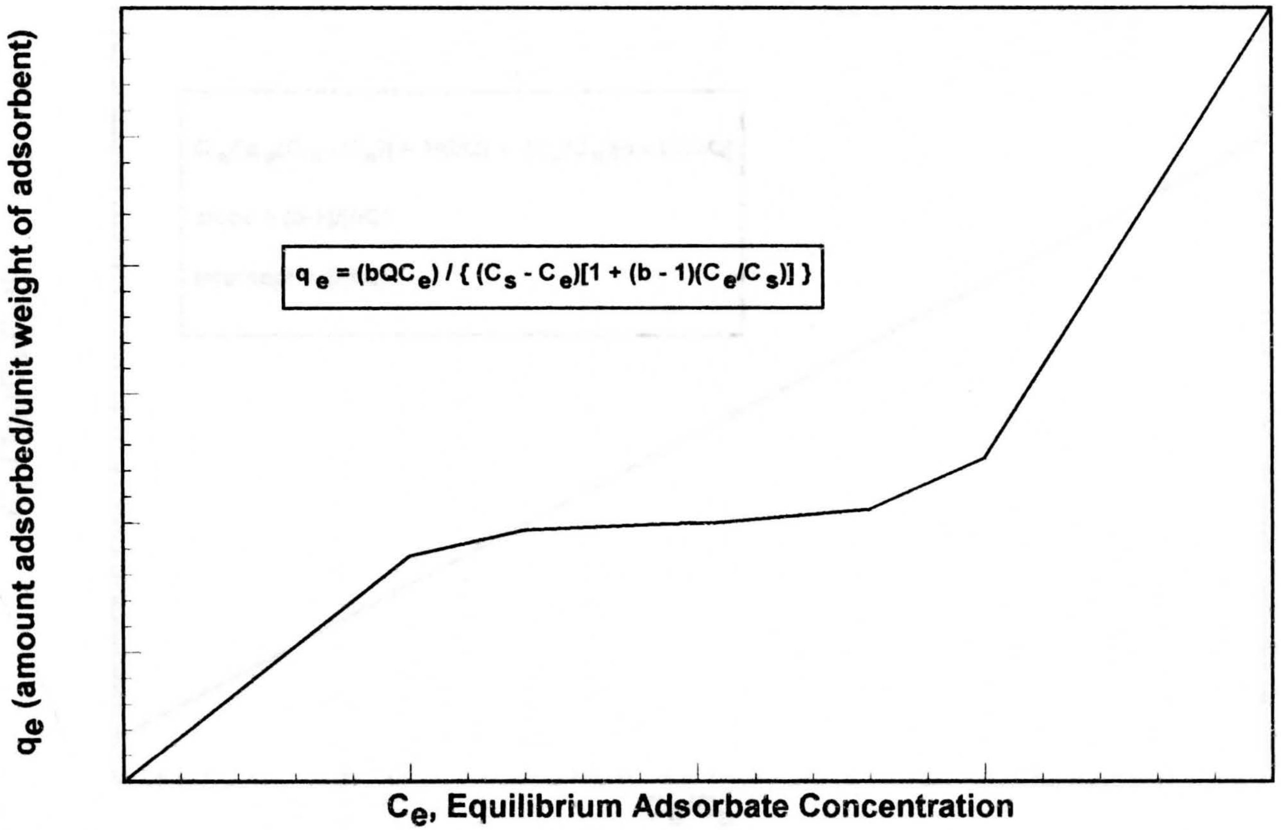


Figure 2-6. Typical BET Isotherm (Source: Weber, 1972)

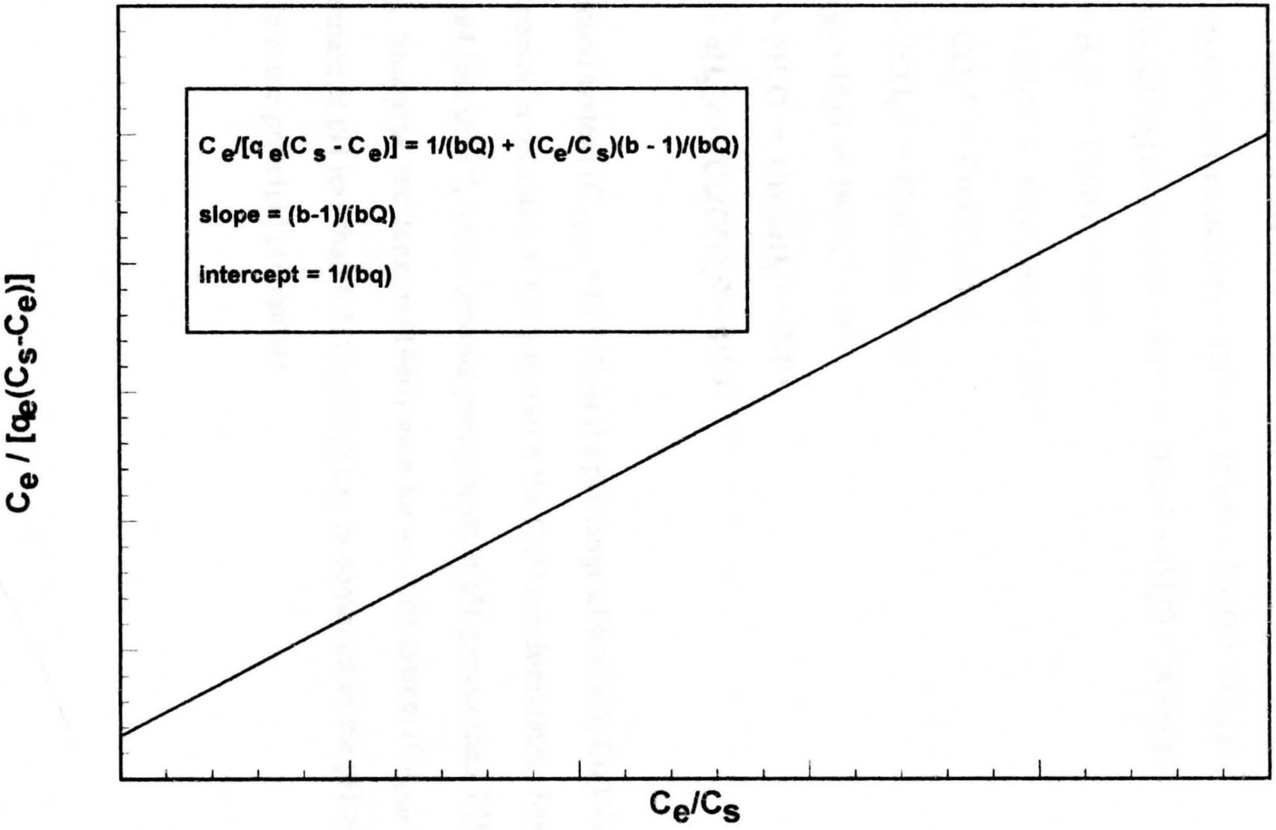


Figure 2-7. Typical Linearized BET Isotherm (Source: Weber, 1972)

2.3.5 Behavior of Copper in Solution

Stumm & Morgan (1981) listed the following series of equilibrium reactions for the behavior of Cu(II) in natural waters which shows the effect of complexing by carbonates:

	Reaction	$LogK_{SO,25C}$
a)	$CuO(s)$ (tenorite) + $2H^{+1} = Cu^{+2} + H_2O$	7.65
b)	$Cu_2(OH)_2CO_3(s)$ (malachite) + $4H^{+1} = 2Cu^{+2} + 3H_2O + CO_2(g)$	14.16
c)	$Cu_3(OH)_2(CO_3)_2(s)$ (azurite) + $6H^{+1} = 3Cu^{+2} + 4H_2O + 2CO_2(g)$	21.24
d)	$Cu^{+2} + H_2O = CuOH^{+1} + H^{+1}$	-8
e)	$2Cu^{+2} + 2H_2O = Cu_2(OH)_2^{+2} + 2H^{+1}$	-10.95
f)	$Cu^{+2} + CO_3^{-2} = Cu(CO_3)(aq)$	6.77
g)	$Cu^{+2} + 2CO_3^{-2} = Cu(CO_3)_2^{-2}(aq)$	10.01
h)	$CO_2(g) + H_2O = HCO_3^{-1} + H^{+1}$	-7.82
i)	$Cu^{+2} + 3H_2O = Cu(OH)_3^{-1} + 3H^{+1}$	-26.3
j)	$Cu^{+2} + 4H_2O = Cu(OH)_4^{-2} + 4H^{+1}$	-39.4

For a closed system ($C_{T,CO3} = 10^{-2}M$) in the pH range of 6 to 9.3, $Cu(CO_3)(aq)$ is the dominant species in solution; at pH less than 6 the Cu^{+2} ion dominates. Malachite precipitates at pH less than 7, while tenorite precipitates at pH greater than 7 [Stumm & Morgan, 1981]. Snoeyink and Jenkins (1980) state for an open system ($C_{T,CO3} = 10^{-3}M$) Cu^{+2} is predominant at pH less than 6.5, $Cu(CO_3)(aq)$ is dominant in the pH range 6.5 to 9.5, and tenorite is the principal precipitate.

PROCEDURES

3.1 Analytical Equipment and Procedures

3.1.1 General Analytical Procedures and Equipment

The procedures for the preparation and storage of all chemicals and chemical solutions used in this study and for the analysis of collected samples were based on Standard Methods for the Examination of Water and Wastewater, Vol. 16 (APHA, AWWA, & WPCF,1985). All glassware and Nalgene® containers used for the storage of standard solutions and samples, and as reaction vessels, were rinsed with deionized water, soaked in 30% (v/v) nitric acid for a minimum of 20 minutes, rinsed five times with deionized water, and air-dried in inverted position on clean laboratory towels.

All experiments were conducted in the Environmental Engineering Laboratory at Youngstown State University. Atomic absorption spectroscopy (AA) was performed on samples using a Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer in flame mode. Table 3-1 gives operating parameters used during AA analysis. The pH of samples was measured using a Fisher Scientific Accumet Model 810 pH Meter. Batch study samples were shaken using a Lab-Line Orbit Shaker set at 200 rpm.

Table 3-1 Atomic Absorption Operating Parameters

Metal Analyzed	Wavelength	Slit Width	Flame Type
Copper	324.8 nm	0.7 nm	air-acetylene
Iron	248.3 nm	0.2 nm	air-acetylene

3.1.2 Nitric Acid Digestion

Selected samples were digested for iron and copper analysis using a nitric acid digestion. A measured volume of the sample to be digested (typically 100 mL) was placed in a 250 mL beaker and 10 mL of redistilled grade nitric acid was added.

The sample was then placed under a ventilation hood on a hot plate, covered with a watch glass, and brought to a boil. Boiling was maintained for two to three hours. Periodically 2 mL of redistilled nitric acid was added to prevent the sample from drying out. This process was maintained until the sample reached a clear color. At this time it was removed from the heat and allowed to cool. After it reached room temperature, the digested sample was transferred to a volumetric flask having a volume equal to the original volume of sample digested. The watchglass and beaker were rinsed with deionized water, which was transferred to the volumetric flask. The solution in the flask was then brought to the correct level with deionized water. The sample was then analyzed using atomic absorption spectroscopy.

Nitric acid digestion was performed on peat ash and sand samples to determine the background concentrations of iron and copper. Samples from initial batch studies were not digested. However, AA analysis of samples which utilized peat as the adsorbent was difficult due to suspected colloidal interference, and later batch samples were digested. It was found that digested samples provided a much more stable reading during AA analysis. Generally, the copper concentrations of digested samples from Batch #4 (Cu/Peat) were significantly greater than that of the corresponding samples prior to digestion. This confirmed that colloidal material was interfering with the AA analysis. and perhaps indicated the copper was either being adsorbed by the colloidal material, or chelated by it. The iron concentration of digested samples from Batch #10 (Fe/Peat) generally were less than those measured prior to digestion, but the results were inconclusive since the experiment involving iron and peat was not repeated.

3.2 Substrate Characterization

3.2.1 Peat Characterization

A 4 cubic foot bale of Canadian *Sphagnum* peat moss was obtained at a local lawn and garden supply center. A visual inspection was performed to determine obvious characteristics, such as color, the extent of degradation, and texture. Several peat samples were analyzed for moisture content by oven-drying at 110 °C for two hours. Ash content was determined by oven-drying for two hours at 110 °C, and firing the dried peat in a muffle furnace for one hour at 550 °C. Two samples of air-dried peat were sieved to determine particle size distribution. The background concentrations of copper and iron in the peat were obtained by ashing several peat samples, performing nitric acid digestion on the ash, and analyzing through flame atomic absorption spectroscopy.

3.2.2 Sand Characterization

The sand used in batch studies was obtained from a quantity stored in the Environmental Laboratory at Youngstown State University, and had been used to conduct other unrelated experiments. It was visually inspected, and portions obviously contaminated (discolored and clumped) were discarded. Moisture content was determined by oven-drying at 110 °C for two hours. A determination of the background concentrations of copper and iron in the sand was attempted by performing nitric acid digestion on oven-dried sand samples, and analyzing through flame atomic absorption spectroscopy. However, the sand grains reacted violently to the heat of digestion, and the samples boiled only for 25 minutes. A sieve analysis was not conducted on the sand.

3.2.3 Yard Waste Compost Characterization

The yard waste compost used in batch experiments was obtained from Browning Ferris Industries, Inc. It was visually inspected, and analyzed for moisture content and ash content using the same procedures as the peat characterization. A background metals analysis was not conducted on the compost, nor was a sieve analysis performed.

3.3 Batch Adsorption Experiments

3.3.1 Batch Study Methods

Batch-type adsorption experiments are a method of determining the adsorptive capacity of a material, and predicting the adsorptive behavior of the material. In essence, batch adsorption studies involve placing a known mass of adsorbent into a reaction vessel containing a measured volume of solution in which the adsorbate is dissolved.

The initial concentration of the adsorbate is measured and recorded before the adsorbent is introduced to the system, or a sample is saved for later analysis by acidifying. After the adsorbent is weighed out and placed in the container of solution, the container is agitated (mixed) at constant temperature for a specified period of time which allows the system to reach equilibrium. After mixing, the solution is separated from the adsorbent, and the final concentration is measured and recorded.

The amount adsorbed is calculated by the equation [US EPA, 1992]:

$$q_e = x/m = V(C_o - C_e)/m \qquad \{\text{Eqn. 3-1}\}$$

where, q_e = x/m = amount of solute adsorbed per unit mass of adsorbent, mg/kg

x = mass of the adsorbent that is adsorbed, mg

m = oven-dried mass of adsorbent added to reaction container, kg

C_o = initial solute concentration before exposure to adsorbent, mg/L

C_e = solute concentration at equilibrium after exposure to adsorbent, mg/L

V = volume of solute solution added to reaction container, L

This procedure is repeated using several different initial concentrations of adsorbate with a constant soil:solution ratio, or by varying the soil:solution ratio with a constant initial adsorbate concentration. The data collected is then examined to determine if it follows one of the adsorption isotherms given in Section 2-3.

Several variables were involved in the batch tests conducted during this study. Various tests were conducted using copper and iron as adsorbates, and peat, sand, and yard waste compost as adsorbents. In order to determine the adsorptive capacity of these typical constructed wetland substrates, three types of batch adsorption experiments were performed.

The first type utilized a constant initial concentration of metallic solution (adsorbate), and the amount of substrate (adsorbent) mixed with a constant volume of solution was varied (i.e., variable soil:solution ratio). The second type of batch study performed utilized a constant soil:solution ratio, and a constant initial concentration of metallic solution, while the time the sample was shaken was varied (i.e., time-variable). The purpose of this test was to determine if a mixing time of 24 hours was sufficient for the samples to reach equilibrium. The third type of batch experiment involved varying the initial solute concentration while keeping the soil:solution ratio constant. The soil:solution ratios used during the time-variable test and the constant ratio test were both selected based on the results generated by the variable ratio tests.

Preliminary studies conducted by introducing varying quantities of peat to equal volumes of tap water resulted in a wide range of solution pH. The pH value tended to decrease as the amount of peat added to solution increased. Since tap water should contain a much greater amount of alkalinity than deionized water, it was expected that the pH of samples prepared with deionized water would be drastically altered. Thus, a buffer was introduced to stock solutions of adsorbate to provide a more stable pH.

Initial tests were buffered with 0.02N K_2HPO_4, but later tests utilized a 0.1N K_2HPO_4 buffer. The phosphate buffer was selected over a carbonate buffer since it may provide a slightly higher partition coefficient, or degree of partitioning between dissolved and adsorbed phases [McIlroy, *et al.*, 1986]. Batches utilizing sand were buffered with 0.02N K_2HPO_4. The batch using yard waste compost was not buffered since preliminary tests showed the addition of varying amounts of compost to solution had a tendency to increase the pH of the solution. Some later batch studies also involved adjusting the pH of solution with the addition of sodium hydroxide after 4 hours of mixing. Even with the initial buffer, the addition of high concentrations of peat reduced the pH considerably. NaOH was added so results would be obtained over a narrower pH range. Table 3-2 gives a general overview of the batch studies performed during this study.

Table 3-2 General Overview of Batch Experiments

BATCH #	ADSORBATE/ ADSORBENT	K2HPO4 BUFFER	NaOH pH ADJUSTMENT	SHAKE TIME	SOIL:SOLUTION RATIO	INITIAL ADSORBATE CONC.	REACTION CONTAINER VOLUME
1	Cu/Peat	0.02N	none	40.5 hr	VARIABLE 1:10, 1:20, 1:25, 1:40, 1:50, 1:60	10 mg/L	50 ml
2	Cu/Peat	0.02N	none	24 hr	VARIABLE 1:100, 1:200, 1:400, 1:500, 1:600, 1:1000	10 mg/L	50 ml
3	Cu/Peat	0.10N	none	24 hr	VARIABLE 1:10, 1:20, 1:40, 1:60, 1:100, 1:200, 1:500, 1:1000, 1:2000, 1:5000, 1:10,000	10 mg/L	125 ml
4	Cu/Peat	0.10N	0.10N	24 hr	VARIABLE 1:10, 1:20, 1:40, 1:60, 1:100, 1:200, 1:500, 1:1000, 1:2000, 1:5000, 1:10,000	10 mg/L	125 ml
5	Cu/Peat	0.10N	1.0N	VARIABLE 24hr 48 hr 72 hr 96 hr 168 hr	CONSTANT 1:40	10 mg/L	125 ml
6	Cu/Peat	0.10N	1.0N	24 hr	CONSTANT 1:1000	VARIABLE 2 mg/L 5 mg/L 10 mg/L 20 mg/L 30 mg/L 40 mg/L	125 ml
7	Cu/Compost	none	1.0N	24 hr	CONSTANT 1:1000	VARIABLE 2 mg/L 5 mg/L 10 mg/L 20 mg/L 30 mg/L 40 mg/L	125 ml
8	Cu/Sand	0.02N	none	18.5 hr	VARIABLE 1:2, 1:3, 1:5, 1:10, 1:25, 1:50	10 mg/L	50 ml
9	Fe/Sand	0.02N	none	24 hr	VARIABLE 1:2, 1:3, 1:5, 1:10, 1:25, 1:50, 1:100, 1:200	10 mg/L	50 ml
10	Fe/Peat	0.10N	1.0N	24 hr	VARIABLE 1:10, 1:20, 1:40, 1:60, 1:100, 1:200, 1:500, 1:1000, 1:2000, 1:5000, 1:10,000	10 mg/L	125 ml

3.4 Column Experiments

3.4.1 Apparatus

In order to test a dynamic system simulating the subsurface conditions in a constructed wetland, a column adsorption test was conducted. The column (shown in Figure 3-1) consisted of two opaque sections of 6-inch (15.2 cm) diameter Schedule 40 PVC pipe. The top was 6 inches (15.2 cm) in length, while the bottom was 24-¼ inches (61.6 cm). The sections were banded together with a rubber sleeve (Fernco type) held in place by two worm-drive clamps. The sleeve allowed easy access to the interior of the column for filling and removal of the substrate, and also provided a water-tight seal between the two sections. A circular screen made of ¼" (6.35 mm) thick Plexiglas (with ¼" (6.35 mm) holes drilled on ½" (12.7 mm) centers and a diameter slightly less than the inside pipe diameter) was inserted in the column on top of the peat layer. Its purpose was to keep the peat from floating within the column.

Overall column height was 30-¼" (76.8 mm). The empty capacity of the entire column was 0.5 ft^3 (13.9 L), while the lower portion of the column had an empty capacity of 0.4 ft^3 (11.1 L). Flat pieces of Plexiglas [(8" x 8" x ¼") or (20.3 cm x 20.3 cm x 6.35 mm)] were attached to each end of the column, providing an effective closure as well as a stable platform. The center of each piece of Plexiglas was tapped to allow connection of influent and effluent hoses to the column via a ½-inch NPT by ½-inch hose barb fitting (12.7 mm x 12.7 mm).

A 5.3 gallon (20 L) Nalgene® carboy was utilized as a reservoir for the copper solution. The carboy was elevated above the top of the column to enable gravity feed of the solution to the column. Norprene™ tubing connected the reservoir to the column. The column effluent hose was connected to a Masterflex L/S™ Variable Flow Console Drive (Model H-07553-60) peristaltic pump with a standard pump head. This pump controlled the discharge rate from the column, and therefore the hydraulic residence time could be controlled.

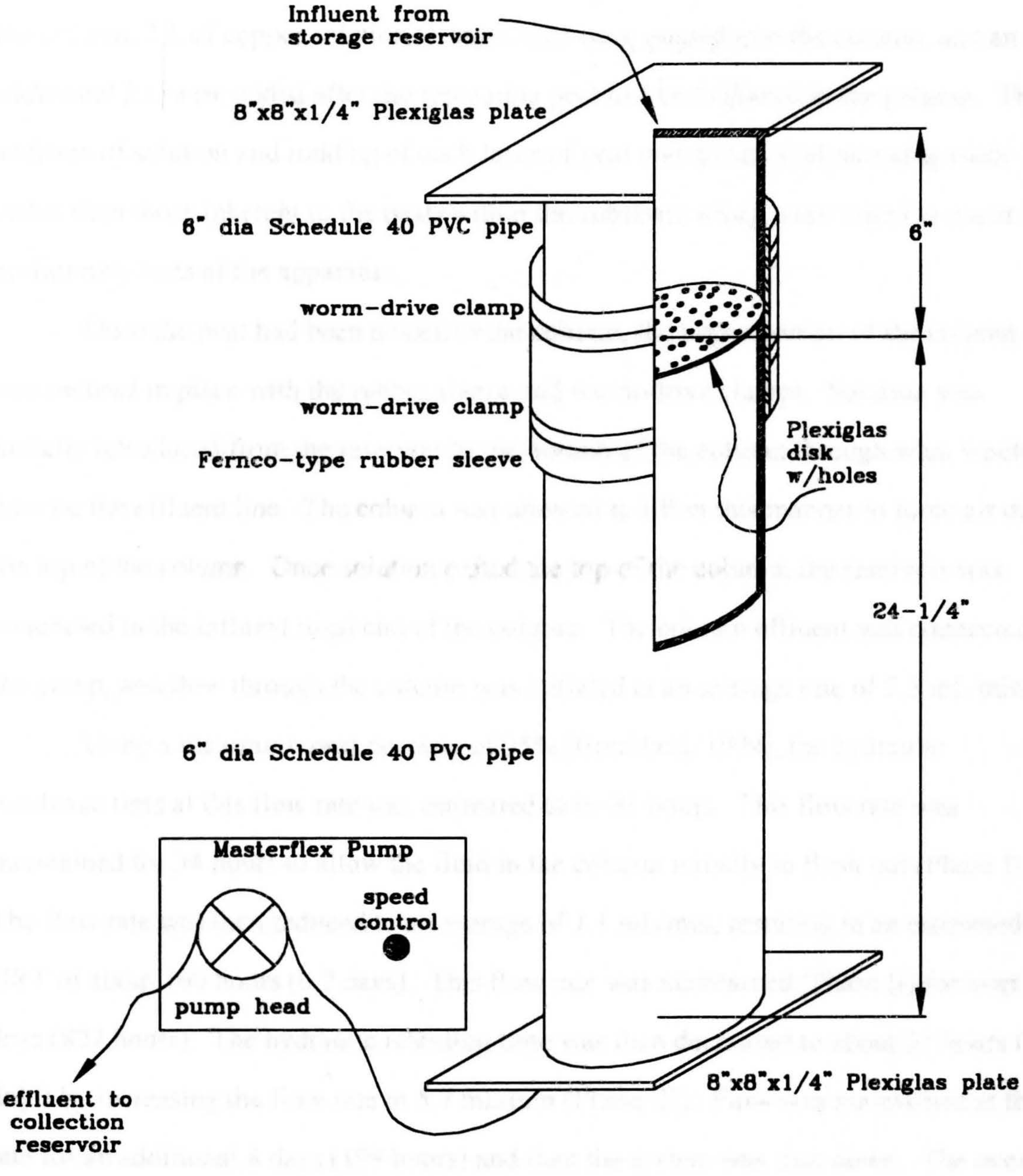


Figure 3-1 Diagram of Column Apparatus

3.4.2 Column Experiment

The lower section of the column was filled to a depth of 24 inches (61 cm) with 1500 grams of air-dried peat by successively adding 6-inch (15.2 cm) layers of peat, and rodding after each addition. When approximately one-half of the peat had been placed in the column, 2 L of copper solution (10mg Cu/L) were poured into the column, and an additional 2 L were added after the remaining peat had been placed in the column. The addition of solution and rodding of each layer of peat was aimed at eliminating voids (other than those inherent to the peat) within the substrate which were found to occur in preliminary tests of the apparatus.

Once the peat had been placed in the column, the upper portion of the column was secured in place with the rubber sleeve and worm-drive clamps. Solution was initially introduced from the reservoir to the bottom of the column through what would later be the effluent line. The column was allowed to fill in this manner to force air out the top of the column. Once solution exited the top of the column, the reservoir was connected to the influent (top) end of the column. The column effluent was connected to the pump, and flow through the column was initiated at an average rate of 5.3 mL/min.

Using a maximum peat porosity of 95% [Couillard, 1994], the hydraulic residence time at this flow rate was estimated to be 33 hours. This flow rate was maintained for 34 hours to allow the fluid in the column initially to flush out (Phase I). The flow rate was then reduced to an average of 1.1 mL/min, resulting in an estimated HRT of about 160 hours (6.7 days). This flow rate was maintained (Phase II) for over 34 days (827 hours). The hydraulic retention time was then decreased to about 31 hours (1.3 days) by increasing the flow rate to 5.7 mL/min (Phase III). Flow was maintained at this rate for an additional 8 days (199 hours) and then the system was shut down. The overall length of time the column was run was slightly more than 44 days (1060 hours).

The copper solution used to fill the column and for the first 78 hours of operation (Phase A) was prepared by diluting a measured volume of 1000 mg/L copper standard solution with deionized water to a concentration of approximately 10 mg/L. No buffer was used. The pH of this solution averaged 4.18. For the next 170 hours (Phase B) the 10 mg/L stock solution was prepared by mixing $CuSO_4 \cdot 5H_2O$ (0.040 g/L) with deionized water with no buffer. The pH of this solution averaged 4.66.

For the next 756 hours (Phase C), the stock solution was prepared by mixing $CuSO_4 \cdot 5H_2O$ (0.040 g/L) with deionized water buffered with 0.0008N K_2HPO_4 (0.0697 g/L). The pH of this solution averaged 6.67. For the remainder of the experiment (Phase D), the stock solution was again prepared by mixing $CuSO_4 \cdot 5H_2O$ (0.040 g/L) with deionized water, but the buffer was increased to 0.001N K_2HPO_4 (0.0871 g/L). The average pH of this mixture was 6.95. These various mixtures were used to examine the effect of the influent pH on the system.

It should be noted that the target value for the influent copper concentration was 10 mg/L, which was reasonably maintained during Phases A and B. However, the higher solution pH values resulting from the addition of the buffer in Phases C and D caused copper to precipitate in the reservoir. In an attempt to keep the precipitate mixed in solution, a magnetic stirrer was added to the apparatus early in Phase C, and the reservoir was periodically shaken manually. Although these measures showed some benefit, the measured values for influent copper varied considerably, and often strayed significantly from the 10 mg/L goal.

The magnetic stirrer was undersized for this application, and did not perform as desired. The general trend in the measured values of the influent copper concentration (see Figure 4-34) showed periods of declining copper concentration as the precipitate formed and settled in the container, followed by abrupt peaks of high concentration occurring when freshly prepared solution was added to the reservoir, or when the reservoir was manually shaken. These higher values were not caused by changing the mass of copper sulfate used to prepare the solution, but by the precipitate becoming more concentrated in the reservoir. Throughout the entire experiment, the copper solution was prepared using the appropriate volume of Copper Reference Standard or mass of copper sulfate to achieve a copper concentration of 10 mg/L based on theoretical calculations.

The system was allowed to operate continuously for a 44 day period beginning on Monday, October 24, 1994 and ending on Wednesday, December 7, 1994. The system was monitored periodically throughout the day on Mondays through Thursdays. Influent samples (100 mL) were collected an average of twice per day, and sampling of effluent (100 mL) averaged three times per day. Typically, the system was allowed to operate unattended from Friday through Sunday, with no sampling during this time. An exception to this was the last weekend of operation in Phase III when the reservoir required refilling prior to Monday due to the higher flow rate. Immediately after collection, the pH of each sample was measured, and then the sample was preserved by acidifying with 0.2 mL of redistilled nitric acid. Periodically during the week, the copper concentration of the preserved samples (not digested) was measured using flame atomic absorption.

A number of samples were randomly chosen for nitric acid digestion. The column effluent did not contain nearly as much suspended colloidal material as the batch study samples, and little difference was noted between samples that were digested and those that were not.

A total of 143.5 L of copper solution was processed by the peat column during the entire Column Experiment (1060 hours). Assuming the average copper concentration of the applied solution was 10 mg/L, the copper loading rate was approximately 22 mg of copper per kg of peat per day.

RESULTS AND DISCUSSION

4.1 Substrate Characterization

4.1.1 Peat

The peat was visually examined and found to be a brown-colored, mixture of finely decomposed powder and fibrous material, slightly moist to the touch. The fibers ranged from very thin (similar in thickness to human hair) to very thick (roots and stalks up to 2 cm wide), and from very short (<5 mm) to relatively long (4-5 cm). Portions of the fibrous material were loosely clumped together, and the powdery, dust-like material was loose, as well as clinging to the fibrous clumps, and thinly coating the roots and stalks.

A sieve analysis was performed on two samples of the peat. The first sample (500g) was sieved through the following screens: 3/4", 1/2", #4 (0.187"), #8 (0.0937"), #20 (0.0331"), #50 (0.0117"), and #100 (0.0059"). A lid was placed on top of the stack of sieves, and a pan on the bottom. All sieves, the lid and the pan were weighed prior to the test, and then stacked according to descending screen size (as listed above).

The 500g of peat placed on the 3/4" sieve, and the stack was placed on a mechanical shaker for 20 minutes. The results of the sieve analysis are given in Table 4-1, and the percent of material passing each sieve is presented on Figure 4-1. A large amount of peat was retained on the #4 sieve. However, a visual inspection showed much of this material appeared to be smaller than the screen openings. This material should have passed the #4 sieve, but did not. Apparently this was because the test utilized too much material to allow adequate shaking, and peat clogged the screen.

A second test was performed using 300g of peat, and utilizing a 1/4" sieve in addition to those previously used. The results of this test are presented in Table 4-2, and the percentage of material passing each sieve is shown on Figure 4-2. This test showed a better distribution, but it was noted that a large amount of material was retained on the 1/4" sieve. Some of this material should have passed through this size screen, but was again "filtered" by the amount of peat retained on the screen itself. These results indicate that due to its extremely non-spherical (i.e., fibrous) shape, peat is difficult to characterize by sieve analysis.

Table 4-1. Sieve Analysis of 500 gram Peat Sample

Sieve	Opening (in.)	Opening (mm)	mass retained (g)	% retained on sieve	% passing sieve
Pan	0.0000	0.0000	31	6.20%	0.0%
#100	0.0059	0.1499	25	5.00%	6.2%
#50	0.0117	0.2972	45	9.00%	11.2%
#20	0.0331	0.8407	25	5.00%	20.2%
#8	0.0937	2.3800	6	1.20%	25.2%
#4	0.1870	4.7498	310	62.00%	26.4%
1/2 in	0.5000	12.7000	58	11.60%	88.4%
3/4 in	0.7500	19.0500	0	0.00%	100.0%
		Totals	500	100%	
Analysis of Data					
			symbol	in.	mm
Diameter Corresponding to 10% Passing			D(10)	0.0104	0.2642
Diameter Corresponding to 30% Passing			D(30)	0.2052	5.2121
Diameter Corresponding to 60% Passing			D(60)	0.3566	9.0576
C(u) = Uniformity Coefficient = D(60) / D(10)					34.29
C(c) = Coefficient of Curvature = [D(30) * D(30)] / [D(10) * D(60)]					11.35
Finess Modulus = Sum of Cumulative Percentages Retained / 100					2.78

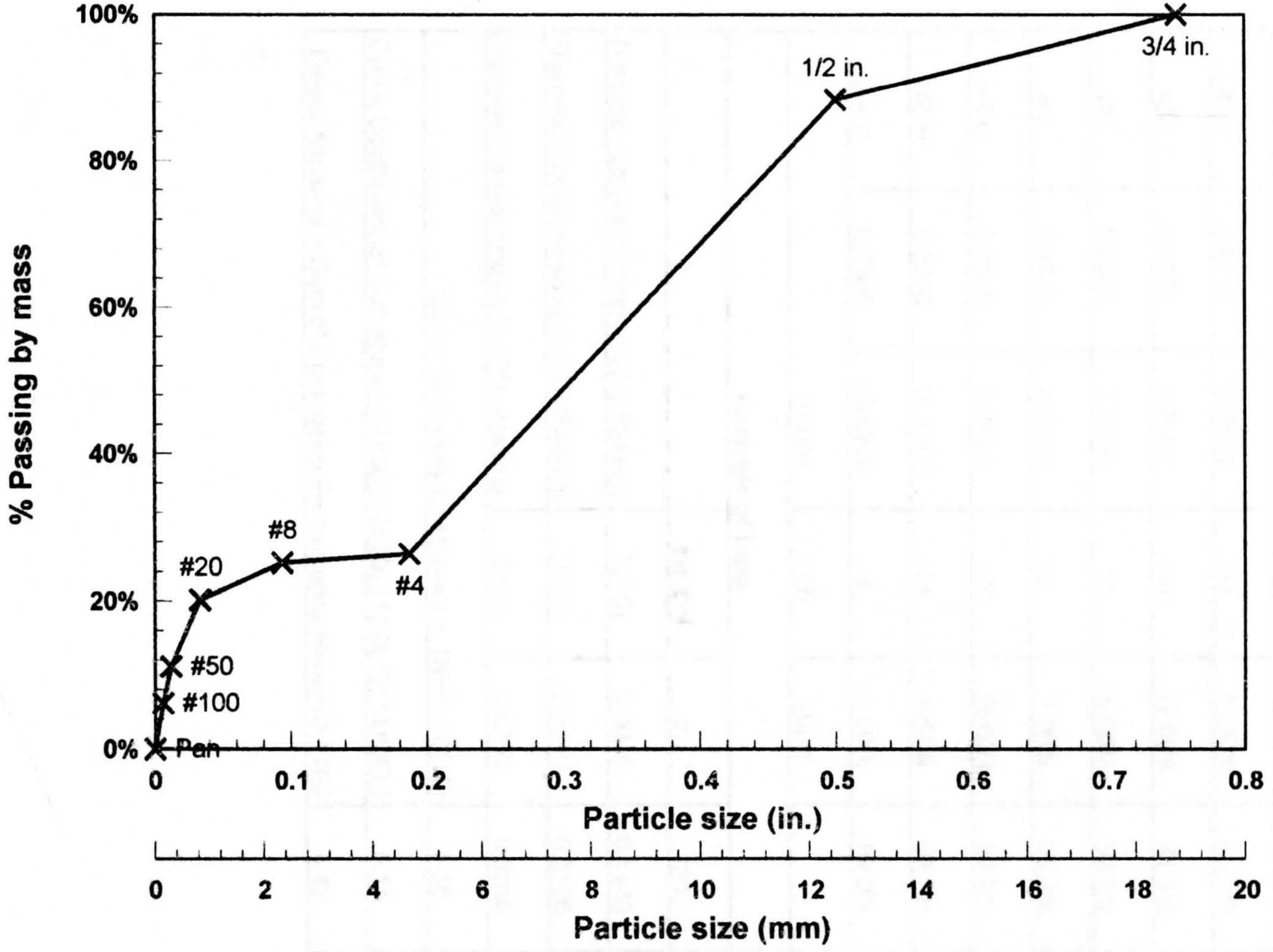


Figure 4-1. Sieve Analysis of 500 gram Peat Sample

Table 4-2. Sieve Analysis of 300 gram Peat Sample

Sieve	Opening (in.)	Opening (mm)	mass retained (g)	% retained on sieve	% passing sieve
Pan	0.0000	0.0000	39	13.00%	0.0%
#100	0.0059	0.1499	30	10.00%	13.0%
#50	0.0117	0.2972	55	18.33%	23.0%
#20	0.0331	0.8407	36	12.00%	41.3%
#8	0.0937	2.3800	15	5.00%	53.3%
#4	0.1870	4.7498	3	1.00%	58.3%
1/4 in	0.2500	6.3500	105	35.00%	59.3%
1/2 in	0.5000	12.7000	14	4.67%	94.3%
3/4 in	0.7500	19.0500	3	1.00%	99.0%
		Totals	300	100%	
		Analysis of Data			
			symbol	in.	mm
Diameter Corresponding to 10% Passing			D(10)	0.0045	0.1143
Diameter Corresponding to 30% Passing			D(30)	0.0240	0.6106
Diameter Corresponding to 60% Passing			D(60)	0.0250	0.6350
C(u) = Uniformity Coefficient = D(60) / D(10)					5.56
C(c) = Coefficient of Curvature = [D(30) * D(30)] / [D(10) * D(60)]					5.14
Finess Modulus = Sum of Cumulative Percentages Retained / 100					4.42

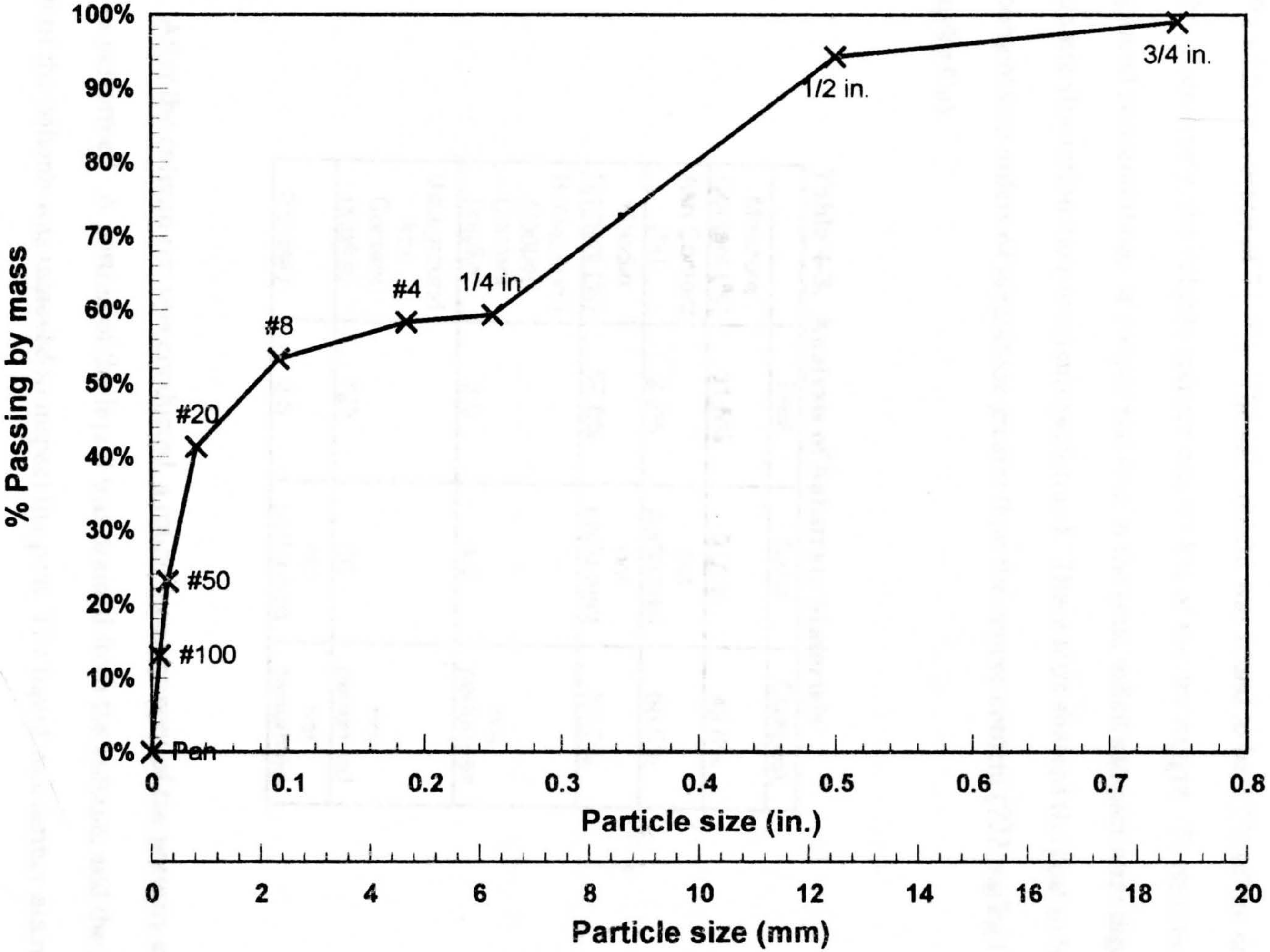


Figure 4-2. Sieve Analysis of 300 gram Peat Sample

Peat samples were also analyzed for moisture content, ash content, and background metals concentrations. The results of these analyses are presented in Table 4-3 along with those for sand and yard waste compost samples. The moisture content of the peat, measured periodically during the entire phase of batch testing, ranged from 20% to 37% with an average of 31.5%. The ash content was found to be 2.2% of the dry weight. Conversely, the volatile content was 97.8% of the dry weight. To determine the background concentrations of copper and iron in the peat, ashed samples were digested, and atomic absorption measurements performed. These tests showed the peat to have an iron content two orders of magnitude greater than the copper content (722 mg/kg Fe vs. 2.9 mg/kg Cu).

Table 4-3. Analysis of Substrate Materials

	Peat	Sand	Compost
Moisture Content (%)	31.5%	0.02%	43.6%
Ash Content (%)	2.2%	not performed	66.5%
Volatile Content (%)	97.8%	not performed	33.5%
Background Copper Content (mg/kg)	2.9	4.0	not performed
Background Iron Content (mg/kg)	722	88	not performed
Porosity	0.5	not performed	not performed

After the column run was conducted, a rough measurement of the porosity of the peat was performed. A portion of the liquid was drained from the column, and the upper section of the column was removed to inspect the peat. The liquid was further drained until the water level was at the surface of the peat in the column. This level was marked, the column was allowed to completely drain, and the effluent was collected. The porosity was found by dividing the volume of voids (assumed to be the volume of water drained) by the total volume of the saturated peat prior to draining the column. This gave a porosity of 0.5 - a value that is probably lower than the actual value since the peat was saturated at the start of this test, and some of the water remained trapped in the voids.

4.1.2 Sand

The sand used in batch experiments was visually inspected, and portions obviously contaminated from previously experiments were discarded. The sand was rinsed with deionized water, and allowed to sit for several days to allow the rinse water to evaporate, and the sand to reach equilibrium with the lab atmosphere. The moisture content was determined to be 0.02%. Samples were dried and baked at 550°C, and 1g of sand was digested. It is not certain if digestion reached completion because when the sand/nitric acid solution was heated, the sand grains reacted violently to the heat by rapidly bouncing around in the boiling solution. Since this caused a hazardous situation (droplets of the solution become airborne within the hood), the samples were removed after only 25 minutes of heating. Background metals analysis of the solution revealed the iron content to be one order of magnitude greater than the copper content (88 mg/kg Fe vs. 4 mg/kg Cu). These results are shown in Table 4-3. Ash content, volatile content, and porosity of the sand were not determined. A grain size distribution was not performed on the sand.

4.1.3 Yard Waste Compost

Samples of yard waste compost were analyzed for moisture content. The moisture content ranged from 40% to 44%, with an average value of 43.6%. The ash content was found to be 66.5%, which is considerably greater than the peat. Conversely, the volatile content was only 33.5%. These values are shown in Table 4-3. No analysis of the background metal concentrations was performed on the yard waste compost, nor was the porosity determined. A sieve analysis of the compost was not conducted.

4.2 Batch Experiments

Ten separate batch studies were conducted. Batch Experiments numbered 1 through 8 utilized copper as the adsorbate, while Batch Experiments 9 and 10 were conducted using iron as the adsorbate. Peat was utilized as the adsorbent in Batches 1 through 6, and 10; yard-waste compost in Batch 7; and sand in Batches 8 and 9. Each set of data was analyzed using standard linear regression to determine whether it followed the Freundlich, Langmuir, or Double Reciprocal Langmuir isotherms. Detailed results of the linear regression analysis for the batch experiments are given in Appendix A.

In general, the adsorption of copper by peat observed in the variable soil:solution Batch Experiments #1 through #4 could be described by the Freundlich isotherm, but not by the Langmuir and Double Reciprocal Langmuir isotherms. However, all three isotherms could be used to describe copper adsorption by peat in Batch Experiment #6. This experiment utilized a constant soil:solution ratio of low concentration (1:1000) and the initial copper in solution was varied from 2 mg/L to 40 mg/L, while the first four experiments used a range of soil:solution ratios and a constant initial concentration of 10 mg/L of copper in solution.

The adsorption of copper by yard waste compost followed the Freundlich isotherm, also. The adsorption of copper by sand could be described by either the Freundlich or Langmuir isotherms, but neither equation fit the data very well. No conclusive determination on the adsorption of iron by either peat or sand could be made based on the limited number of experiments conducted using these constituents.

4.2.1 Batch Experiment #1 - Copper/Peat Variable Soil:Solution Ratio

4.2.1.1 Results of Batch Experiment #1

A 10 mg/L Cu stock solution was prepared by diluting Copper Reference Solution (1000 mg/L ± 1%) with deionized water and buffered with 0.02N K_2HPO_4. Next, 30 mL of this solution was placed into each of 10 plastic, 50 mL centrifuge tubes. The pH of this solution was measured as 8.37, and the initial Cu concentration was found subsequently by atomic absorption to be 9.79 mg/L. Peat was added to six of the tubes in sufficient quantity to achieve the desired soil:solution ratios of 1:10 (3.00 g peat), 1:20 (1.50 g), 1:25 (1.20 g), 1:40 (0.75 g), 1:50 (0.60 g), and 1:60 (0.50 g). No peat was added to the other four tubes in order to quantify the adsorption of copper to the container.

The centrifuge tubes were placed on the shaker at 200 rpm for 40.5 hours. They were removed and each mixture was filtered through a Whatman GF/C glass fiber filter. The filter and the filtered material were discarded, and the pH of the filtrate of each sample was measured. As expected, the addition of peat caused the pH of the solution to decrease considerably, and as the amount of peat added to the solution increased, the equilibrium pH decreased. The equilibrium pH of the 1:10 sample was 3.31, while the pH was 5.37 for the 1:60 sample.

The equilibrium copper concentrations were determined by AA analysis, and ranged from 0.05 mg/L for the 1:10 sample to 0.11 mg/L for the 1:60 sample. Adsorption to the container was obtained from analyzing the blank samples, and averaged 0.13 mg/L. Equation 3-1 was modified to account for container adsorption (C_c), assuming that containers with peat added would adsorb the same amount of copper as those with no peat, resulting in the following equation:

$$q_e = x/m = V(C_o - C_e - C_c)\,/m \qquad \{\text{Eqn. 4-1}\}$$

The amount of copper adsorbed by the peat for each sample was calculated using Equation 4-1. A summary of the results obtained during Batch Experiment #1 is presented in Table 4-4. A plot of the amount of copper adsorbed versus the equilibrium copper concentration is presented in Figure 4-3.

Table 4-4 Summary of Results from Batch Experiment #1

Soil:Solution Ratio	1:10	1:20	1:25	1:40	1:50	1:60
Initial Cu Concentration (mg/L)	9.79	9.79	9.79	9.79	9.79	9.79
Adsorbate Volume (ml)	30	30	30	30	30	30
Initial pH	8.37	8.37	8.37	8.37	8.37	8.37
Adsorbent added (g)	3.00	1.50	1.20	0.75	0.60	0.50
Equilibrium pH	3.31	3.84	4.36	4.89	5.14	5.37
Equilibrium Cu Concentration (mg/L)	0.05	0.08	0.09	0.09	0.10	0.11
Container Adsorption (mg/L)	0.13	0.13	0.13	0.13	0.13	0.13
Amount Adsorbed (mg/L)	9.61	9.58	9.57	9.57	9.56	9.55
Percent Adsorbed by Adsorbent	98.16%	97.85%	97.75%	97.75%	97.65%	97.55%
Amount Adsorbed (mg/kg)	96	192	239	383	478	573

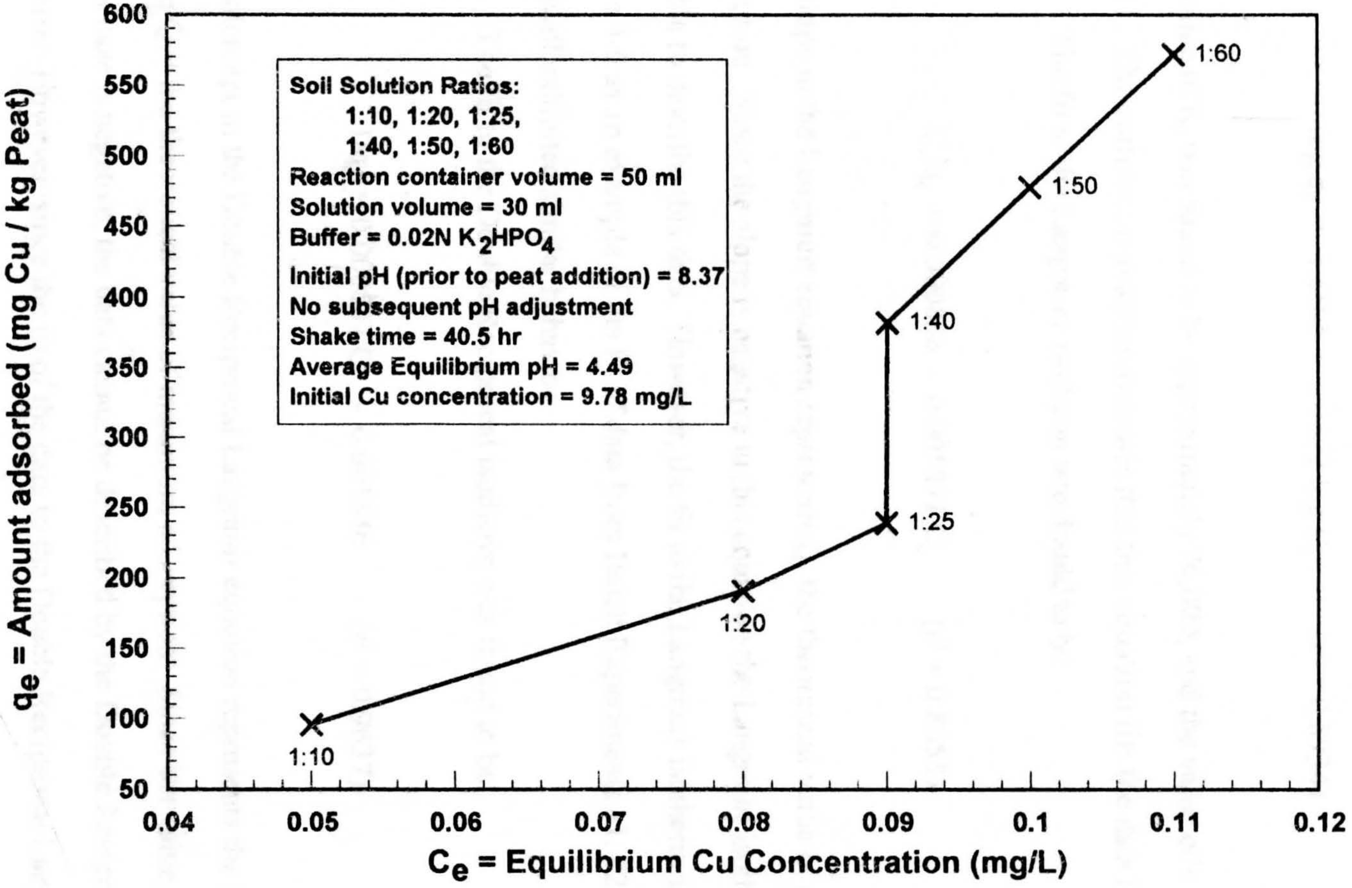


Figure 4-3. Batch Experiment #1 - Cu/Peat with Variable Soil:Solution Ratio

4.2.1.2 Analysis of Batch Experiment #1

The fit to the Freundlich isotherm equation is plotted in Figure 4-4. The equation was found to be:

$$\log q_e = 4.8806 + 2.2672 \log C_e \qquad (r^2 = 0.8934) \qquad \{\text{Eqn. 4-2}\}$$

The value of K_f was found to be approximately 76,000, and the value of n equal to 0.4411. The correlation analysis indicates that this equation fits the data fairly well.

The fit to the Langmuir isotherm was found to be:

$$C_e/q_e = 0.000836 - 0.005891\, C_e \qquad (r^2 = 0.8355) \qquad \{\text{Eqn. 4-3}\}$$

The slope in the Langmuir equation represents Q, the theoretical value of maximum adsorption. Since the slope is negative in this equation the Langmuir isotherm is not suitable to describe this data. However, the fit to the Langmuir isotherm is shown in Figure 4-5 as an example of the fit of data from Batch Experiments #1, #2, #3 and #4, which all exhibited similar behavior.

The fit to the Double Reciprocal isotherm was found to be:

$$1/q_e = 0.000807/C_e - 0.005546 \qquad (r^2 = 0.9637) \qquad \{\text{Eqn. 4-4}\}$$

The intercept in the Double Reciprocal Langmuir equation represents the term 1/Q, where Q is the theoretical value of maximum adsorption. Since the value of the intercept in this case is negative, the data cannot be described by the Double Reciprocal Langmuir isotherm. However, since the fit of the data to the Double Reciprocal Langmuir is representative of the first four batch experiments, it is shown in Figure 4-6.

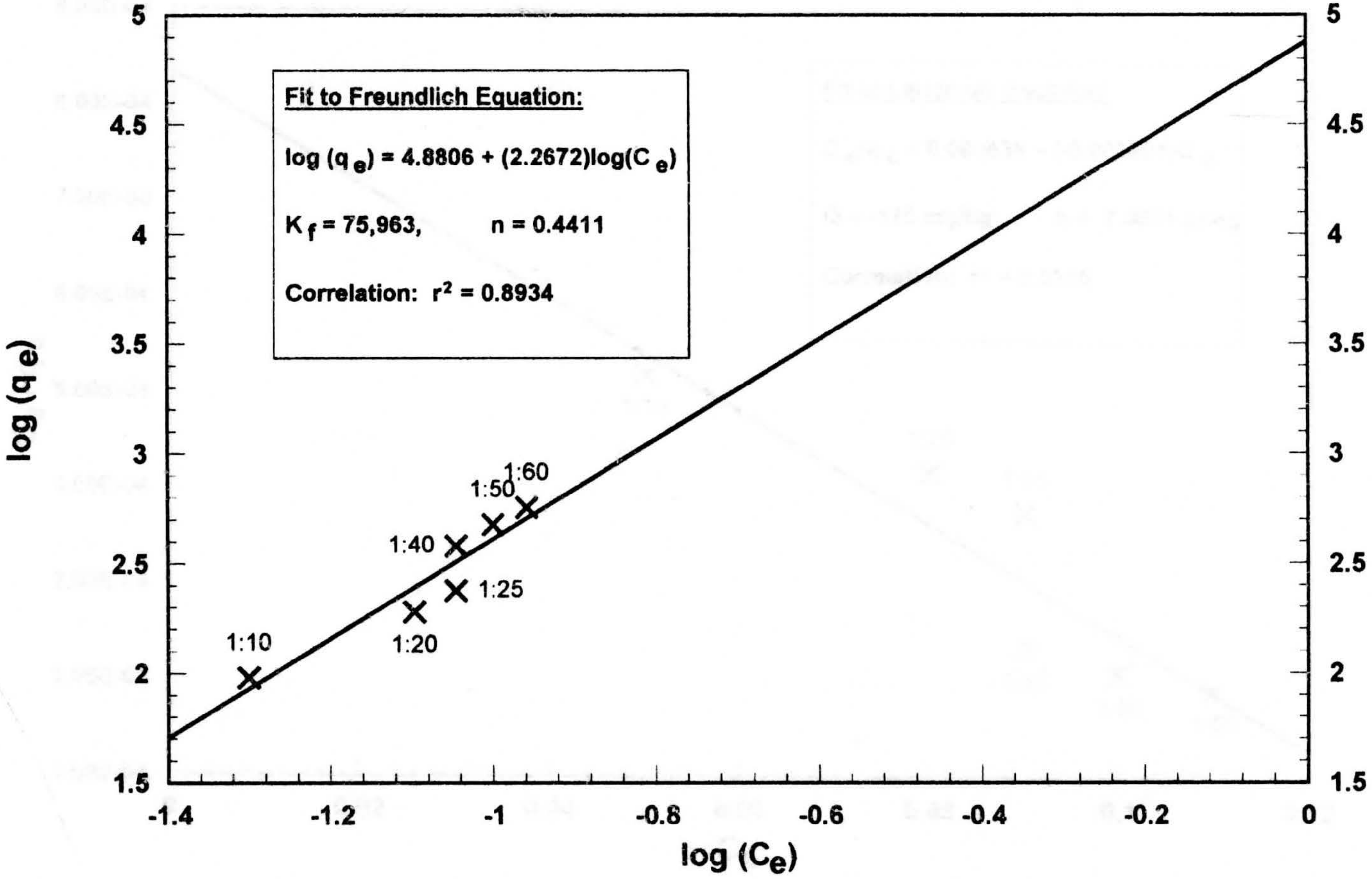


Figure 4-4. Batch Experiment #1 - Cu/Peat with Variable Soil:Solution Ratio - Freundlich Isotherm

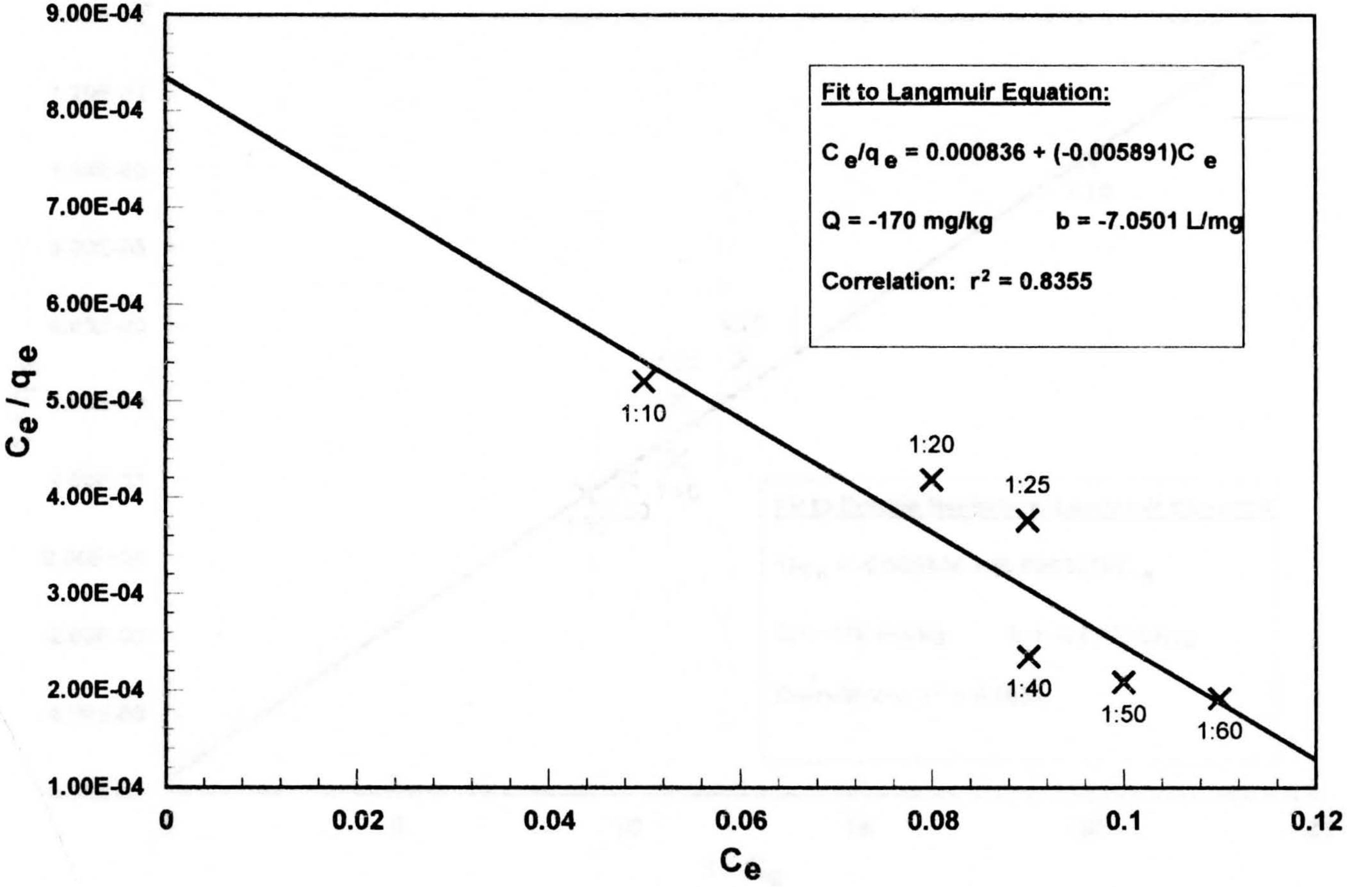


Figure 4-5. Batch Experiment #1 - Cu/Peat with Variable Soil:Solution Ratio - Langmuir Isotherm

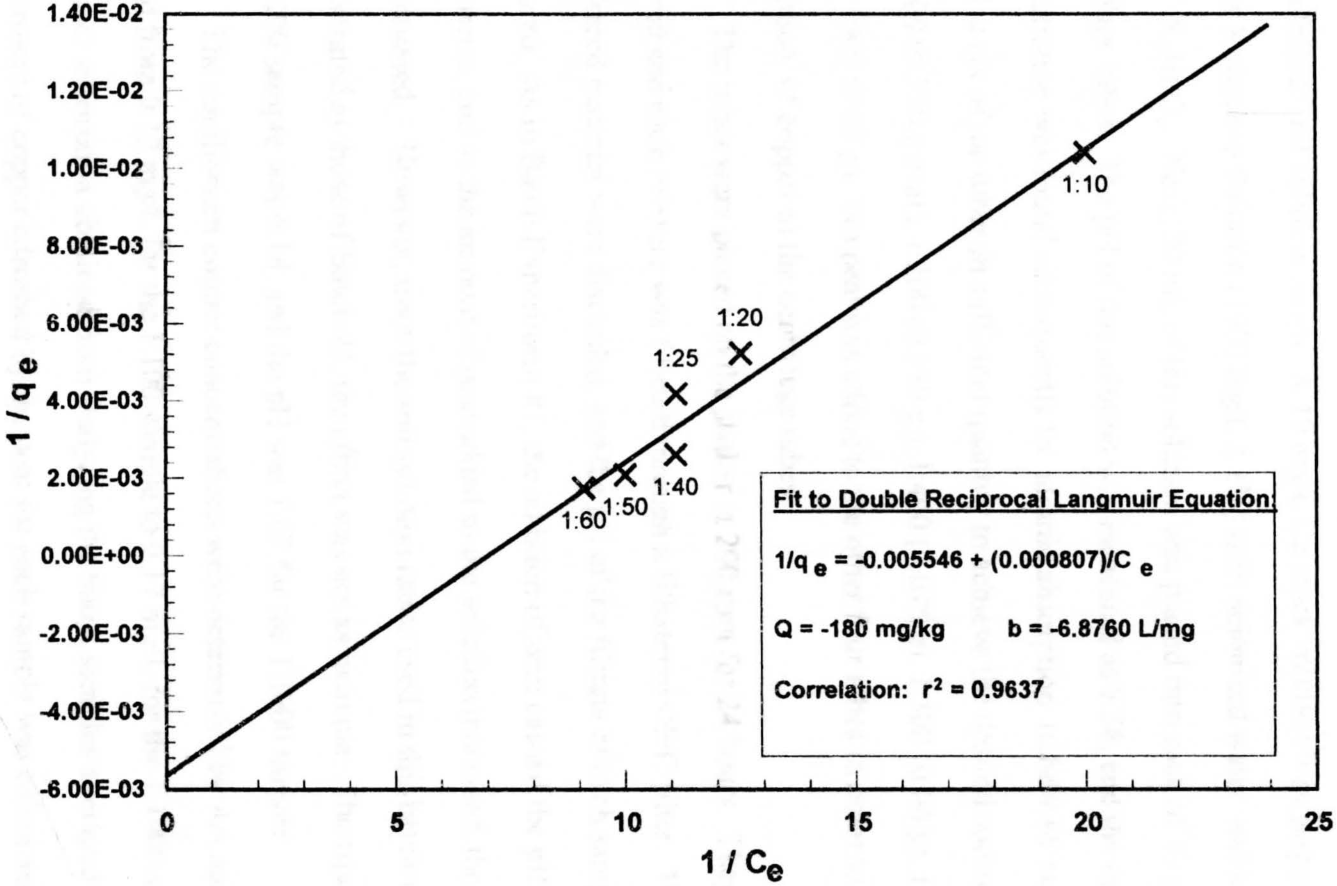


Figure 4-6. Batch Experiment #1 - Cu/Peat with Variable Soil:Solution Ratio -Double Reciprocal Langmuir Isotherm

4.2.2 Batch Experiment #2 - Copper/Peat with Variable Soil:Solution Ratio

4.2.2.1 Results of Batch Experiment #2

Since over 97% of the copper in solution was adsorbed by the peat in all samples from Batch Experiment #1, a second experiment was conducted at lower (less concentrated) soil:solution ratios. A 10 mg/L Cu stock solution was prepared by diluting Copper Reference Solution (1000 mg/L ± 1%) with deionized water and buffered with 0.02N K_2HPO_4. Next, 30 mL of this solution was placed into each of 10 plastic, 50 mL centrifuge tubes. The pH of this solution was measured as 8.38, and the initial Cu concentration was found subsequently by atomic absorption to be 9.68 mg/L. Peat was added to six of the tubes in sufficient quantity to achieve the desired soil:solution ratios of 1:100 (0.300 g peat), 1:200 (0.150 g), 1:400 (0.075 g), 1:500 (0.06 g), 1:600 (0.05 g), and 1:1000 (0.03 g). No peat was added to the other four tubes in order to quantify the adsorption of copper to the centrifuge tubes.

The tubes were placed on the shaker at 200 rpm for 24 hours. They were removed and each mixture was filtered through a Whatman GF/C filter. The filter and the filtered material were discarded, and the pH of the filtrate of each sample was measured. As in Batch Experiment #1, the addition of peat caused the pH of the solution to decrease, and as the amount of peat added to the solution increased, the equilibrium pH decreased. However, since the soil:solution ratios used in this batch were not as concentrated as those of Batch #1, the effect was not as extreme. The equilibrium pH of the 1:100 sample was 6.18, and the pH was 7.67 for the 1:1000 sample.

The equilibrium copper concentrations were determined by AA analyses, and ranged from 0.12 mg/L for the 1:100 sample to 0.17 mg/L for the 1:1000 sample. The container adsorption obtained from analyzing the blank samples averaged 0.11 mg/L. The amount of copper adsorbed by the peat for each sample was calculated using Equation 4-1. A summary of the results is presented in Table 4-5. A plot of the amount of copper adsorbed versus the equilibrium copper concentration is shown in Figure 4-7.

Table 4-5 Summary of Results from Batch Experiment #2

Soil:Solution Ratio	1:100	1:200	1:400	1:500	1:600	1:1000
Initial Cu Concentration (mg/L)	9.68	9.68	9.68	9.68	9.68	9.68
Adsorbate Volume (ml)	30	30	30	30	30	30
Initial pH	8.38	8.38	8.38	8.38	8.38	8.38
Adsorbent added (g)	0.300	0.150	0.075	0.060	0.050	0.030
Equilibrium pH	6.18	6.88	7.31	7.40	7.47	7.67
Equilibrium Cu Concentration (mg/L)	0.12	0.14	0.15	0.15	0.15	0.17
Container Adsorption (mg/L)	0.11	0.11	0.11	0.11	0.11	0.11
Amount Adsorbed (mg/L)	9.45	9.43	9.42	9.42	9.42	9.40
Percent Adsorbed by Adsorbent	97.62%	97.42%	97.31%	97.31%	97.31%	97.11%
Amount Adsorbed (mg/kg)	945	1886	3768	4710	5652	9400

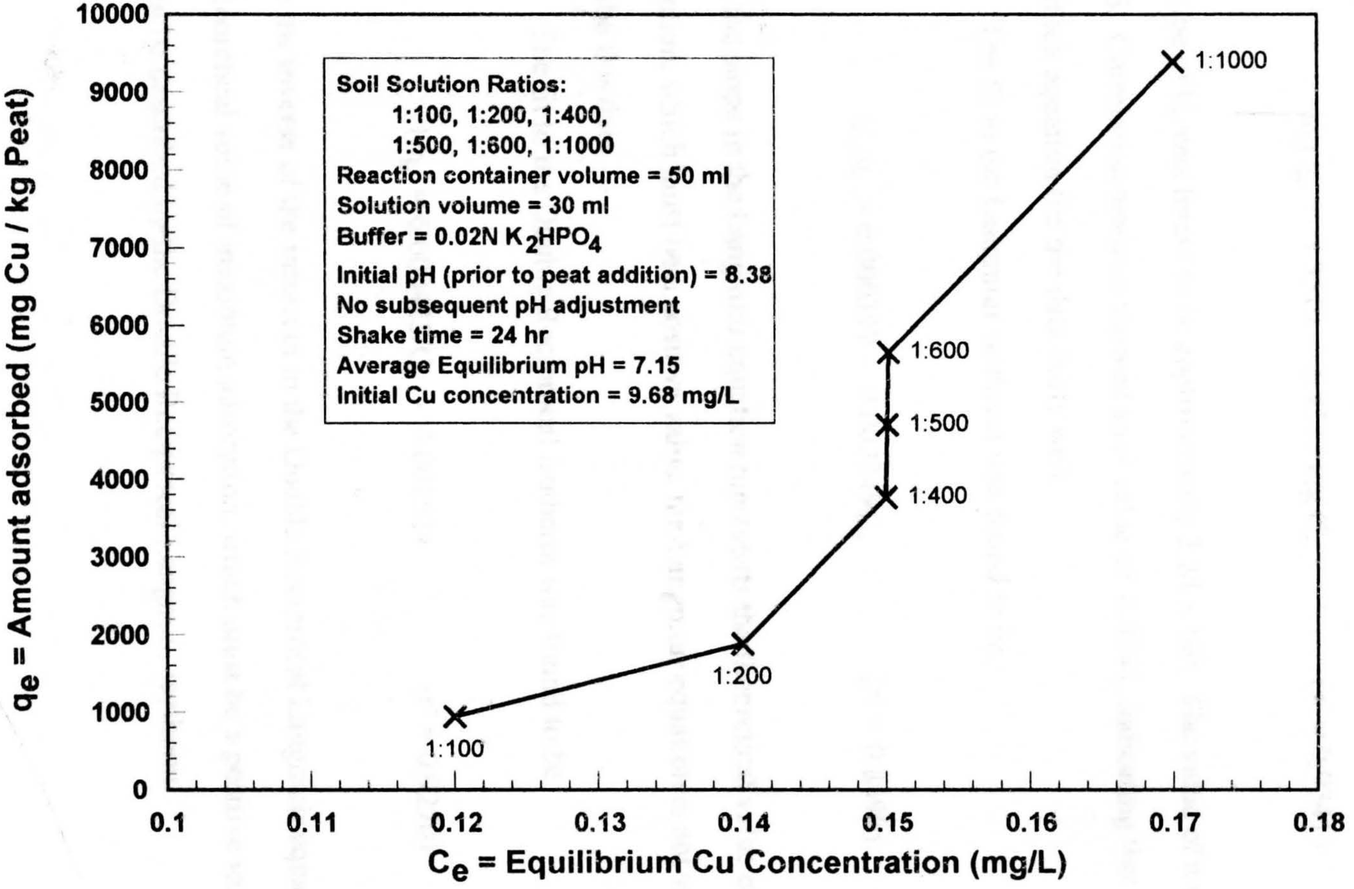


Figure 4-7. Batch Experiment #2 - Cu/Peat with Variable Soil:Solution Ratio

4.2.2.2 Analysis of Batch Experiment #2

The fit to the Freundlich isotherm equation is plotted in Figure 4-8. The equation was found to be:

$$\log q_e = 9.3510 + 6.9539 \log C_e \qquad (r^2 = 0.9341) \qquad \{\text{Eqn. 4-5}\}$$

The value of K_f was found to be approximately 2.24 x 10^9. The value of n equaled 0.1438. Correlation analysis showed an r^2 value of 0.9341, indicating that the Freundlich equation fits the data fairly well.

The fit to the Langmuir isotherm was found to be:

$$C_e/q_e = 0.000397 - 0.002349C_e \qquad (r^2 = 0.8690) \qquad \{\text{Eqn. 4-6}\}$$

Since the slope in the Langmuir equation represents the theoretical value of maximum adsorption, which must be a positive value, the Langmuir equation is not suitable to describe this data.

The fit to the Double Reciprocal isotherm was found to be:

$$1/q_e = 0.000423/C_e - 0.002524 \qquad (r^2 = 0.9270) \qquad \{\text{Eqn. 4-7}\}$$

Since the inverse of the intercept in the Double Reciprocal Langmuir equation represents the theoretical value of maximum adsorption, which must be a positive value, the data cannot be described by the Double Reciprocal Langmuir isotherm.

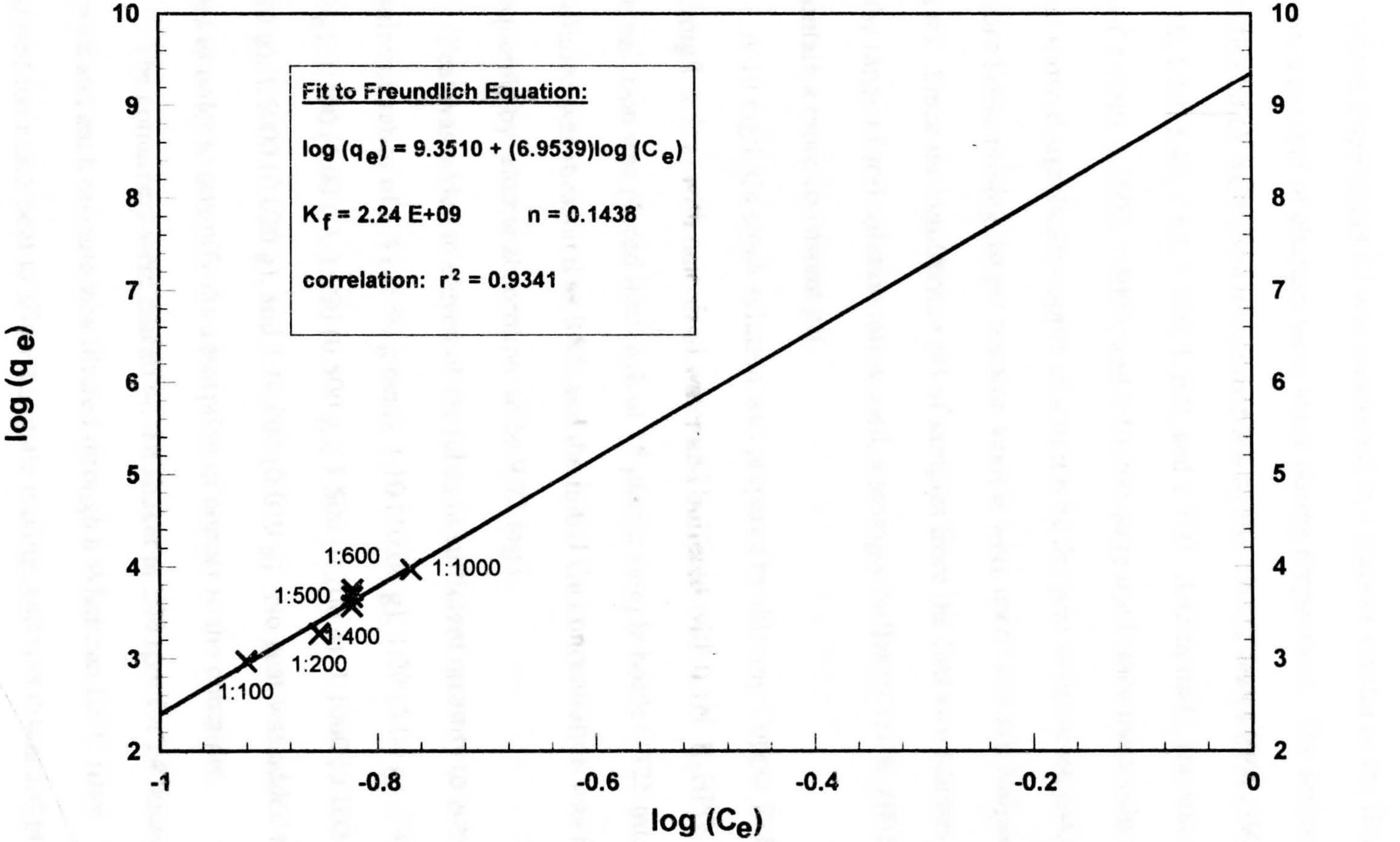


Figure 4-8. Batch Experiment #2 - Cu/Peat with Variable Soil:Solution Ratio - Freundlich Isotherm

4.2.3 Batch Experiment #3 - Copper/Peat with Variable Soil:Solution Ratio

4.2.3.1 Results of Batch Experiment #3

Batch Experiment #3 was conducted in a manner similar to the first two batches. However, a number of changes were made during preparation. The soil:solution ratios used in this batch were those recommended by the United States EPA (1992), namely 1:4, 1:10, 1:20, 1:40, 1:60, 1:100, 1:200, and 1:500. Additionally, the less concentrated ratios of 1:1000, 1:2000, 1:5000, and 1:10,000 were used since the results of the first two batches showed significant copper adsorption by the peat at the more concentrated ratios. To insure better mixing, larger reaction vessels were used (125 mL Nalgene® bottles) in Batch #3. Since the equilibrium pH of samples from the first two batches varied widely over the range of soil:solution ratios used, a stronger buffer (0.1N K_2HPO_4) was applied to maintain a more consistent pH.

A 10 mg/L Cu stock solution was prepared by diluting Copper Reference Solution (1000 mg/L ± 1%) with deionized water and buffered with 0.1N K_2HPO_4. Next, 100 mL of this solution was placed into each of 16 plastic sample bottles (125 mL). The pH of this solution was measured as 8.85, and the initial Cu concentration was found subsequently by atomic absorption to be 9.73 mg/L.

Peat was added to eleven of the tubes in sufficient quantity to achieve the desired soil:solution ratios of 1:4 (25.00 g peat), 1:10 (10.00 g), 1:20 (5.00 g), 1:40 (2.50 g), 1:60 (1.67 g), 1:100 (1.00 g), 1:200 (0.500 g), 1:500 (0.200 g), 1:1000 (0.100 g), 1:2000 (0.050 g), 1:5000 (0.020 g), and 1:10,000 (0.010 g). No peat was added to the other four bottles in order to quantify the adsorption of copper to the container.

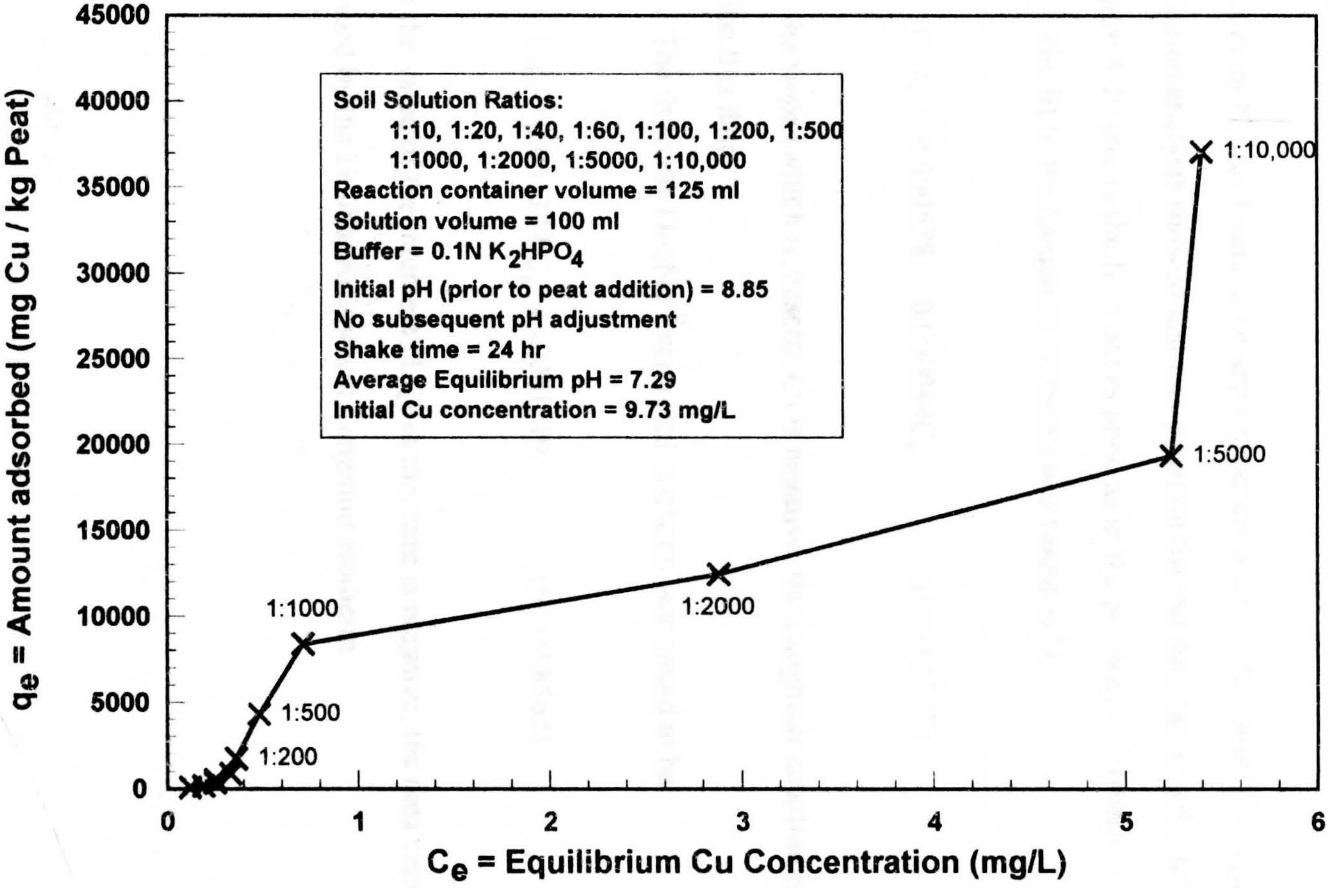
The containers were placed on the shaker at 200 rpm for 24 hours. They were removed and each mixture was filtered through a Whatman GF/C filter. The 1:4 sample contained too much peat to allow adequate mixing, and was discarded prior to evaluation. For all other samples, the filter and the filtered material were discarded, and the pH of the filtrate was measured. Even with the stronger buffer, the addition of peat caused the pH of the solution to decrease, and as the amount of peat added to the solution increased, the equilibrium pH decreased. However, with the exception of the 1:10 sample, the pH change for the more concentrated samples (1:20, 1:40 and 1:60) was not as great as in Batch Experiment #1. The equilibrium pH of the 1:10 sample was 3.42, and the pH was 8.61 for the 1:10,000 sample. The pH remained greater than 7.0 for the majority of samples.

The equilibrium copper concentrations ranged from 0.12 mg/L for the 1:10 sample to 5.40 mg/L for the 1:10,000 sample. The container adsorption obtained from analyzing the blank samples averaged 0.62 mg/L, considerably higher than the two previous batches and probably due to the higher solution pH created by using a stronger buffer. The amount of copper adsorbed by the peat for each sample was calculated using Equation 4-1. A summary of the results obtained during Batch Experiment #3 is presented in Table 4-6.

A plot of the amount of copper adsorbed versus the equilibrium copper concentration is shown in Figure 4-9. This graph shows abrupt changes in the shape of the curve, dividing it into essentially three regions. The first region contains the concentration of data points ranging from the 1:10 sample up to the 1:1000 sample. The slope of the curve is relatively steep in this region. The slope decreases considerably in the region from the 1:1000 to 1:5000 samples, indicating that the available adsorption sites on the peat in these samples may have been filled. The slope then increases dramatically between the 1:5000 and 1:10,000 samples suggesting a considerable amount of adsorption occurred at the 1:10,000 sample. However, this is attributed to copper precipitating from solution due to the higher equilibrium pH of the solution. The same phenomena was observed in Batch Experiment #4.

Table 4-6 Summary of Results from Batch Experiment #3

Soil:Solution Ratio	1:10	1:20	1:40	1:60	1:100	1:200	1:500	1:1000	1:2000	1:5000	1:10,000
Initial Cu Concentration (mg/L)	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73	9.73
Adsorbate Volume (ml)	100	100	100	100	100	100	100	100	100	100	100
Initial pH	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85
Adsorbent added (g)	10.00	5.00	2.50	1.67	1.00	0.50	0.20	0.10	0.05	0.02	0.01
Equilibrium pH	3.42	5.81	6.74	7.05	7.35	7.69	8.05	8.29	8.48	8.66	8.61
Equilibrium Cu Concentration (mg/L)	0.12	0.19	0.25	0.25	0.33	0.36	0.48	0.71	2.88	5.24	5.40
Container Adsorption (mg/L)	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
Amount Adsorbed (mg/L)	8.99	8.92	8.86	8.86	8.78	8.75	8.63	8.40	6.23	3.87	3.71
Percent Adsorbed by Adsorbent	92.39%	91.68%	91.06%	91.06%	90.24%	89.93%	88.69%	86.33%	64.03%	39.77%	38.13%
Amount Adsorbed (mg/kg)	90	178	354	531	878	1,750	4,315	8,400	12,460	19,350	37,100



Soil Solution Ratios:
1:10, 1:20, 1:40, 1:60, 1:100, 1:200, 1:500
1:1000, 1:2000, 1:5000, 1:10,000
Reaction container volume = 125 ml
Solution volume = 100 ml
Buffer = 0.1N K_2HPO_4
Initial pH (prior to peat addition) = 8.85
No subsequent pH adjustment
Shake time = 24 hr
Average Equilibrium pH = 7.29
Initial Cu concentration = 9.73 mg/L

Figure 4-9. Batch Experiment #3 - Cu/Peat with Variable Soil:Solution Ratio

4.2.3.2 Analysis of Batch Experiment #3

The fit to the Freundlich isotherm equation was found to be:

$$\log q_e = 3.5841 + 1.3958 \log C_e \qquad (r^2 = 0.8697) \qquad \{\text{Eqn 4-8}\}$$

The value of K_f was found to be approximately 3,800. The value of n equaled 0.7164. Correlation analysis showed that this equation fits the data fairly well, but the plot shown in Figure 4-10 shows the fit is not as good as in the previous experiments.

The fit to the Langmuir isotherm was found to be:

$$C_e/q_e = 0.000578 - 0.000084C_e \qquad (r^2 = 0.1727) \qquad \{\text{Eqn 4-9}\}$$

Since the slope (which represents Q) is negative, the Langmuir equation is not suitable to describe this data.

The fit to the Double Reciprocal isotherm was found to be:

$$1/q_e = 0.001277/C_e - 0.001519 \qquad (r^2 = 0.8562) \qquad \{\text{Eqn 4-10}\}$$

Since the value of the intercept (1/Q) in this case is negative, the data cannot be described by the Double Reciprocal Langmuir isotherm.

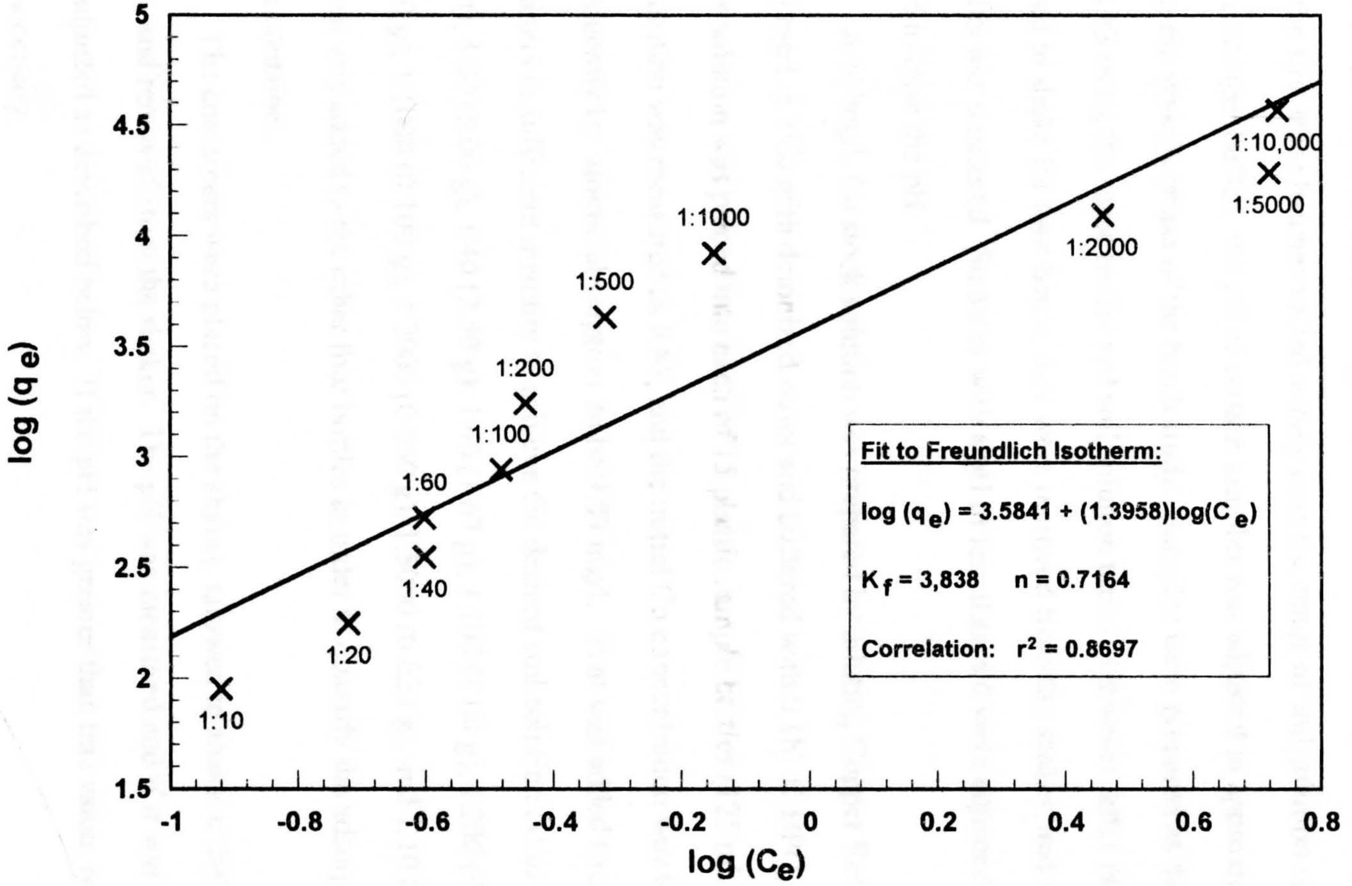


Figure 4-10. Batch Experiment #3 - Cu/Peat with Variable Soil:Solution Ratio - Freundlich Isotherm

4.2.4 Batch Experiment #4 - Copper/Peat with Variable Soil:Solution Ratio

4.2.4.1 Results of Batch Experiment #4

Batch Experiment #4 was conducted in a manner similar to Batch Experiment #3. However, certain procedural changes were made. Since the equilibrium pH of samples from the first three batches varied widely over the range of soil:solution ratios used, even with a stronger buffer, the pH of certain samples was adjusted to approximately 8.0 during the shaking phase of the batch study. Samples were prepared as they were in Batch #3 using the same buffer and soil:solution ratios. However, after they were allowed to shake for four hours, they were removed from the shaker, and the pH of the samples was measured. Samples with a pH of less than 8.0 were adjusted by adding 0.1N NaOH to raise the pH.

A 10 mg/L Cu stock solution was prepared by diluting Copper Reference Solution (1000 mg/L ± 1%) with deionized water and buffered with 0.1N K_2HPO_4. Next, 100 mL of this solution was placed into each of 15 plastic sample bottles (125 mL). The pH of this solution was measured as 8.88, and the initial Cu concentration was found subsequently by atomic absorption to be 9.89 mg/L. Peat was added to eleven of the containers in sufficient quantity to achieve the desired soil:solution ratios of 1:10 (10.00 g peat), 1:20 (5.00 g), 1:40 (2.50 g), 1:60 (1.67 g), 1:100 (1.00 g), 1:200 (0.500 g), 1:500 (0.200 g), 1:1000 (0.100 g), 1:2000 (0.050 g), 1:5000 (0.020 g), and 1:10,000 (0.010 g). No peat was added to the other four bottles in order to quantify the adsorption of copper to the container.

The containers were placed on the shaker, allowed to shake at 200 rpm for 4 hours, and removed from the shaker. The pH was measured and if it was less than 8.0, it was adjusted as described below. If the pH was greater than this value, no adjustment was necessary.

Measurement of the pH began with the most concentrated sample (1:10) which was found to have a 4-hour pH of 4.57. Repeatedly, 1-2 mL of 0.1N NaOH was added to the sample and the pH measured. It was hoped to raise the pH of all samples to about 8.0, but it was found that the 1:10 sample still only had a pH of 5.95 when the container was completely full after the addition of 35.9 mL of 0.1N NaOH. The 1:20 sample behaved similarly - it was only possible to raise the pH from 5.84 to 7.06 with 33.6 mL of NaOH. This indicated that a more concentrated solution of NaOH should have been used for pH adjustment.

All samples from the ratios of 1:40 to1:200 showed an initial 4-hour pH of less than 8.0, and were treated through the addition of 0.1N NaOH to raise the pH above this value. The 1:500 and 1:1000 samples showed initial 4-hr pH values above 8.0. The pH values of the1:2000, 1:5000 and 1:10,000 samples were not measured. The adjustment of pH was not necessary for any of these samples (1:500 to 1:10,000).

The samples were returned to the shaker, and allowed to shake for a total of 24 hours from their initial placement on the shaker. Then they were removed and each mixture was filtered through a Whatman GF/C filter. The filter and the filtered material were discarded, and the pH of each filtrate was measured. The pH of samples from ratios 1:40 to 1:200, which had been adjusted to approximately 8.0 after four hours, dropped slightly, but were all still within one pH unit of the 1:10,000 sample. Even the 1:10 and 1:20 samples did not show an appreciable drop in pH after adjustment. The equilibrium pH of the 1:10 sample was 5.72, and the pH was 8.67 for the 1:10,000 sample. The final pH measured greater than 7.6 for the majority of samples. Thus, the aim of obtaining a smaller range of equilibrium pH values was achieved.

Analytical results were similar to those of Batch Experiment #3. The equilibrium copper concentrations ranged from 0.09 mg/L for the 1:10 sample to 5.11 mg/L for the 1:10,000 sample. The container adsorption obtained from analyzing the blank samples averaged 0.60 mg/L. The amount of copper adsorbed by the peat for each sample was calculated using Equation 4-1. However, for those samples which underwent pH adjustment, the measured value for the initial copper concentration in solution was adjusted to account for dilution which occurred when the NaOH was added. A summary of the results obtained during Batch Experiment #4 is presented in Table 4-7. A plot of the amount of copper adsorbed versus the equilibrium copper concentration is shown as the solid line on Figure 4-11.

No samples from Batch Experiments #1, #2, or #3 were treated by nitric acid digestion. However, fluctuations in the performance of the atomic absorption spectrophotometer were thought to be the result of colloidal interference. The effective pore size of the Whatman GF/C filters used in phase separation was 1.2 microns. Colloidal material typically is classified by size in the range of 10^{-3} microns to 1 micron (Tchobanoglous and Schroeder, 1985). Therefore, essentially all of the colloidal material present in solution can pass through the GF/C filter.

To determine the effect of colloidal material on the AA analysis, the samples from Batch Experiment #4 were analyzed prior to digestion, and then were treated by nitric acid digestion. The digested samples were then analyzed by AA. The amount of copper adsorbed by the peat for each digested sample was calculated using Equation 4-1, again accounting for the dilution caused by the addition of NaOH to some samples. A plot of the amount of copper adsorbed versus the equilibrium copper concentration for the digested samples is shown as the dashed line on Figure 4-11. The shape of these curves is very similar to that of Figure 4-9.

Atomic absorption analyses of the digested samples gave much more consistent results with less signal noise. This strongly supported the hypothesis that colloidal material was hindering the analysis of the batch solutions. The digested samples showed an average increase of 27% in the copper concentration compared to the values measured for the samples prior to digestion. The large increase in the copper concentration of the digested samples suggests that the copper was being adsorbed by the colloidal material present in the peat.

Table 4-7 Summary of Results from Batch #4

Soil:Solution Ratio	1:10	1:20	1:40	1:60	1:100	1:200	1:500	1:1000	1:2000	1:5000	1:10,000
Initial Cu Concentration (mg/L)	9.89	9.89	9.89	9.89	9.89	9.89	9.89	9.89	9.89	9.89	9.89
Adsorbate Volume (ml)	100	100	100	100	100	100	100	100	100	100	100
Initial pH	8.88	8.88	8.88	8.88	8.88	8.88	8.88	8.88	8.88	8.88	8.88
Adsorbent added (g)	10.00	5.00	2.50	1.67	1.00	0.50	0.20	0.10	0.05	0.02	0.01
pH after 4 hr shaking	4.57	5.84	6.74	7.05	7.35	7.70	8.08	8.36	N/P	N/P	N/P
0.1N NaOH added (ml)	35.9	33.6	27.6	17.9	10.1	3.9	0.0	0.0	0.0	0.0	0.0
Adjusted 4 hr pH	5.95	7.06	8.01	8.03	8.01	8.02	N/A	N/A	N/A	N/A	N/A
Adjusted Cu Conc. in Solution	7.28	7.40	7.75	8.39	8.98	9.52	9.89	9.89	9.89	9.89	9.89
Equilibrium pH	5.72	6.88	7.66	7.76	7.84	7.96	8.05	8.26	8.47	8.65	8.67
Undigested Results											
Equilibrium Cu Concentration (mg/L)	0.09	0.15	0.29	0.29	0.29	0.31	0.31	0.52	1.80	4.91	5.11
Container Adsorption (mg/L)	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Amount Adsorbed (mg/L)	6.59	6.65	6.86	7.50	8.09	8.61	8.98	8.77	7.49	4.38	4.18
Percent Adsorbed by Adsorbent	90.52%	89.87%	88.52%	89.39%	90.09%	90.44%	90.80%	88.68%	75.73%	44.29%	42.26%
Amount Adsorbed (mg/kg)	90	178	350	529	891	1,789	4,490	8,770	14,980	21,900	41,800
Digested Results											
Digested Equilibrium Cu Concentration (mg/L)	0.15	0.22	0.33	0.33	0.36	0.40	0.44	0.55	2.19	5.93	5.97
Amount Adsorbed (mg/L)	6.53	6.58	6.82	7.46	8.02	8.52	8.85	8.74	7.10	3.36	3.32
Percent Adsorbed by Adsorbent	89.69%	88.92%	88.00%	88.91%	89.31%	89.49%	89.48%	88.37%	71.79%	33.97%	33.57%
Amount Adsorbed (mg/kg)	89	176	348	527	883	1,770	4,425	8,740	14,200	16,800	33,200

(N/P = test not performed; N/A = not applicable)

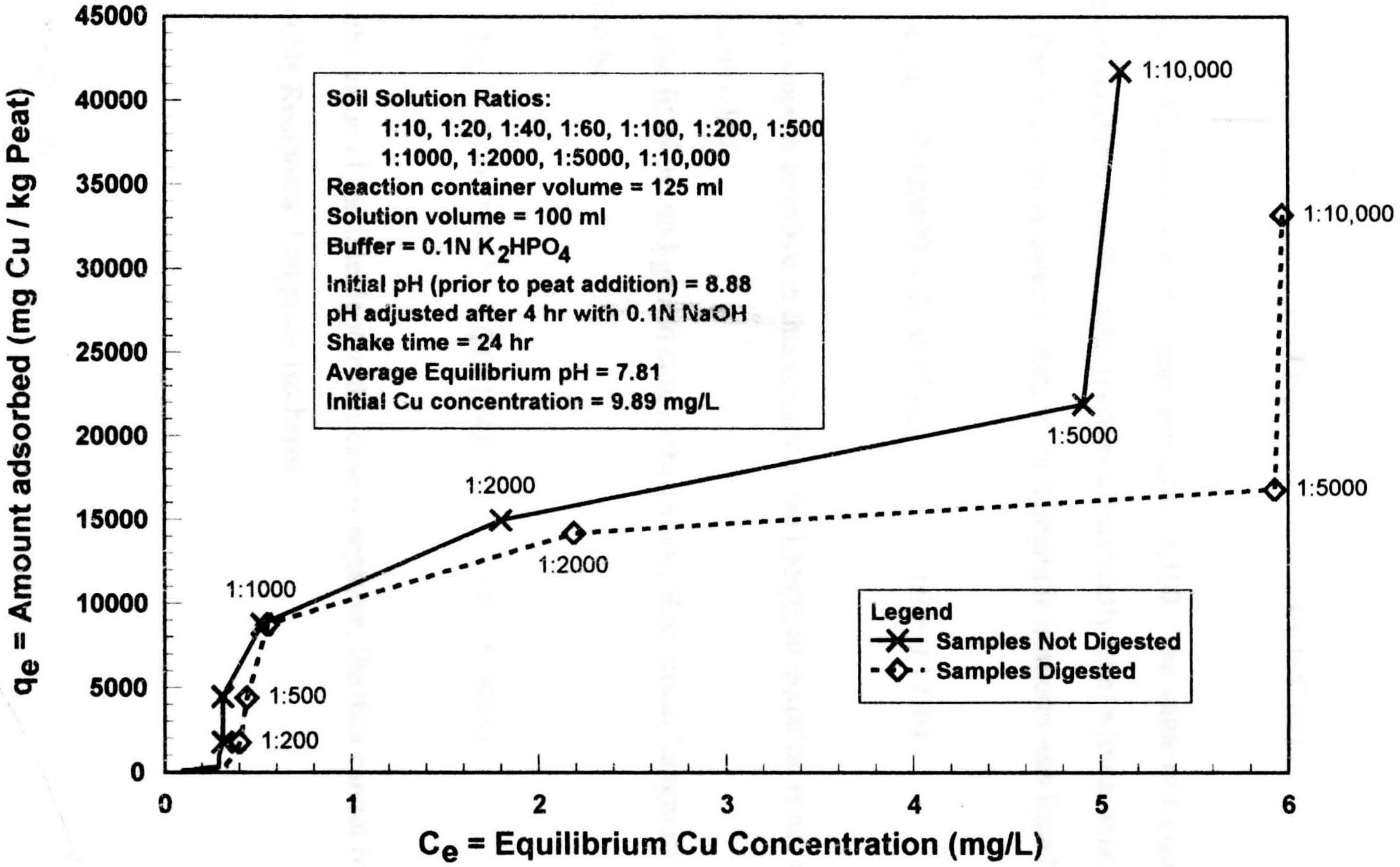


Figure 4-11. **Batch Experiment #4 - Cu/Peat with Variable Soil:Solution Ratio**

4.2.4.2 Analysis of Batch Experiment #4 - Undigested Samples

The fit of the undigested data to the Freundlich isotherm equation is plotted in Figure 4-12. This equation was found to be:

$$\log q_e = 3.7079 + 1.3997 \log C_e \qquad (r^2 = 0.8232) \qquad \{\text{Eqn. 4-11}\}$$

The value of K_f was found to be approximately 5,100. The value of n equaled 0.7144. The graph indicates that this data deviates substantially from a linear relationship.

The fit of the undigested data to the Langmuir isotherm was found to be:

$$C_e/q_e = 0.000490 - 0.000076C_e \qquad (r^2 = 0.1710) \qquad \{\text{Eqn. 4-12}\}$$

Since the slope is negative in this equation, the Langmuir equation is not suitable to describe this data.

The fit of the undigested data to the Double Reciprocal Langmuir isotherm was found to be:

$$1/q_e = 0.001025/C_e - 0.001342 \qquad (r^2 = 0.9018) \qquad \{\text{Eqn. 4-13}\}$$

Since the value of the intercept in this case is negative, the data cannot be described by the Double Reciprocal Langmuir isotherm.

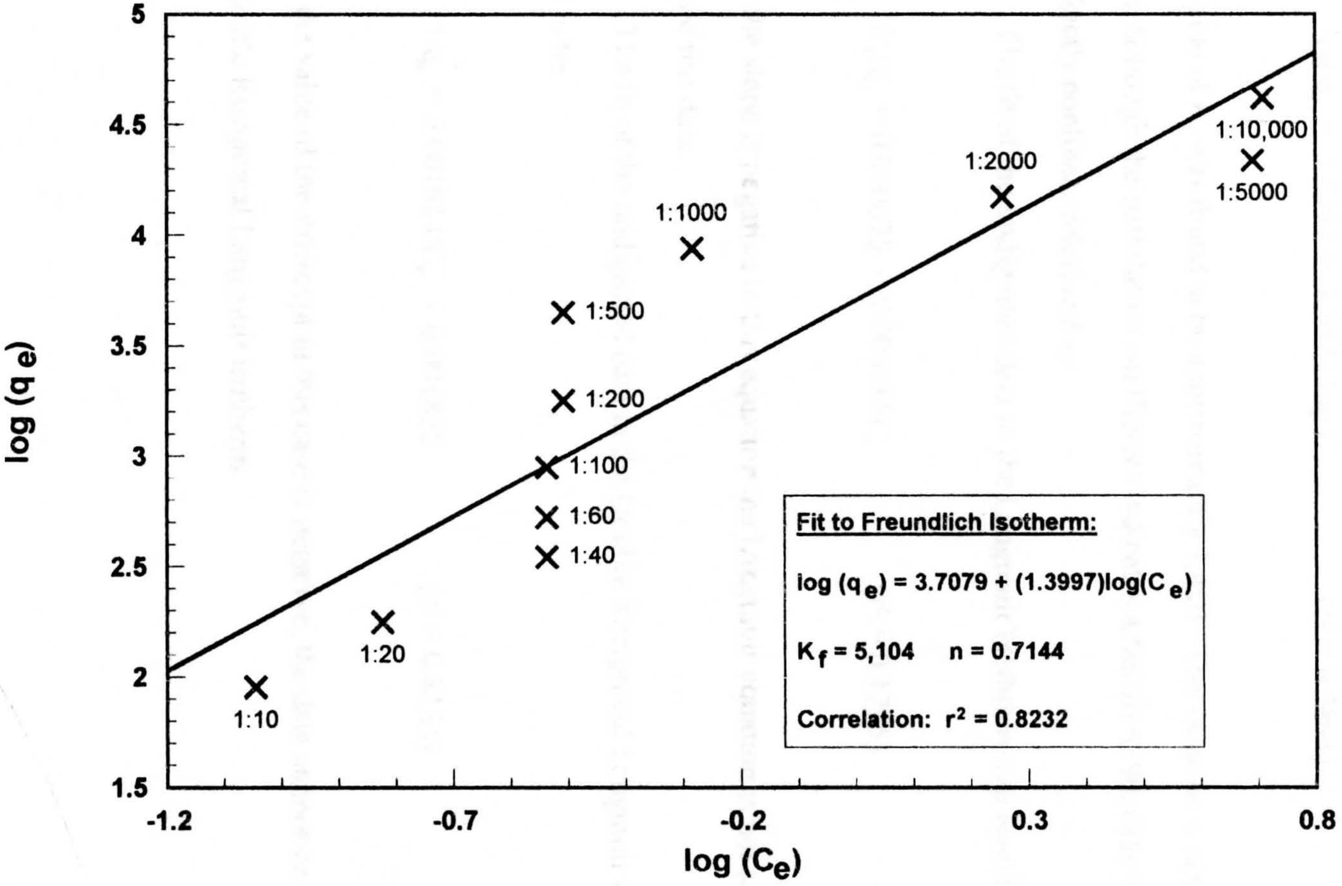


Figure 4-12. **Batch Experiment #4 (Undigested)-**
Cu/Peat with Variable Soil:Solution Ratio - Freundlich Isotherm

4.2.4.3 Analysis of Batch Experiment #4 - Digested Samples

The fit of the digested data to the Freundlich isotherm equation is plotted in Figure 4-13. This equation was found to be:

$$\log q_e = 3.5391 + 1.3871 \log C_e \qquad (r^2 = 0.7801) \qquad \{\text{Eqn. 4-14}\}$$

The value of K_f was found to be approximately 3,460. The value of n equaled 0.7209. Again, although the correlation coefficient indicates a fair fit to the data, the graph shows a distinctly nonlinear relationship.

The fit of the undigested data to the Langmuir isotherm was found to be:

$$C_e/q_e = 0.000675 - 0.000085C_e \qquad (r^2 = 0.1295) \qquad \{\text{Eqn. 4-15}\}$$

Since the slope is negative in this equation the Langmuir equation is not suitable to describe this data.

The fit of the undigested data to the Double Reciprocal Langmuir isotherm was found to be:

$$1/q_e = 0.001614/C_e - 0.001855 \qquad (r^2 = 0.8185) \qquad \{\text{Eqn. 4-16}\}$$

Since the value of the intercept in this case is negative, the data cannot be described by the Double Reciprocal Langmuir isotherm.

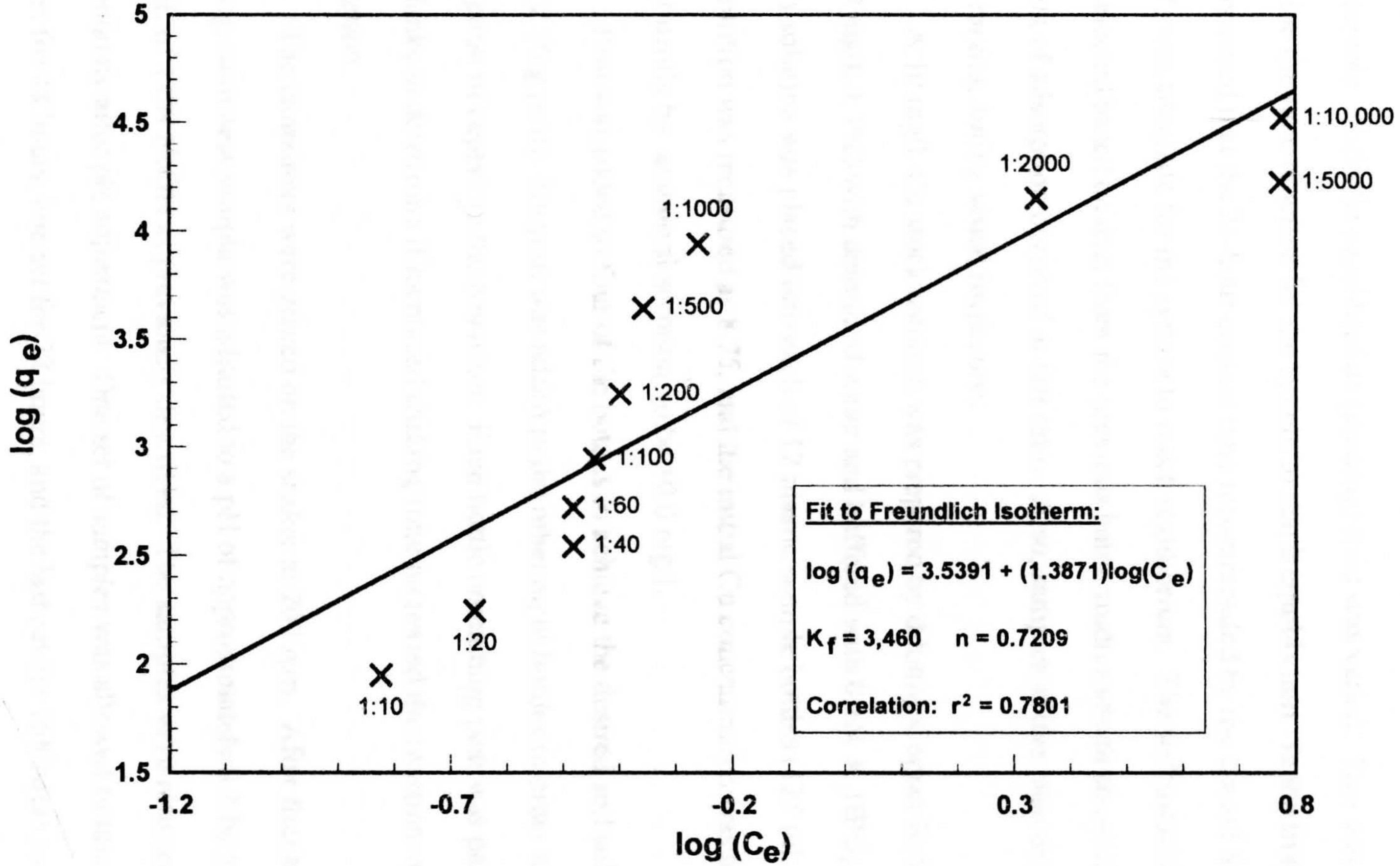


Figure 4-13. Batch Experiment #4 (Digested) - Cu/Peat with Variable Soil:Solution Ratio - Freundlich Isotherm

4.2.5 Batch Experiment #5 - Copper/Peat with Variable Equilibration Time

Batch Experiment #5 was conducted in a manner similar to the previous experiments. The major difference was that the same soil:solution ratio was used for each sample, while the equilibration (shaking) time was varied. This was done to examine the time required for the system to reach equilibrium. In the first four batches it was assumed that the 24-hour contact time recommended by the United States EPA (1992) was adequate for the system to reach equilibrium. The soil:solution ratio of 1:40 was selected based on data from the previous batch studies which showed a significant amount of adsorption occurred at this ratio. Also, samples at this ratio displayed very good mixing during visual inspection.

A 10 mg/L Cu stock solution was prepared by diluting Copper Reference Solution (1000 mg/L ± 1%) with deionized water and buffered with 0.1N K_2HPO_4. Next, 100 mL of this solution was placed into each of 12 plastic sample bottles (125 mL). The pH of this solution was measured as 8.75, and the initial Cu concentration was found subsequently by atomic absorption to be 10.0 mg/L.

Peat was added to four of the bottles to achieve the desired soil:solution ratio of 1:40 (2.50 g peat). No peat was added to the other eight bottles in order to quantify the adsorption of copper to the container. Each bottle containing peat was paired with two of the blanks to determine if increased shaking time increased the reaction vessel adsorption.

The containers were placed on the shaker at 200 rpm. After four hours of shaking, each peat sample was adjusted to a pH of approximately 8.3 by the addition of 3.0 mL of 1.0N NaOH as previously described. The samples were returned to the shaker immediately after pH adjustment. One set of samples was allowed to mix for 24 hours, one set for 48 hours, one set for 72 hours, and the last set for 168 hours (measured from the time samples were initially placed on the shaker). At each of these times, the set of samples (one mixture containing peat plus two blanks) was removed from the shaker, and each mixture was filtered through a Whatman GF/C filter. The filter and the filtered material were discarded, and the pH of each blank and of each filtered peat solution was measured. The samples were preserved by acidifying with 0.2 mL of redistilled nitric acid for later analysis. All peat solutions were later digested. The equilibrium pH of the 24-hour sample was 7.80, and decreased as the mixing time increased to a value of 7.54 for the 168-hour sample.

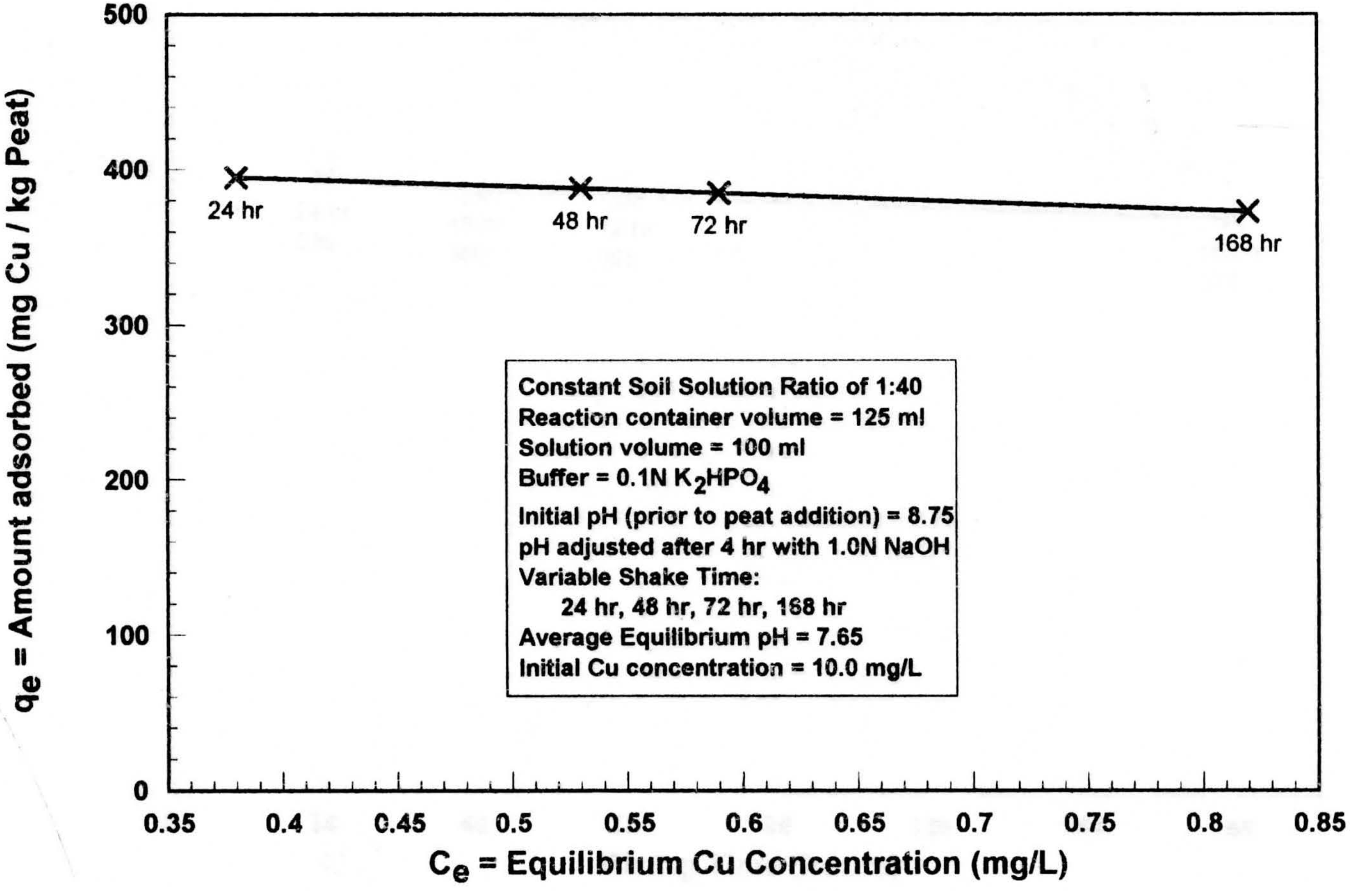
The equilibrium copper concentrations ranged from 0.38 mg/L for the 24-hour sample to 0.82 mg/L for the 168-hour sample. The container adsorption was 0.04 mg/l for the 24-hour sample and 0.06 mg/L for the 72-hour sample, but more than doubled to 0.14 mg/L for the 168-hr sample. These values were significantly lower than those found for Batch Experiments #3 and #4, which were conducted using the same buffer at slightly higher initial pH values (8.85 and 8.88 respectively). It is possible that an adsorption edge exists for the container material at pH values of 8.75 to 8.85.

The amount of copper adsorbed by the peat for each sample was calculated using Equation 4-1. A summary of the results obtained is presented in Table 4-8. A plot of the amount of copper adsorbed versus the equilibrium copper concentration is given in Figure 4-14. Figure 4-15 shows the amount of copper adsorbed versus mixing time, and Figure 4-16 shows the pH versus mixing time for the time-variable batch experiment.

The results of this batch study show that a mixing time of 24 hours is optimal in order to achieve the highest amount of copper adsorption by the peat. The amount of copper adsorbed decreased as the mixing time was increased from 24 hours to 168 hours. Since the amount of copper adsorbed by the container increased as the mixing time was increased, it appears that the peat was competing with the container to adsorb copper ions from solution.

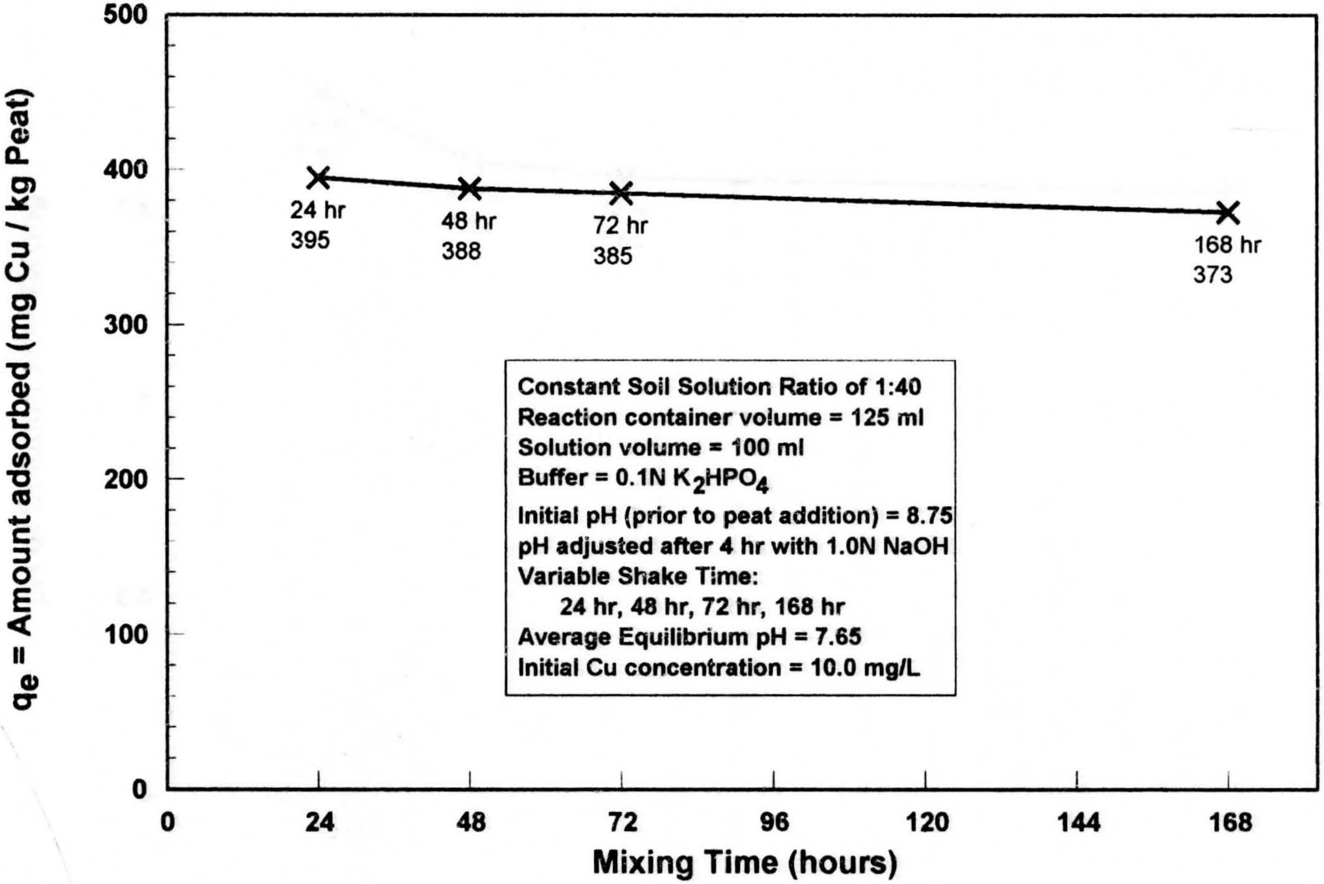
Table 4-8 Summary of Results from Batch Experiment #5

Shake Time	24 hr	48 hr	72 hr	168 hr
Initial Cu Concentration (mg/L)	10.0	10.0	10.0	10.0
Adsorbate Volume (ml)	100	100	100	100
Initial pH	8.75	8.75	8.75	8.75
Adsorbent added (g)	2.50	2.50	2.50	2.50
pH after 4 hr shaking	6.78	6.79	6.79	6.80
1.0N NaOH added (ml)	3.0	3.0	3.0	3.0
Adjusted 4 hr pH	8.31	8.30	8.31	8.32
Adjusted Cu Conc. in Solution	9.71	9.71	9.71	9.71
Equilibrium pH	7.80	7.62	7.58	7.54
HNO3 added as Preservative (ml)	0.2	0.2	0.2	0.2
Readjusted Cu Concentration	9.69	9.69	9.69	9.69
Digested Results				
Equilibrium Cu Concentration (mg/L)	0.38	0.53	0.59	0.82
Container Adsorption (mg/L)	0.04	0.05	0.06	0.14
Amount Adsorbed (mg/L)	9.27	9.11	9.04	8.73
Percent Adsorbed by Adsorbent	95.48%	93.83%	93.11%	89.92%
Amount Adsorbed (mg/kg)	382	375	372	360



Constant Soil Solution Ratio of 1:40
Reaction container volume = 125 ml
Solution volume = 100 ml
Buffer = 0.1N K_2HPO_4
Initial pH (prior to peat addition) = 8.75
pH adjusted after 4 hr with 1.0N NaOH
Variable Shake Time:
24 hr, 48 hr, 72 hr, 168 hr
Average Equilibrium pH = 7.65
Initial Cu concentration = 10.0 mg/L

Figure 4-14. **Batch Experiment #5 - Cu/Peat - Constant Soil:Solution Ratio, Variable Equilibration Time**



Constant Soil Solution Ratio of 1:40
Reaction container volume = 125 ml
Solution volume = 100 ml
Buffer = 0.1N K_2HPO_4
Initial pH (prior to peat addition) = 8.75
pH adjusted after 4 hr with 1.0N NaOH
Variable Shake Time:
24 hr, 48 hr, 72 hr, 168 hr
Average Equilibrium pH = 7.65
Initial Cu concentration = 10.0 mg/L

Figure 4-15. **Batch Experiment #5 - Cu/Peat - Adsorption vs. Mixing Time**

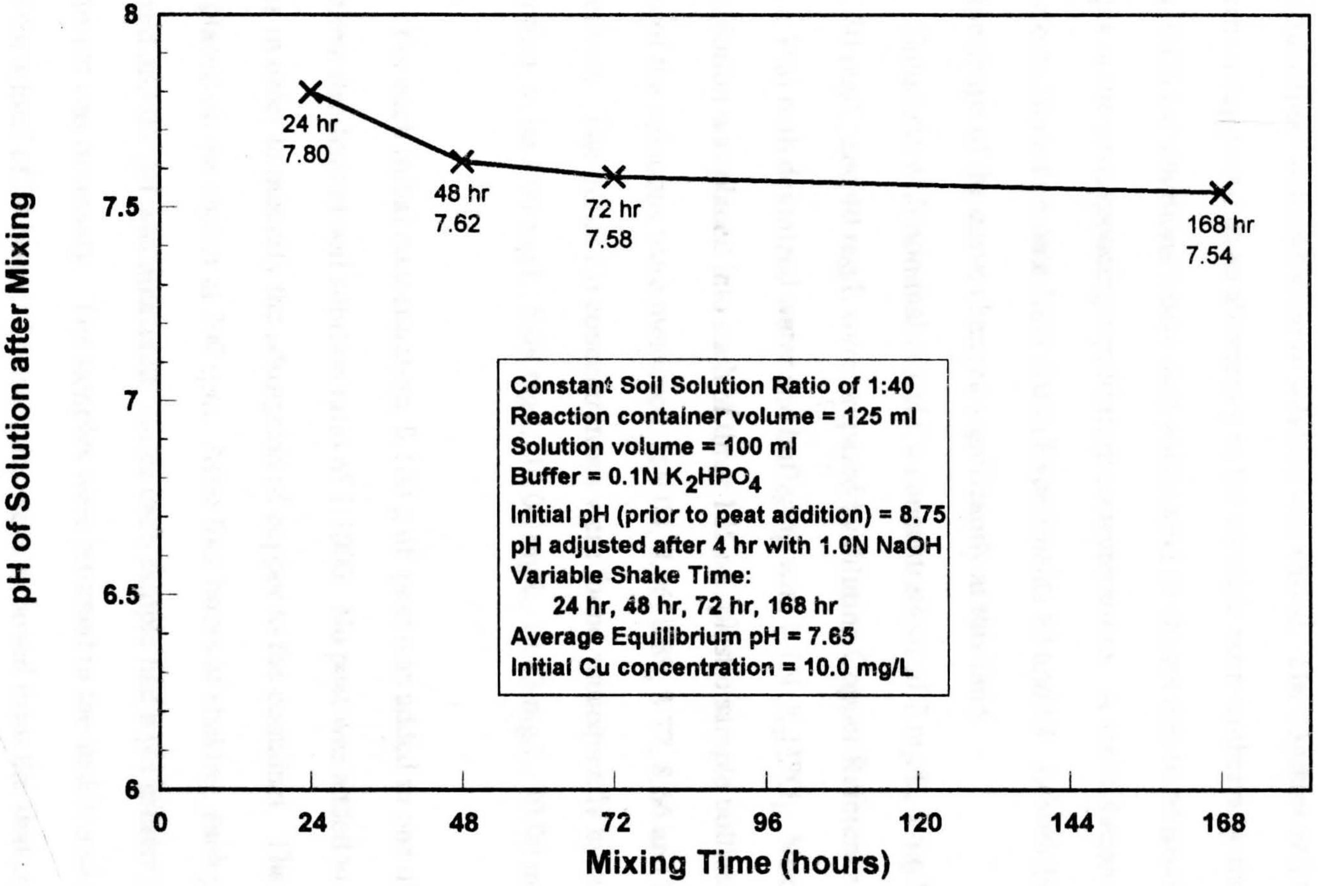


__Figure 4-16.__ **Batch Experiment #5 - Cu/Peat - pH of Solution after Mixing vs. Mixing Time**

4.2.6 Batch Experiment #6 - Copper/Peat with Constant Soil:Solution Ratio

4.2.6.1 Results of Batch Experiment #6

Batch Experiment #6 was conducted in a manner similar to the previous batches. The major difference was that the same soil:solution ratio was used for all samples, while the initial copper concentration in solution was varied. The constant soil:solution ratio isotherm is suggested as an alternative to the variable ratio isotherm by the United States EPA (1992) for situations where data points tend to cluster due to relatively small changes in the corresponding equilibrium concentrations. A soil:solution ratio of 1:1000 was selected based on data from Batch Experiments #3 and #4. In both Figures 4-9 and 4-11 the shape of the curve changed significantly at this ratio.

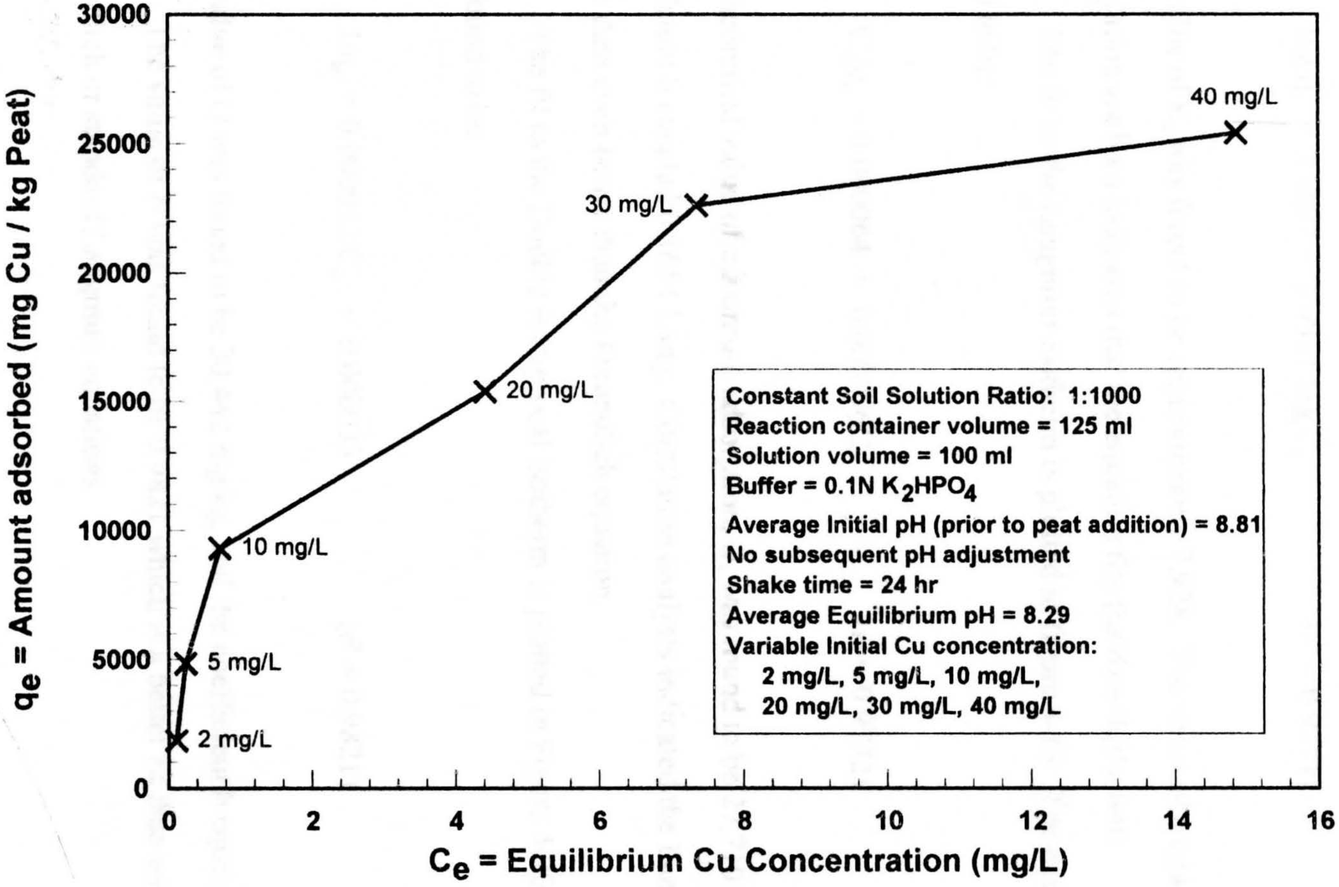
Solutions with nominal initial Cu concentrations of 2 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, and 40 mg/L were prepared by diluting Copper Reference Solution (1000 mg/L ± 1%) with deionized water and buffering with 0.1N K_2HPO_4. Next, 100 mL of each solution was placed into each of three 125 mL plastic sample bottles. The initial pH values of the solutions were measured at 9.04, 8.96, 8.89, 8.77, 8.66 and 8.56, respectively. The initial Cu concentrations were found subsequently by atomic absorption to be 1.99 mg/L, 5.09 mg/L, 10.06 mg/L, 19.83 mg/L, 30.00 mg/L, and 40.33 mg/L.

For each initial concentration, 0.100 g of peat was added to one of the containers to achieve the desired soil:solution ratio of 1:1000. No peat was added to the other two bottles in order to quantify the adsorption of copper to the container. The containers were placed on the shaker at 200 rpm. After four hours of shaking, each peat sample was removed and the pH was measured. Since each sample had a pH greater than 8.2, no pH adjustment was necessary. The samples were returned to the shaker and allowed to shake for a total of 24 hours. The samples were removed from the shaker, and each mixture was filtered through a Whatman GF/C filter. The filter and the filtered material were discarded, and the pH of each blank and each filtered peat solution was measured. All peat solutions were later digested.

The equilibrium pH ranged from 8.21 for the 40 mg/L sample to 8.34 for the 2 mg/L sample. The equilibrium copper concentrations ranged from 0.11 mg/L for the 2 mg/L sample to 14.86 mg/L for the 40 mg/L sample. The container adsorption was very small, varying from 0.0 mg/L to 0.03 mg/L. The amount of copper adsorbed by the peat for each sample was calculated using Equation 4-1. A summary of the results obtained during Batch Experiment #6 is presented in Table 4-9. A plot of the amount of copper adsorbed versus the equilibrium copper concentration is shown in Figure 4-17.

Table 4-9 Summary of Results from Batch Experiment #6

Soil:Solution Ratio	1:1000	1:1000	1:1000	1:1000	1:1000	1:1000
Nominal Initial Cu Concentration (mg/L)	2	5	10	20	30	40
Measured Initial Cu Concentration (mg/L)	1.99	5.09	10.06	19.83	30.00	40.33
Adsorbate Volume (ml)	100	100	100	100	100	100
Initial pH	9.04	8.96	8.89	8.77	8.66	8.56
Adsorbent added (g)	0.100	0.100	0.100	0.100	0.100	0.100
pH after 4 hr shaking	8.44	8.37	8.37	8.32	8.24	8.22
1.0N NaOH added (ml)	0.0	0.0	0.0	0.0	0.0	0.0
Adjusted 4 hr pH	N/A	N/A	N/A	N/A	N/A	N/A
Adjusted Cu Conc. in Solution	1.99	5.09	10.06	19.83	30.00	40.33
Equilibrium pH	8.34	8.35	8.32	8.28	8.23	8.21
Digested Results						
Equilibrium Cu Concentration (mg/L)	0.11	0.24	0.72	4.42	7.36	14.86
Container Adsorption (mg/L)	0.03	0.00	0.03	0.01	0.03	0.03
Amount Adsorbed (mg/L)	1.85	4.85	9.31	15.40	22.61	25.44
Percent Adsorbed by Adsorbent	92.96%	95.28%	92.54%	77.66%	75.37%	63.08%
Amount Adsorbed (mg/kg)	1,850	4,850	9,310	15,400	22,610	25,440



Constant Soil Solution Ratio: 1:1000
Reaction container volume = 125 ml
Solution volume = 100 ml
Buffer = 0.1N K_2HPO_4
Average Initial pH (prior to peat addition) = 8.81
No subsequent pH adjustment
Shake time = 24 hr
Average Equilibrium pH = 8.29
Variable Initial Cu concentration:
2 mg/L, 5 mg/L, 10 mg/L,
20 mg/L, 30 mg/L, 40 mg/L

Figure 4-17. Batch Experiment #6 - Cu/Peat (Digested) - Constant Soil:Solution Ratio

4.2.6.2 Analysis of Batch Experiment #6

The fit to the Freundlich isotherm equation is plotted in Figure 4-18. The equation was found to be:

$$\log q_e = 3.8992 + 0.4921 \log C_e \qquad (r^2 = 0.9371) \qquad \{\text{Eqn. 4-17}\}$$

The value of K_f was found to be approximately 7,928. The value of n equaled 2.0319. Correlation analysis indicated that the equation fits the data fairly well.

The fit to the Langmuir isotherm is plotted in figure 4-19. The equation was found to be:

$$C_e/q_e = 0.000064 + 0.000036C_e \qquad (r^2 = 0.9772) \qquad \{\text{Eqn. 4-18}\}$$

The theoretical value of maximum adsorption, Q, was found to be 27,710 mg/kg, and the coefficient b equaled 0.5654 L/mg. Correlation analysis indicated the Langmuir equation fit the data even better than the Freundlich equation.

The fit to the Double Reciprocal isotherm is plotted in Figure 4-20. The equation was found to be:

$$1/q_e = 0.000053/C_e + 0.000033 \qquad (r^2 = 0.9821) \qquad \{\text{Eqn. 4-19}\}$$

The value of Q was found to be 30,442 mg/kg, and the coefficient b equaled 0.6148 L/mg. The value of r^2 was found to be 0.9821 which is a better fit than either the Freundlich or standard Langmuir equations.

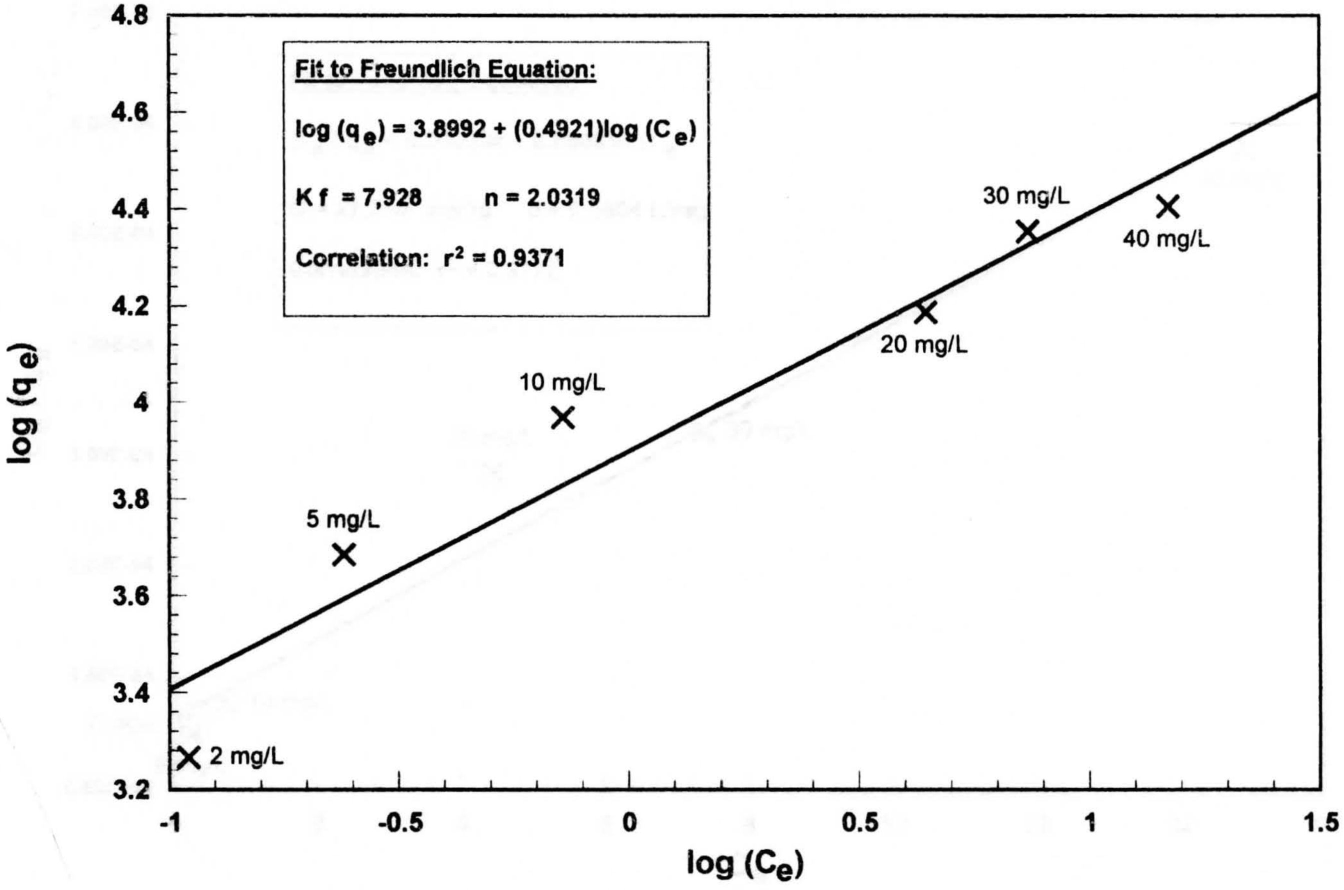


Figure 4-18. **Batch Experiment #6 - Cu/Peat (Digested) - Freundlich Isotherm**

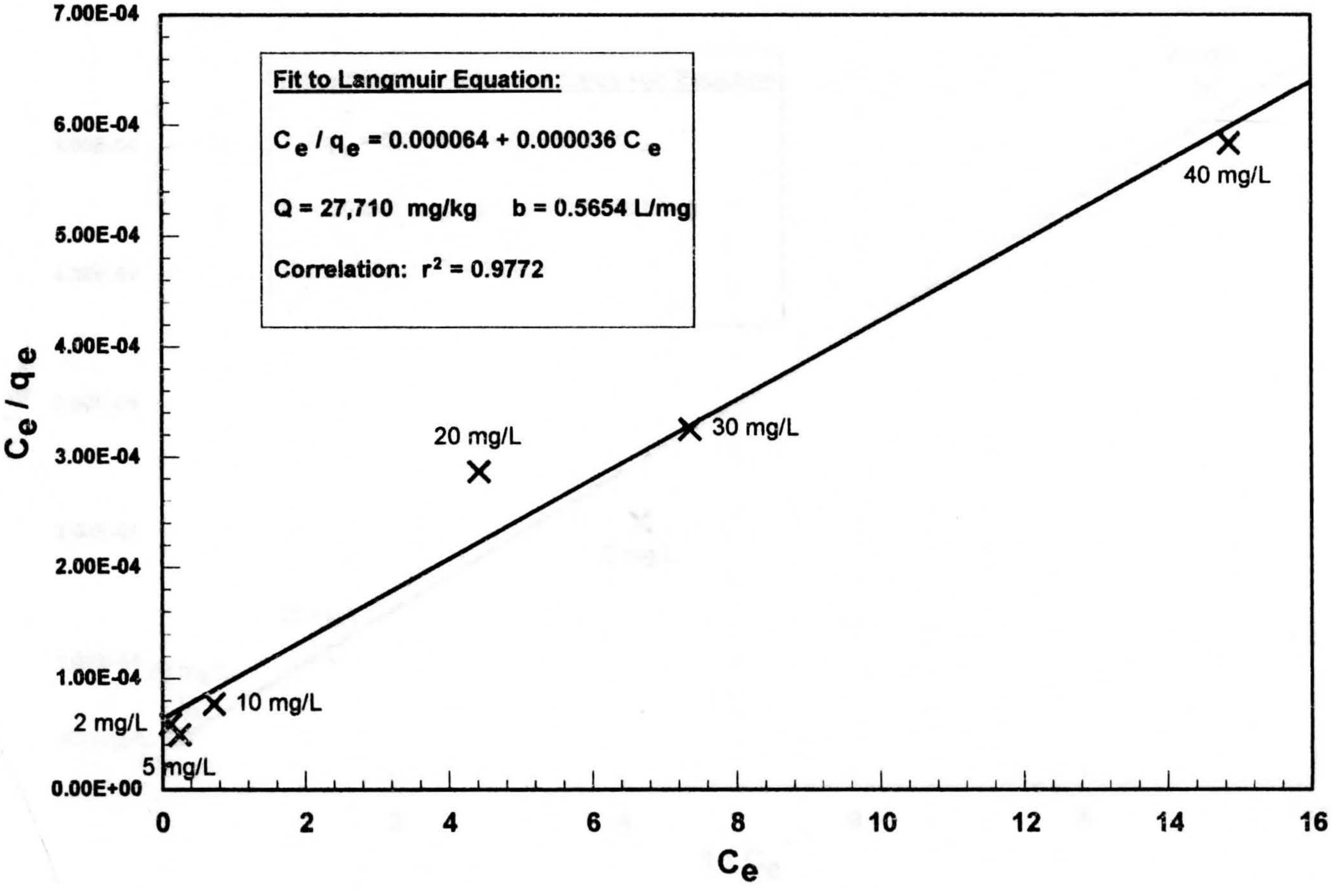


Figure 4-19. Batch Experiment #6 - Cu/Peat (Digested) - Langmuir Isotherm

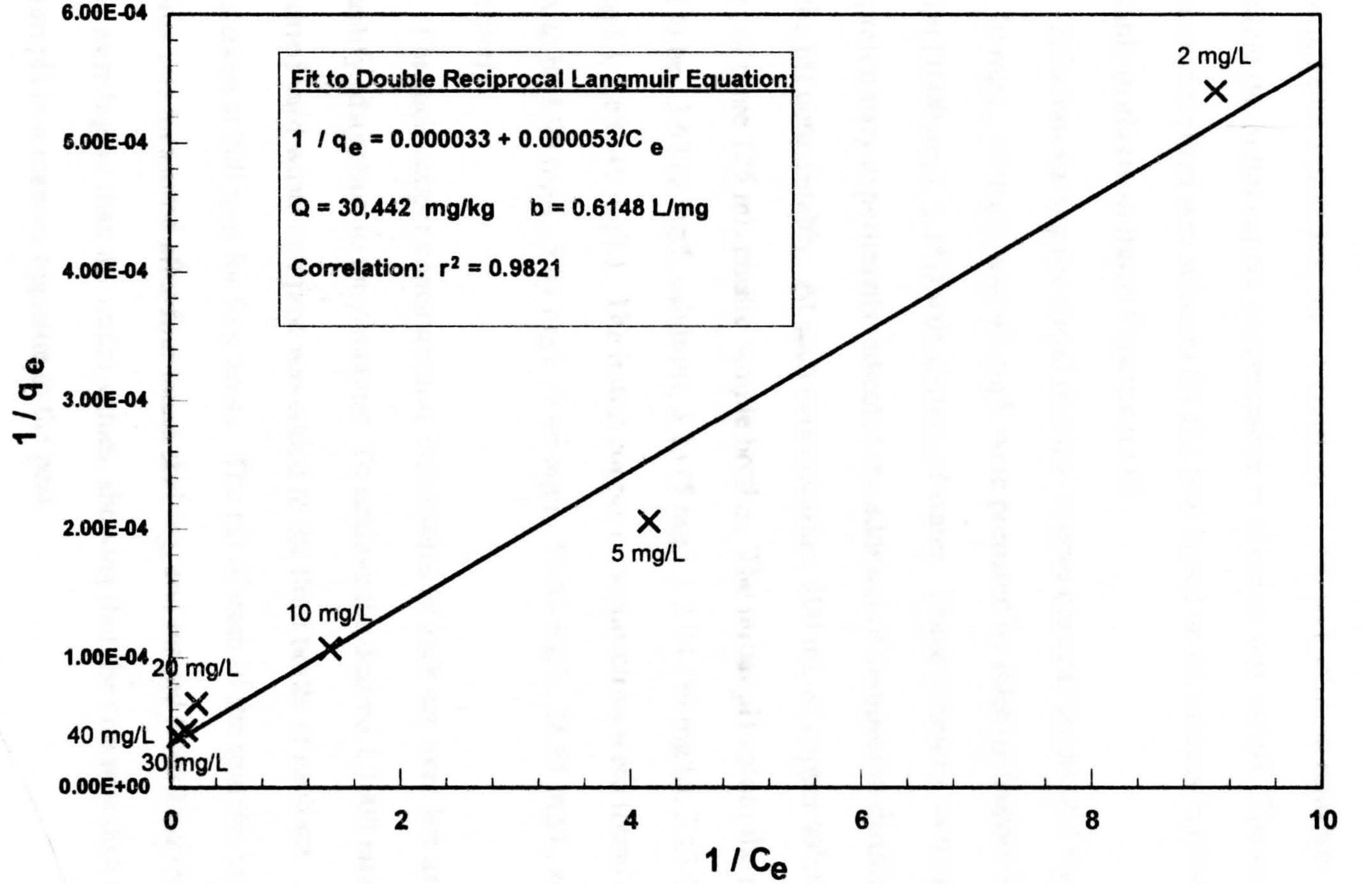


Figure 4-20. Batch Experiment #6 - Cu/Peat (Digested) - Double Reciprocal Langmuir Isotherm

4.2.7 Batch Experiment #7 - Copper/Compost with Constant Soil:Solution Ratio

4.2.7.1 Results of Batch Experiment #7

Yard waste compost was used instead of peat as the adsorbent in Batch Experiment #7. The sample utilized was finished, screened compost obtained from Browning Ferris Industries, Inc. A constant 1:1000 soil:solution ratio was utilized in this trial, while the initial copper concentration in solution was varied. The constant soil:solution method was selected for this trial based on its success in generating an acceptable isotherm in Batch Experiment #6.

Solutions having the initial nominal copper concentrations of 2 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, and 40 mg/L were prepared by diluting Copper Reference Solution (1000 mg/L ± 1%) with deionized water. These solutions were not buffered since preliminary experiments indicated the addition of compost to distilled water would raise the pH considerably. At each concentration, 100 mL of copper solution was added to a set of three 125 mL plastic sample bottles. The initial pH values the solutions were found to be: 3.62 (2 mg/L solution), 3.23 (5 mg/L), 2.94 (10 mg/L), 2.63 (20 mg/L), 2.48 (30 mg/L), 2.63 (40 mg/L). The initial copper concentrations were found subsequently by AA to be 1.99 mg/L, 5.01 mg/L, 9.46 mg/L, 19.40 mg/L, 28.81 mg/L, and 37.77 mg/L, respectively.

For each copper concentration, two bottles of each set were left as blanks in order to quantify adsorption to the container. To achieve the desired 1:1000 ratio, 0.100 g of oven-dried yard waste compost was added to the third bottle of each set. The containers were shaken at 200 rpm for four hours. The pH of each of the samples containing compost was measured after four hours shaking, and ranged from 3.6 to 6.4. These pH values were higher than the initial values, showing that the compost does influence solution pH in a manner opposite to the peat.

However, for the purpose of comparing the capacities of copper adsorption by peat and yard waste compost, this pH range was too broad, and much lower than that of the copper/peat experiments. Therefore, one to three drops of 1.0N NaOH were added to each sample to raise the pH value to the range of 7.2 to 7.7. The samples were returned to the shaker until the equilibration time reached 24 hours. The mixtures were then filtered through a Whatman GF/C filter, and the filters and residuals were discarded. The pH of each filtered compost solution and each blank was measured. The copper content of each sample was then measured by atomic absorption. Digestion was not performed on the compost samples.

The equilibrium pH ranged from 6.23 for the 40 mg/L sample to 6.96 for the 2 mg/L sample. Copper adsorption by the container varied considerably, and generally became greater as the initial copper concentration increased, ranging from 0.07 mg/L of copper adsorbed for the 2 mg/L sample to 3.67 mg/L of copper adsorbed for the 30 mg/L sample. These values of adsorption by the container were not expected since the lower pH of the blank samples (average = 2.9) ordinarily should inhibit the adsorption of cations from solution. A possible explanation is that in the previous batch experiments the phosphate buffer limited the amount of copper adsorbed by the container in the blank samples. Orthophosphates and polyphosphates are often used in water treatment as a corrosion inhibitor. In the batch experiments which utilized the phosphate buffer, the inside surface of the container may have been more susceptible to receiving a phosphate coating than to adsorbing copper from solution.

A summary of the results obtained during Batch Experiment #7 is presented in Table 4-10. On Figure 4-21 the amount of copper adsorbed by the compost versus the equilibrium copper concentration is shown.

Table 4-10 Summary of Results from Batch Experiment #7

Soil:Solution Ratio	1:1000	1:1000	1:1000	1:1000	1:1000	1:1000
Nominal Initial Cu Concentration (mg/L)	2	5	10	20	30	40
Measured Initial Cu Concentration (mg/L)	1.99	5.01	9.46	19.40	28.81	37.77
Adsorbate Volume (ml)	100	100	100	100	100	100
Initial pH	3.62	3.23	2.94	2.63	2.48	2.36
Adsorbent added (g)	0.100	0.100	0.100	0.100	0.100	0.100
pH after 4 hr shaking	6.42	5.88	5.30	4.60	3.52	3.59
1.0N NaOH added (drops)	2 drops	3 drops	5 drops	6 drops	6 drops	6 drops
Adjusted 4 hr pH	7.35	7.46	7.60	7.66	7.34	7.23
Adjusted Cu Conc. in Solution	1.99	5.01	9.46	19.40	28.81	37.77
Equilibrium pH	6.96	6.92	6.72	6.63	6.24	6.23
Undigested Results						
Equilibrium Cu Concentration (mg/L)	0.14	0.25	0.50	1.34	1.95	2.62
Container Adsorption (mg/L)	0.07	0.32	1.05	1.99	3.67	2.91
Amount Adsorbed (mg/L)	1.78	4.44	7.91	16.07	23.19	32.24
Percent Adsorbed by Adsorbent	89.45%	88.62%	83.62%	82.84%	80.49%	85.36%
Amount Adsorbed (mg/kg)	1,780	4,440	7,910	16,070	23,190	32,240

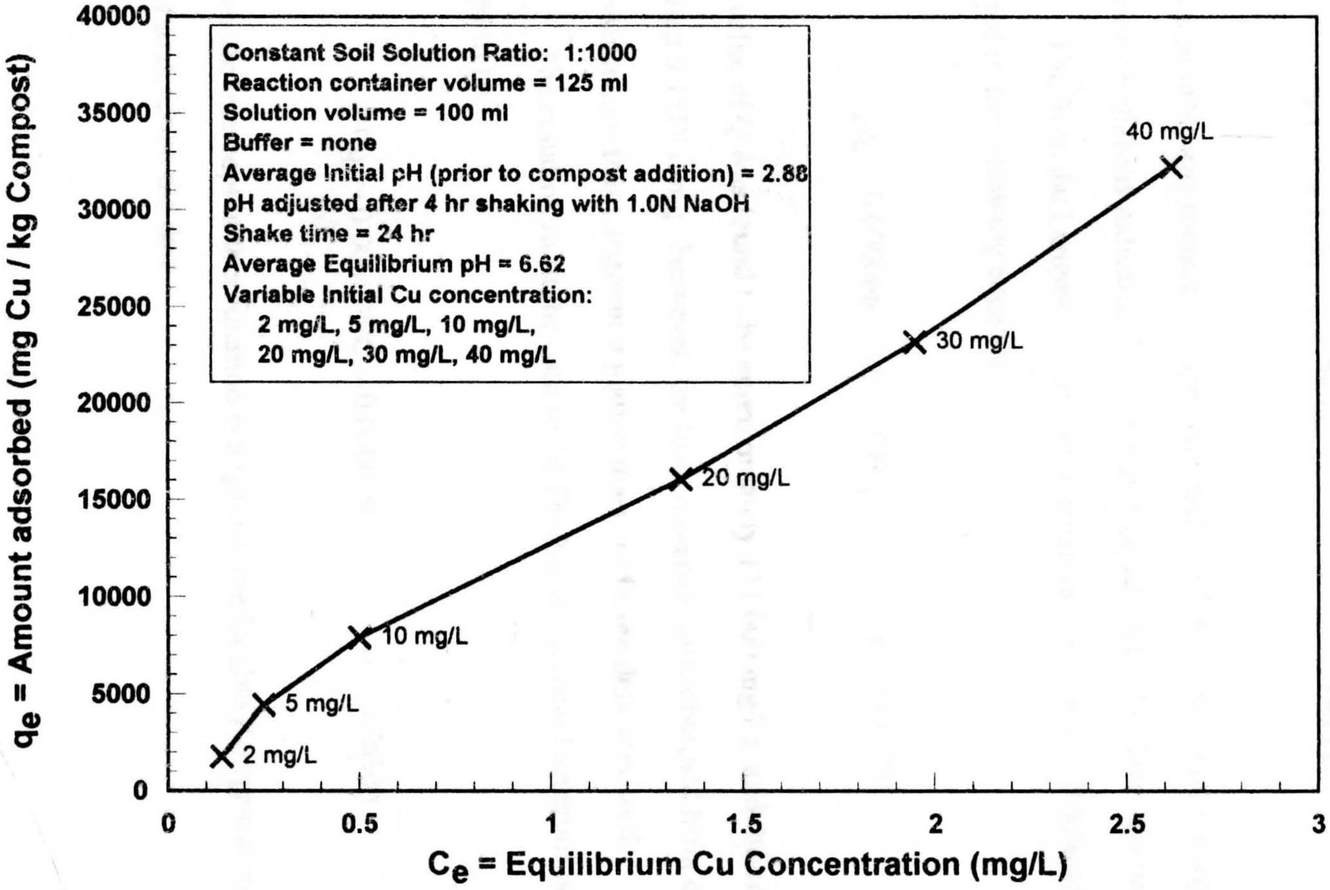


Figure 4-21. Batch Experiment #7 - Cu/Compost with Constant Soil:Solution Ratio

4.2.7.2 Analysis of Batch Experiment #7

The fit of the data to the Freundlich Isotherm is plotted in Figure 4-22. The equation was found to be:

$$\log q_e = 4.1204 + 0.9185 \log C_e \qquad (r^2 = 0.9839) \qquad \{\text{Eqn. 4-20}\}$$

The value of K_f was found to be approximately 13,200. The value of n equaled 1.0887. Correlation analysis indicated the Freundlich equation fit this data very well.

The fit to the Langmuir isotherm is given in Figure 4-23. Regression analysis resulted in the following equation:

$$C_e/q_e = 0.000066 + 0.000008C_e \qquad (r^2 = 0.4278) \qquad \{\text{Eqn. 4-21}\}$$

The value of Q was found to be approximately 131,000 mg/kg, and the coefficient b equaled 0.1159 L/mg. However, the low r-squared value obtained from correlation analysis means that Langmuir equation does not fit the data very well.

The equation to fit the data to the Double Reciprocal Langmuir isotherm was found to be:

$$1/q_e = 0.000075/C_e - 0.000009 \qquad (r^2 = 0.9693) \qquad \{\text{Eqn. 4-22}\}$$

Since the intercept in this equation is negative, the Double Reciprocal model cannot be used to describe the data.

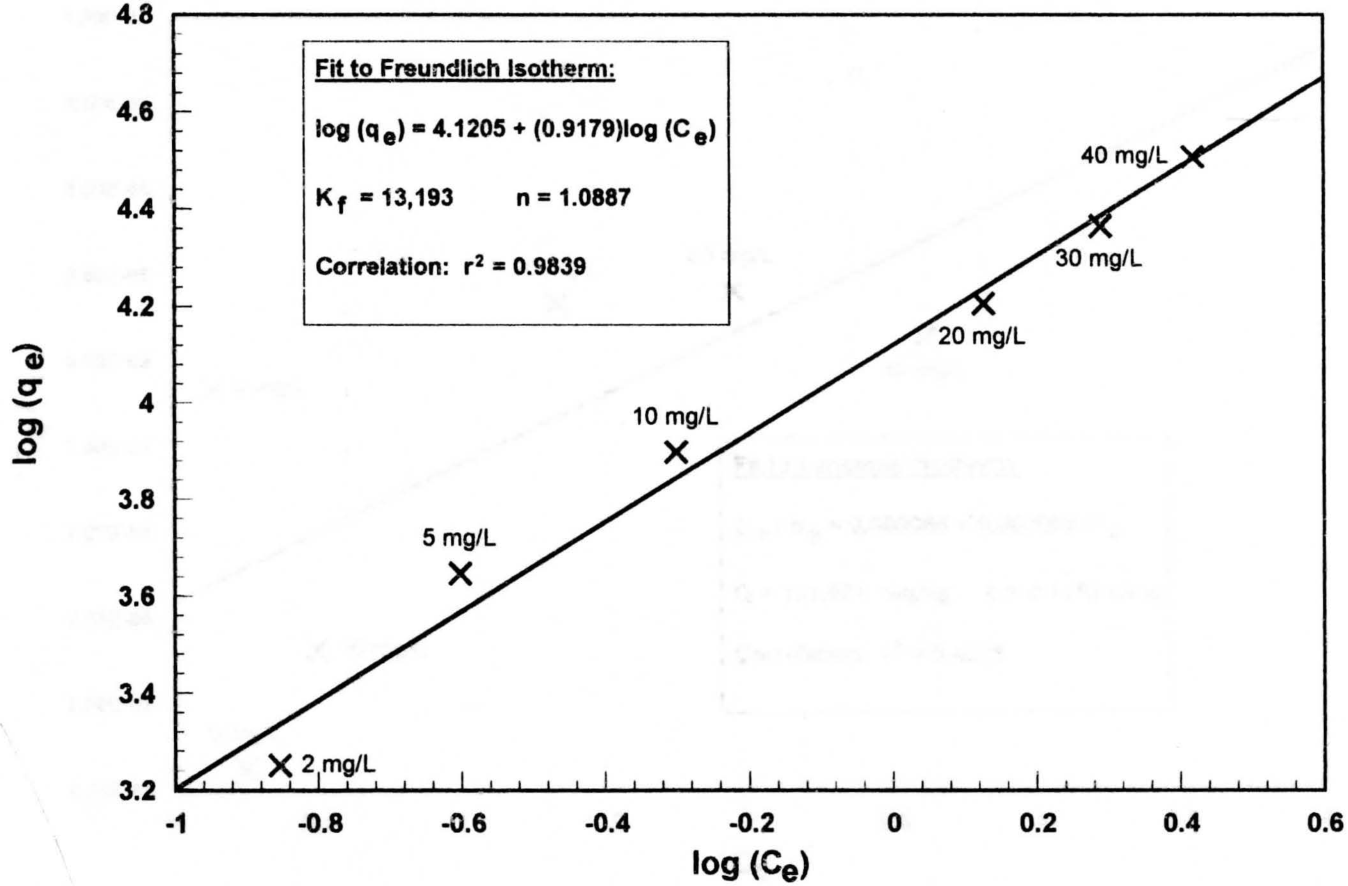


Figure 4-22. Batch Experiment #7 - Cu/Compost - Freundlich Isotherm

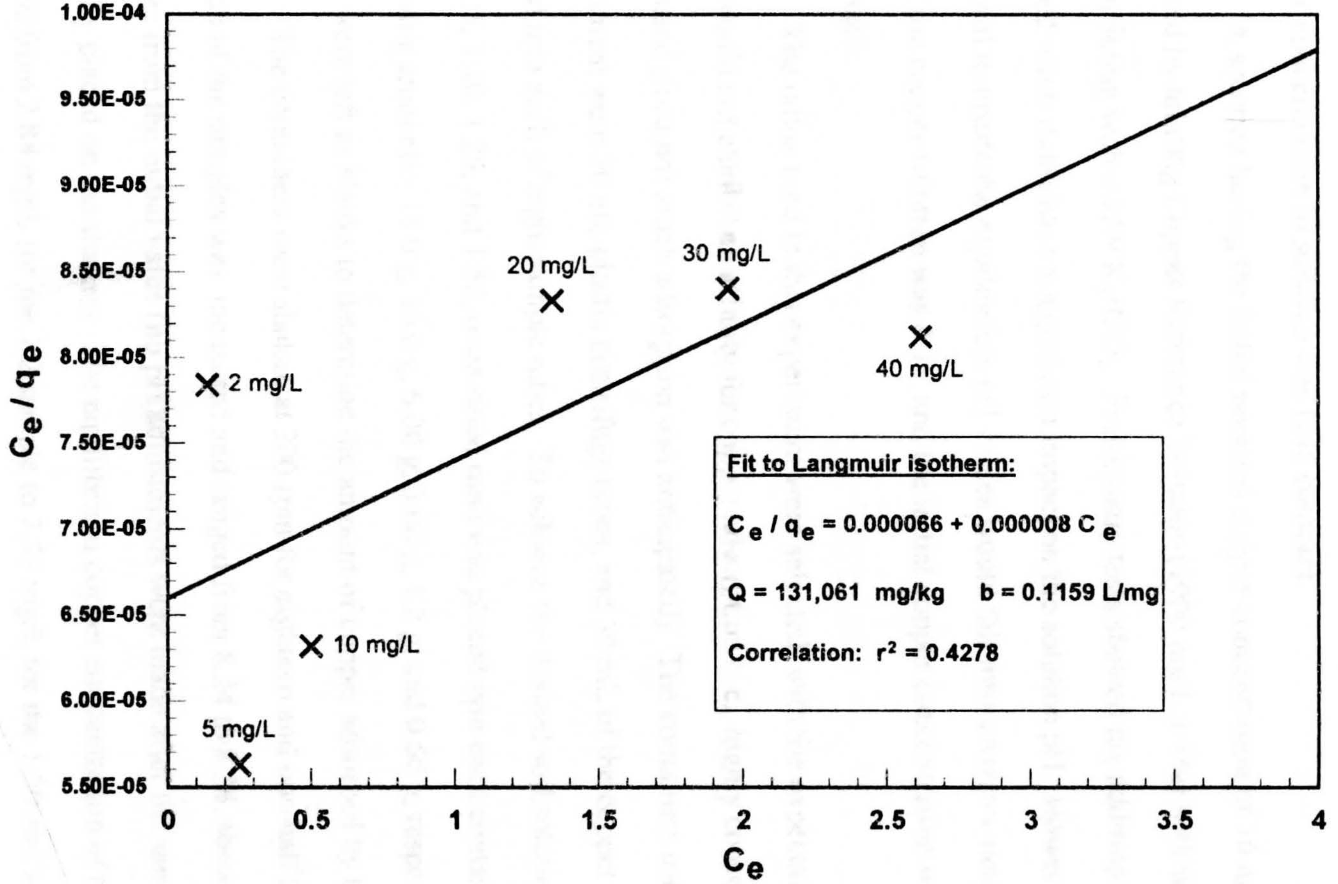


Figure 4-23. Batch Experiment #7 - Cu/Compost - Langmuir Isotherm

4.2.8 Batch Experiment #8 - Copper/Sand with Variable Soil:Solution Ratio

4.2.8.1 Results of Batch Experiment #8

In Batch Experiment #8, sand was used as the adsorbent and copper was used as the adsorbate. Variable soil:solution ratios were utilized in this trial, while the initial copper concentration in solution was held constant.

A solution having the initial nominal copper concentration of 10 mg/L was prepared by diluting Copper Reference Solution (1000 mg/L ± 1%) with deionized water and buffering with 0.02N K_2HPO_4. Preliminary tests showed the addition of sand to distilled water didn't have a significant impact on the solution pH. However, the buffer was used to insure the equilibrium pH values would fall into a narrow range. The initial pH of the copper solution was 8.36, and the initial copper concentration was measured as 9.46 mg/L.

The ratios used in this experiment were selected with the expectation that the sand would not exhibit an affinity for copper adsorption (i.e., highly concentrated ratios were used since not much adsorption was anticipated). The containers used in this experiment were 50 mL plastic centrifuge tubes, and 30 mL of the copper solution was placed into each of eight sample tubes. To achieve the desired soil:solution ratios of 1:2, 1:3, 1:5, 1:10, 1:25, and 1:50, oven-dried sand was placed into each container in the following amounts: 15.0 g, 10.0 g, 6.00 g, 3.00 g, 1.2 g, and 0.60 g, respectively. Two tubes were left as blanks to determine the amount of copper adsorbed by the container.

The containers were shaken at 200 rpm for eighteen and one-half hours. The pH of each of the samples was measured and ranged from 8.24 to 8.36, showing little change from the initial value (no pH adjustments were made after the samples were initially placed on the shaker). The equilibrium copper concentration of the samples ranged from 2.88 mg/L for the 1:2 sample to 7.35 mg/L for the 1:50 soil:solution ratio sample. The container adsorption was found to average 0.10 mg/L. The amount of copper adsorbed at each soil:solution ratio was calculated using Equation 4-1.

A summary of the results obtained from Batch Experiment #8 is presented in Table 4-11. As expected, the amount of copper adsorbed by the sand was considerably less than the values obtained for copper adsorption by peat. A plot of the amount of copper adsorbed versus the equilibrium copper concentration is shown in Figure 4-24.

Comparing Figures 4-9, 4-11, and 4-24, it appears that whenever the equilibrium copper concentration exceeds about 5 mg/L, the adsorption (mg/kg) dramatically increases, regardless of the adsorbent (peat or sand). This is probably attributable to precipitation caused by exceeding the copper solubility limit, which is a function of solution pH.

Table 4-11 Summary of Results from Batch Experiment #8

Soil:Solution Ratio	1:2	1:3	1:5	1:10	1:25	1:50
Initial Cu Concentration (mg/L)	9.46	9.46	9.46	9.46	9.46	9.46
Adsorbate Volume (ml)	30	30	30	30	30	30
Initial pH	8.36	8.36	8.36	8.36	8.36	8.36
Adsorbent added (g)	15.0	10.0	6.00	3.00	1.20	0.60
Equilibrium pH	8.30	8.26	8.24	8.28	8.30	8.36
Equilibrium Cu Concentration (mg/L)	2.88	5.35	5.99	6.90	7.31	7.35
Container Adsorption (mg/L)	0.10	0.10	0.10	0.10	0.10	0.10
Amount Adsorbed (mg/L)	6.48	4.01	3.37	2.46	2.05	2.01
Percent Adsorbed by Adsorbent	68.50%	42.39%	35.62%	26.00%	21.67%	21.25%
Amount Adsorbed (mg/kg)	13	12	17	25	51	101

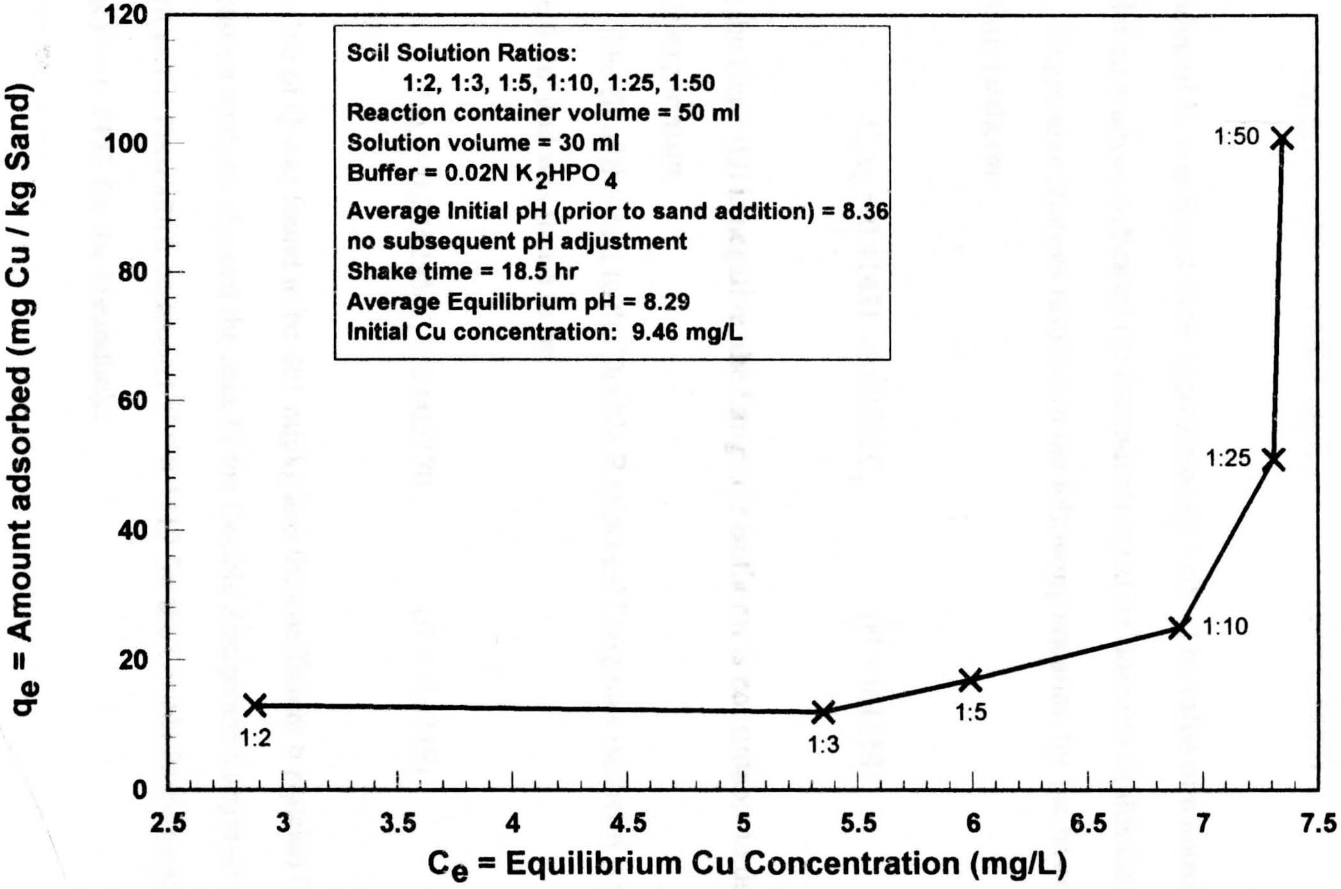


Figure 4-24. **Batch Experiment #8 - Cu/Sand with Variable Soil:Solution Ratio**

4.2.8.2 Analysis of Batch Experiment #8

The fit of the data to the Freundlich Isotherm is plotted in Figure 4-25. The equation was found to be:

$$\log q_e = 0.2257 + 1.5833 \log C_e \qquad (r^2 = 0.4483) \qquad \{\text{Eqn. 4-23}\}$$

The value of K_f was found to be approximately 1.68. The value of n equaled 0.6316. Correlation analysis indicated the Freundlich equation does not fit this data very well.

Regression analysis resulted in the following equation for the fit of the data to the Langmuir isotherm:

$$C_e/q_e = 0.41431 - 0.02722C_e \qquad (r^2 = 0.1154) \qquad \{\text{Eqn. 4-24}\}$$

Since the slope (Q) is negative, the Langmuir isotherm is not suitable to describe the data for this experiment.

The fit of the data to the Double Reciprocal Langmuir isotherm is plotted on Figure 4-26, and was found to be:

$$1/q_e = 0.246295/C_e + 0.002170 \qquad (r^2 = 0.4419) \qquad \{\text{Eqn. 4-25}\}$$

The value of Q was found to be 461 mg/kg and the coefficient b equaled 0.0088 L/mg. Correlation analysis showed the data fit the Double Reciprocal Langmuir equation about as well as the Freundlich equation ($r^2 = 0.4419$ for the Double Reciprocal Langmuir versus $r^2 = 0.4483$ for the Freundlich).

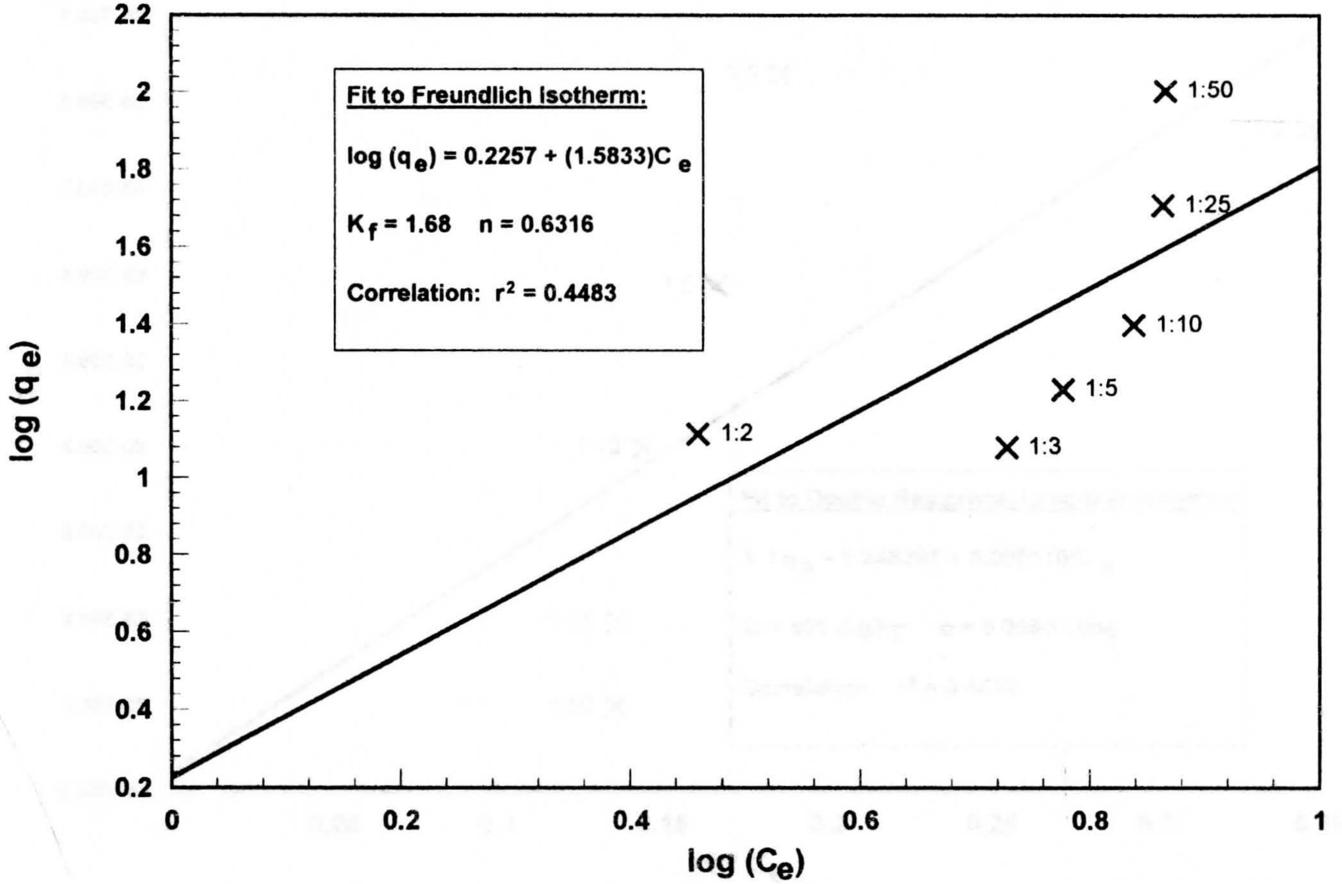


Figure 4-25. Batch Experiment #8 - Cu/Sand - Freundlich Isotherm

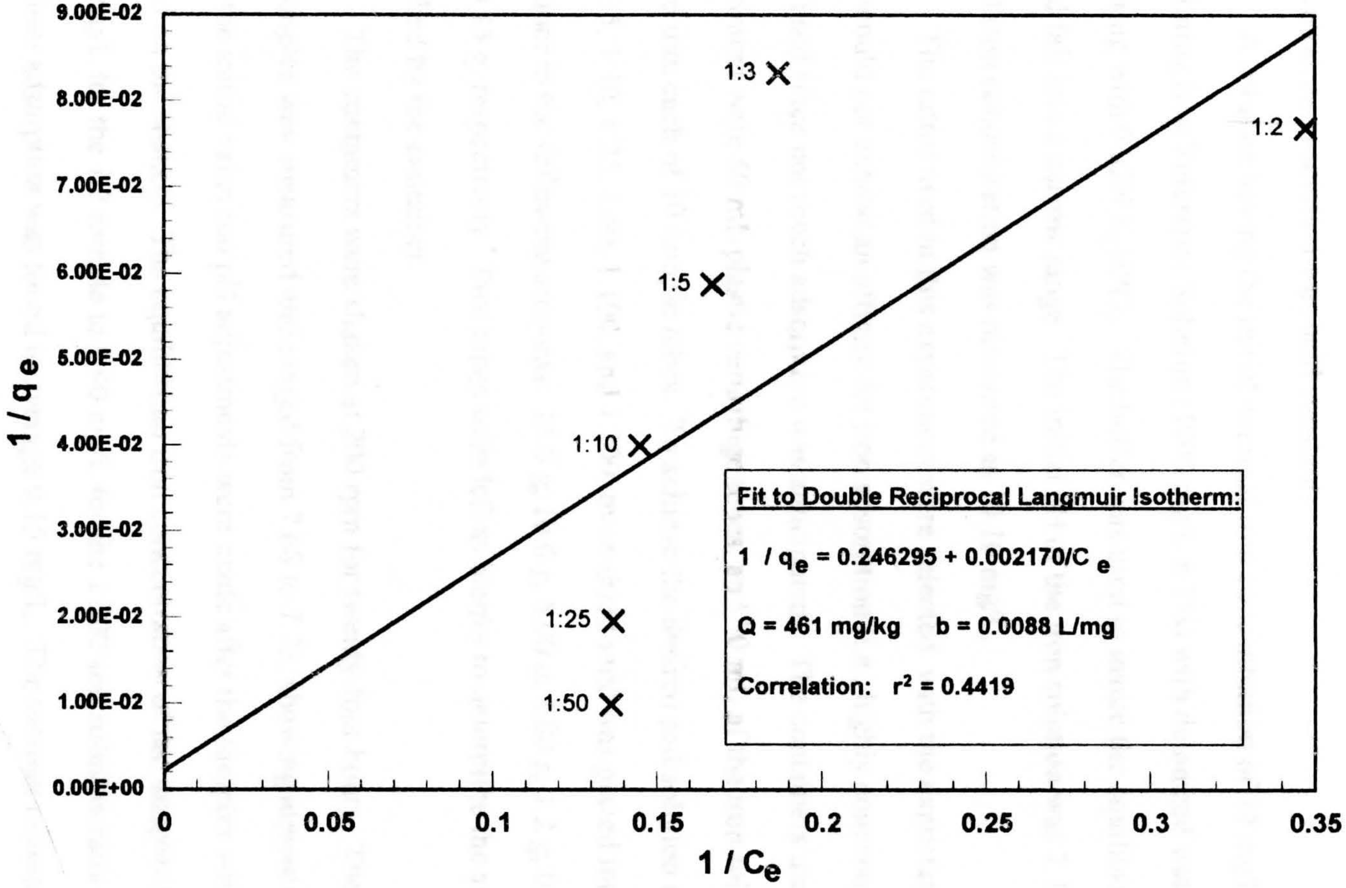


Figure 4-26. Batch Experiment #8 - Cu/Sand - Double Reciprocal Langmuir Isotherm

4.2.9 Batch Experiment #9 - Iron/Sand with Variable Soil:Solution Ratio

4.2.9.1 Results of Batch Experiment #9

Sand was used as the adsorbent in Batch Experiment #9, and iron was used as the adsorbate. Variable soil:solution ratios were utilized in this trial, while the initial iron concentration in solution was held constant.

A solution having the initial nominal iron concentration of 10 mg/L was prepared by diluting Iron Reference Solution (1000 mg/L ± 1%) with deionized water and buffering with 0.02N K_2HPO_4. The buffer was used to insure the equilibrium pH values would fall into a narrow range. The initial pH of the iron solution was 7.73, and the initial iron concentration was measured as 10.10 mg/L.

The ratios used in this experiment were selected with the expectation that the sand would not exhibit an affinity for iron adsorption (i.e., highly concentrated ratios were used since not much adsorption was anticipated). The containers used in this experiment were 50 mL plastic centrifuge tubes, and 30 mL of the iron solution was placed into each of 10 sample tubes. To achieve the desired soil:solution ratios of 1:2, 1:3, 1:5, 1:10, 1:25, 1:50, 1:100, and 1:200, oven-dried sand was placed into each container in the following amounts: 15.0 g, 10.0 g, 6.00 g, 3.00 g, 1.2 g, 0.60 g, 0.30 g, and 0.15 g, respectively. Two tubes were left as blanks to determine the amount of iron adsorbed by the container.

The containers were shaken at 200 rpm for twenty-four hours. The pH of each of the samples was measured and ranged from 7.68 to 7.72, showing almost no change from the initial value (no pH adjustments were made after the samples were initially placed on the shaker). The equilibrium iron concentration of the samples ranged from 5.14 mg/L for the 1:2 sample to 9.90 mg/L for the 1:200 soil:solution ratio sample. The container adsorption was found to average 0.15 mg/L. The amount of iron adsorbed at each soil:solution ratio was calculated using Equation 4-1.

A summary of the results obtained from Batch Experiment #9 is presented in Table 4-12. As expected, the values obtained for the amount of iron adsorbed by the sand were very small. A plot of the amount of iron adsorbed versus the equilibrium iron concentration is shown in Figure 4-27.

Table 4-12 Summary of Results from Batch Experiment #9

Soil:Solution Ratio	1:2	1:3	1:5	1:10	1:25	1:50	1:100	1:200
Initial Fe Concentration (mg/L)	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10
Adsorbate Volume (ml)	30	30	30	30	30	30	30	30
Initial pH	7.73	7.73	7.73	7.73	7.73	7.73	7.73	7.73
Adsorbent added (g)	15.0	10.0	6.00	3.00	1.20	0.60	0.30	0.15
Equilibrium pH	7.71	7.71	7.72	7.72	7.72	7.68	7.72	7.72
Equilibrium Fe Concentration (mg/L)	5.14	5.45	7.23	9.60	9.81	9.81	9.83	9.90
Container Adsorption (mg/L)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Amount Adsorbed (mg/L)	4.81	4.5	2.72	0.35	0.14	0.14	0.12	0.05
Percent Adsorbed by Adsorbent	47.62%	44.55%	26.93%	3.47%	1.39%	1.39%	1.19%	0.50%
Amount Adsorbed (mg/kg)	9.6	13.5	13.6	3.5	3.5	7.0	12.0	10.0

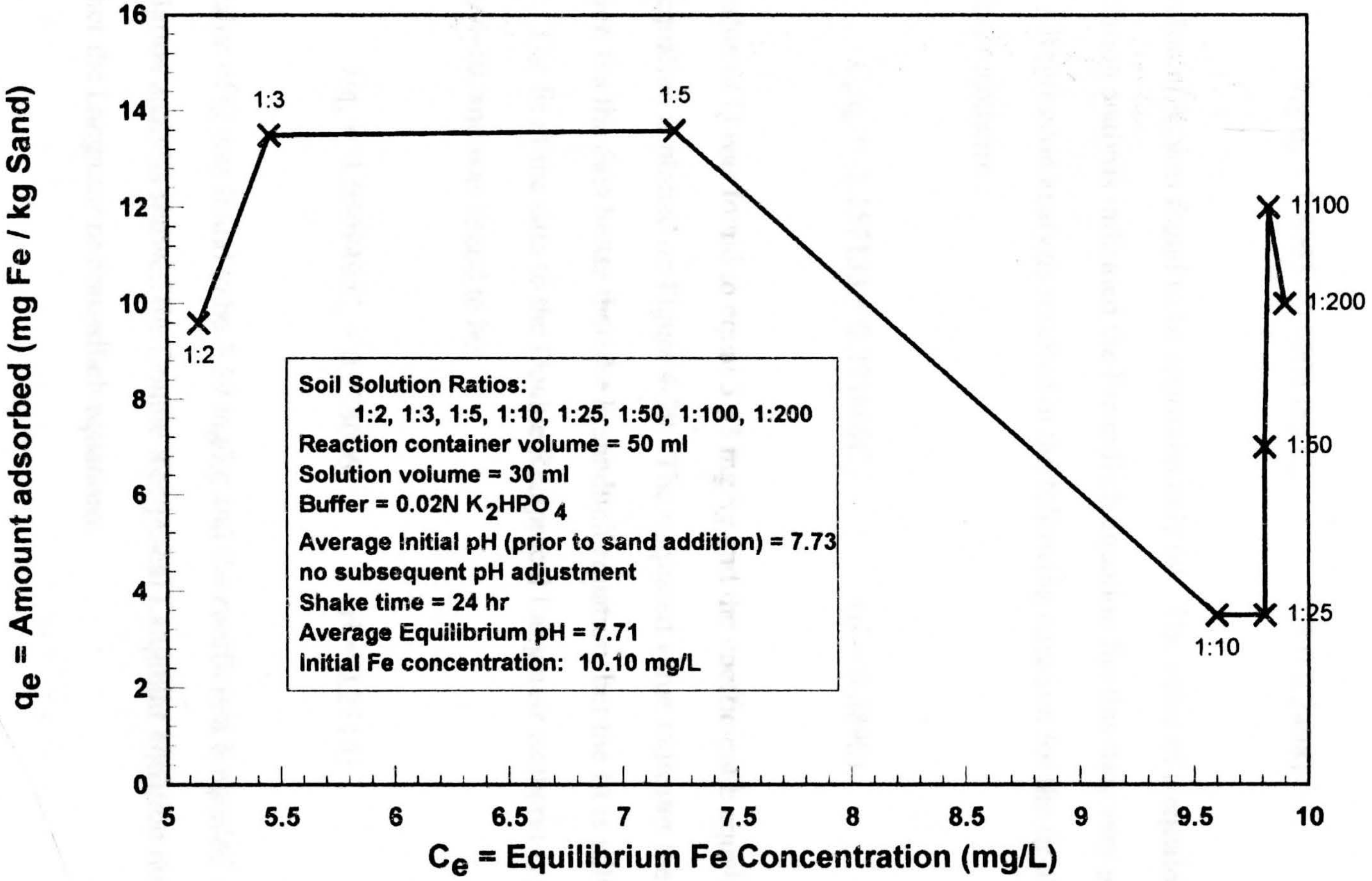


Figure 4-27. Batch Experiment #9 - Fe/Sand with Variable Soil:Solution Ratio

4.2.9.2 Analysis of Batch Experiment #9

The fit of the data to the Freundlich Isotherm is plotted in Figure 4-28. The equation was found to be:

$$\log q_e = 1.8063 - 0.9906 \log C_e \qquad (r^2 = 0.2498) \qquad \{\text{Eqn. 4-26}\}$$

The value of K_f was found to be approximately 64. The value of n equaled -1.0095. Correlation analysis indicated the Freundlich equation fits this data very poorly.

Regression analysis resulted in the following equation for the fit of the data to the Langmuir isotherm :

$$C_e/q_e = -1.157133 + 0.291809C_e \qquad (r^2 = 0.3890) \qquad \{\text{Eqn. 4-27}\}$$

The value of Q was found to equal 3.43 mg/kg and the coefficient b equaled -0.2522. This equation is plotted on Figure 4-29. The r-squared value indicates the Langmuir equation fits the data better than the Freundlich equation, but the fit is still poor.

The fit of the data to the Double Reciprocal Langmuir isotherm is plotted on Figure 4-30, and was found to be:

$$1/q_e = -1.050949/C_e + 0.278606 \qquad (r^2 = 0.2115) \qquad \{\text{Eqn. 4-28}\}$$

The value of Q was found to be 3.59 mg/kg and the coefficient b equaled -0.2651 L/mg. Correlation analysis showed the Double Reciprocal Langmuir equation did not fit as well as either the Langmuir or Freundlich equations.

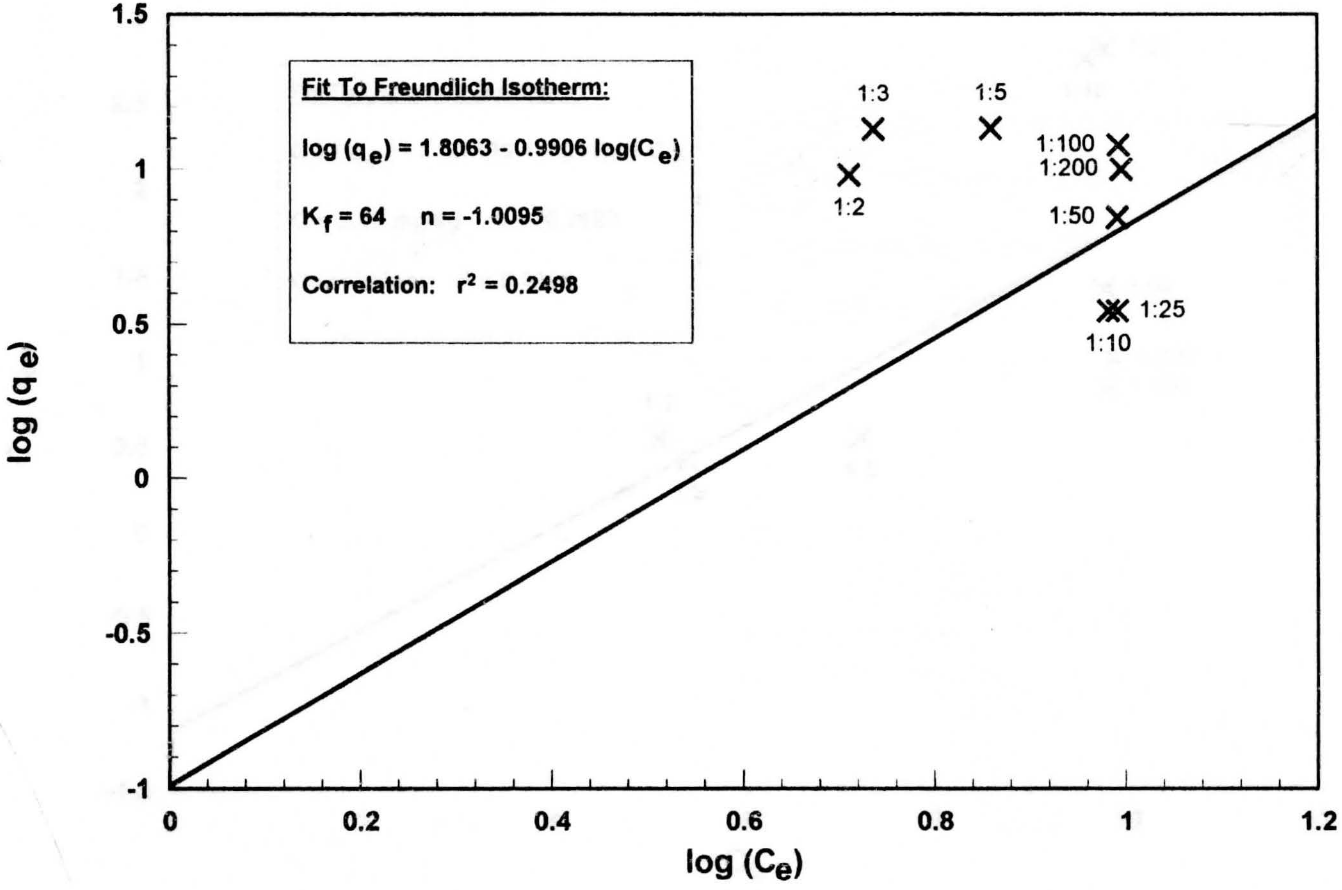


Figure 4-28. Batch Experiment #9 - Fe/Sand - Freundlich Isotherm

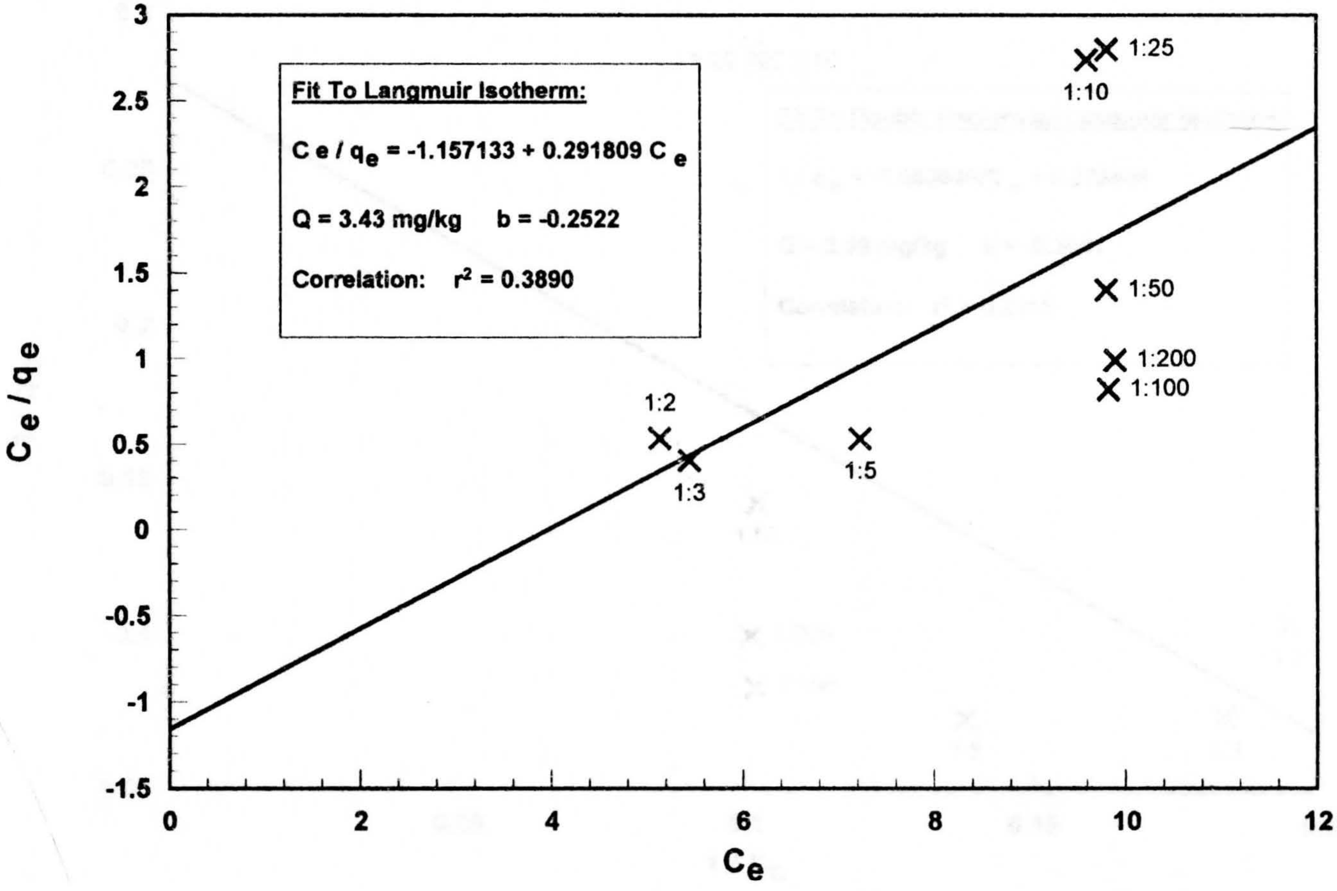


Figure 4-29. Batch Experiment #9 - Fe/Sand - Langmuir Isotherm

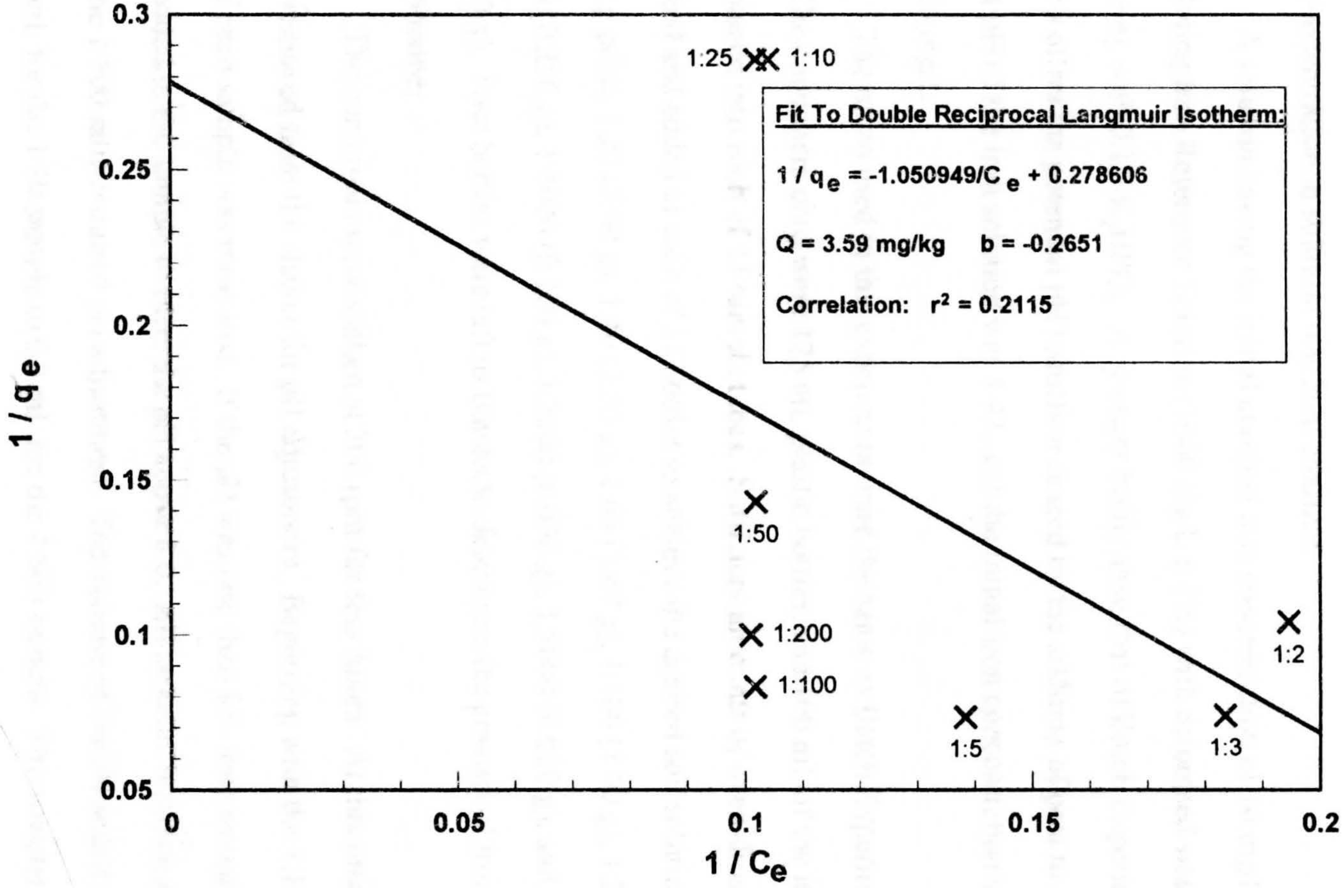


Figure 4-30. Batch Experiment #9 - Fe/Sand - Double Reciprocal Langmuir Isotherm

4.2.10 Batch Experiment #10 - Iron/Peat with Variable Soil:Solution Ratio

4.2.10.1 Results of Batch Experiment #10

Iron was used as the adsorbate in Batch Experiment #10, and peat was utilized as the adsorbent. Variable soil:solution ratios were utilized in this trial, while the initial iron concentration in solution was held constant.

A solution having the initial nominal iron concentration of 10 mg/L was prepared by diluting Iron Reference Solution (1000 mg/L ± 1%) with deionized water and buffering with 0.1N K_2HPO_4. A stronger buffer than that of Batch Experiment #9 was used to offset the potential pH reduction caused by the addition of peat to solution. The initial pH of the iron solution was 8.42, and the initial iron concentration was measured as 9.60 mg/L.

The ratios used in this experiment were the same as Batch Experiments #3 and #4. The containers used were 125 mL plastic bottles, and 100 mL of the iron solution was placed into each of 15 sample tubes. Sufficient amounts of oven-dried peat were weighed and added to each of 11 bottles to achieve the desired soil:solution ratios of 1:10 (10.0 g peat), 1:20 (5.00 g), 1:40 (2.50 g), 1:60 (1.67 g), 1:100 (1.00 g), 1:200 (0.500 g), 1:500 (0.200 g), 1:1000 (0.100 g), 1:2000 (0.050 g), 1:5000 (0.020 g), and 1:10,000 (0.010 g). Four bottles were left as blanks to determine the amount of iron adsorbed by the container.

The containers were shaken at 200 rpm for four hours. At this time the samples were removed from the shaker for pH adjustment. Beginning with the 1:10 sample, the pH of each sample was measured. If the pH was less than 8.0, then enough 1.0N NaOH was added to the sample to raise the pH above 8.0. All samples between the 1:10 ratio and the 1:500 ratio required pH adjustment. The volume of NaOH added ranged from 11.0 mL for the 1:10 sample to 0.2 mL for the 1:500 sample. The samples were returned to the shaker and allowed to mix for a total of twenty-four hours.

After 24 hours, the samples were removed from the shaker, and separated by filtering through a Whatman GF/C glass fiber filter. Equilibrium pH values ranged from 7.23 for the 1:10 ratio sample to 8.37 for the 1:10,000 ratio sample.

The equilibrium iron concentration of the samples did not follow the expected pattern established during the copper batch experiments where the copper concentration in solution was lowest at the most concentrated soil:solution ratio (e.g., 1:10), increased over the range of ratios used, and was highest at the least concentrated ratio (e.g., 1:10,000). Instead, the equilibrium iron concentration for all samples which were treated with NaOH to raise the pH showed the opposite trend - the iron concentration was lowest at the 1:500 sample and increased over the range of more highly concentrated samples to the 1:10 sample. The iron concentration increased over the range of low concentration samples (1:1000 to 1:10,000) as expected. Overall, the iron concentration in solution ranged from 4.05 mg/L to 9.41 mg/L and followed this pattern:

1:500 < 1:200 < 1:100 < 1:60 < 1:40 < 1:20 < 1:10 < 1:1000 < 1:2000 < 1:5000 < 1:10,000

The container adsorption was found to average 0.18mg/L. The amount of iron adsorbed at each soil:solution ratio was calculated using Equation 4-1. A summary of the results obtained from Batch Experiment #10 is presented in Table 4-13. Figure 4-31 shows a plot of the amount of iron adsorbed versus the equilibrium iron concentration.

The samples were treated by nitric acid digestion after the analysis presented above. Equilibrium iron concentration of the digested samples showed a pattern very similar to the untreated samples, although the concentration of the 1:10 sample was much lower than expected from the untreated sample data. The amount of iron adsorbed at each soil:solution ratio for the digested samples was calculated using Equation 4-1. These results are given in Table 4-13, also. The amount of iron adsorbed versus the equilibrium iron concentration is shown on Figure 4-32.

The curves in Figures 4-31 and 4-32 do not resemble typical adsorption isotherms. These results are believed to reflect a complex combination of mechanisms, including a pH adsorption edge, iron speciation, and complexation by colloidal material. The values obtained for iron adsorption by peat (mg/kg) are considerably less than the values obtained for copper adsorption by peat (mg/kg) by about one order of magnitude.

Based on this data, the results of the analysis for the background concentrations of copper and iron in the peat, and the affinities for cation exchange and chelation presented in Section 2.3.3.3, the following hypothesis may be formed. It can be reasoned that if a given mass of peat contains a constant, finite number of adsorption sites, then the adsorption observed in these experiments was influenced more by the presence of carboxylic, phenolic hydroxyl, and heterocyclic groups of humic colloids (resulting in cation exchange) than by the presence of polar multidentate ligands such as alcohols and aldehydes (which would result in cation chelation).

Further study involving solutions made of a mixture of copper, iron, and/or other metals should be conducted to examine the effects of competition for available adsorption sites between metals encountered in treatment wetlands.

Table 4-13 Summary of Results from Batch Experiment #10

Soil:Solution Ratio	1:10	1:20	1:40	1:60	1:100	1:200	1:500	1:1000	1:2000	1:5000	1:10,000
Initial Fe Concentration (mg/L)	9.60	9.60	9.60	9.60	9.60	9.60	9.60	9.60	9.60	9.60	9.60
Adsorbate Volume (ml)	100	100	100	100	100	100	100	100	100	100	100
Initial pH	8.42	8.42	8.42	8.42	8.42	8.42	8.42	8.42	8.42	8.42	8.42
Adsorbent added (g)	10.00	5.00	2.50	1.67	1.00	0.50	0.20	0.10	0.05	0.02	0.01
pH after 4 hr shaking	4.65	5.90	6.73	7.02	7.28	7.59	7.88	8.03	N/P	N/P	N/P
1.0N NaOH added (ml)	11.0	5.5	2.8	2.2	1.5	0.5	0.2	0.0	0.0	0.0	0.0
Adjusted 4 hr pH	8.05	8.04	8.05	8.38	8.19	8.03	8.05	N/A	N/A	N/A	N/A
Adjusted Fe Conc. in Solution	8.65	9.10	9.34	9.39	9.46	9.55	9.58	9.60	9.60	9.60	9.60
Equilibrium pH	7.23	7.40	7.70	7.93	8.01	8.03	8.14	8.12	8.24	8.34	8.37
Undigested Results											
Equilibrium Fe Concentration (mg/L)	7.19	6.95	6.89	6.17	6.14	4.74	4.05	7.80	9.16	9.35	9.41
Container Adsorption (mg/L)	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Amount Adsorbed (mg/L)	1.28	1.97	2.27	3.04	3.14	4.63	5.35	1.62	0.26	0.07	0.01
Percent Adsorbed by Adsorbent	14.78%	21.64%	24.29%	32.40%	33.18%	48.49%	55.85%	16.88%	2.71%	0.73%	0.10%
Amount Adsorbed (mg/kg)	14	42	93	186	319	931	2,681	1,620	520	350	100
Digested Results											
Digested Equilibrium Fe Concentration (mg/L)	5.84	7.16	7.20	5.94	5.89	4.31	3.70	7.44	9.06	9.41	9.21
Amount Adsorbed (mg/L)	2.63	1.76	1.96	3.27	3.39	5.06	5.70	1.98	0.36	0.01	0.21
Percent Adsorbed by Adsorbent	30.39%	19.34%	20.97%	34.85%	35.82%	53.00%	59.50%	20.63%	3.75%	0.10%	2.19%
Amount Adsorbed (mg/kg)	29	37	81	200	344	1,018	2,856	1,980	720	50	2,100

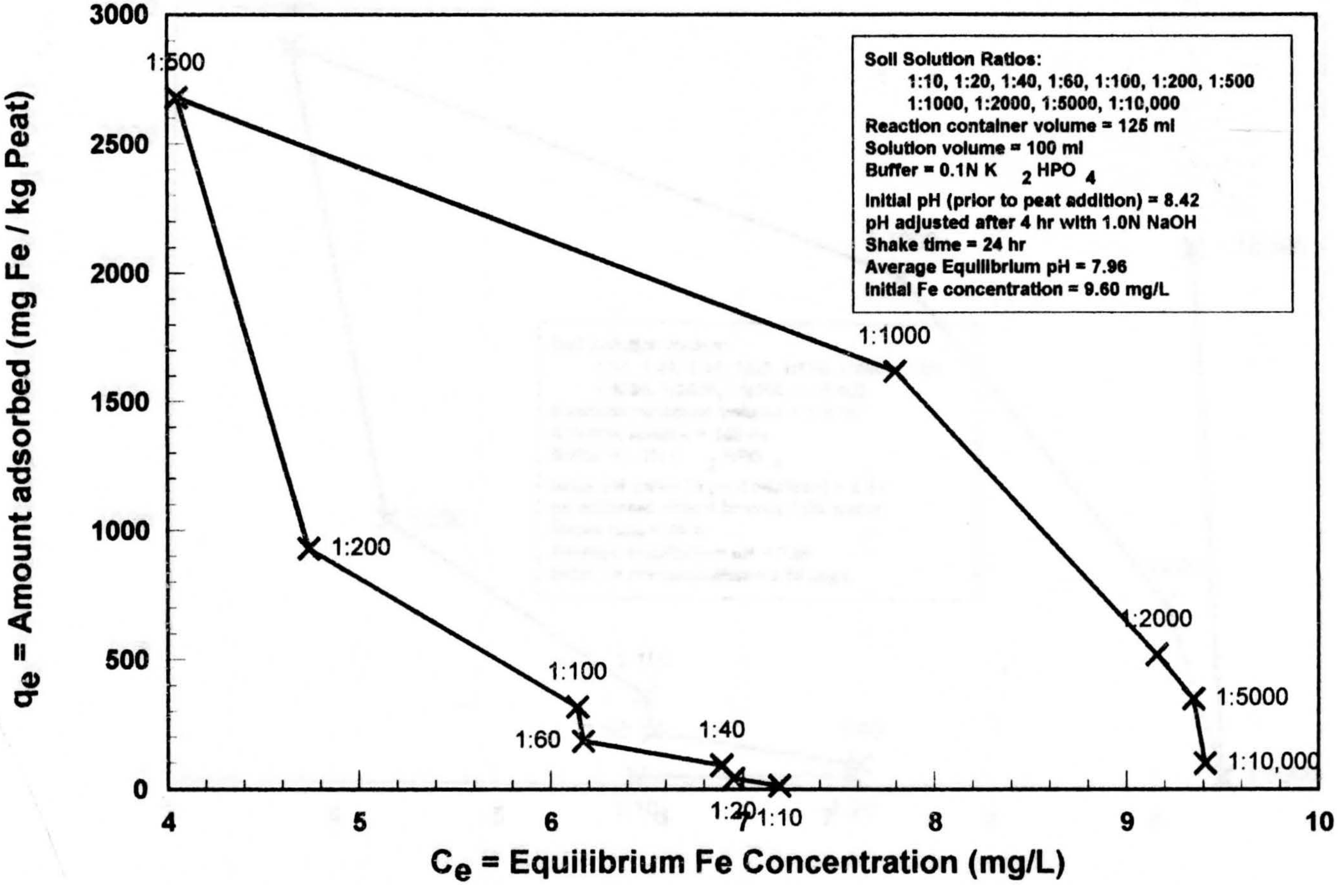


Figure 4-31. Batch Experiment #10 (Undigested) - Fe/Peat with Variable Soil:Solution Ratio

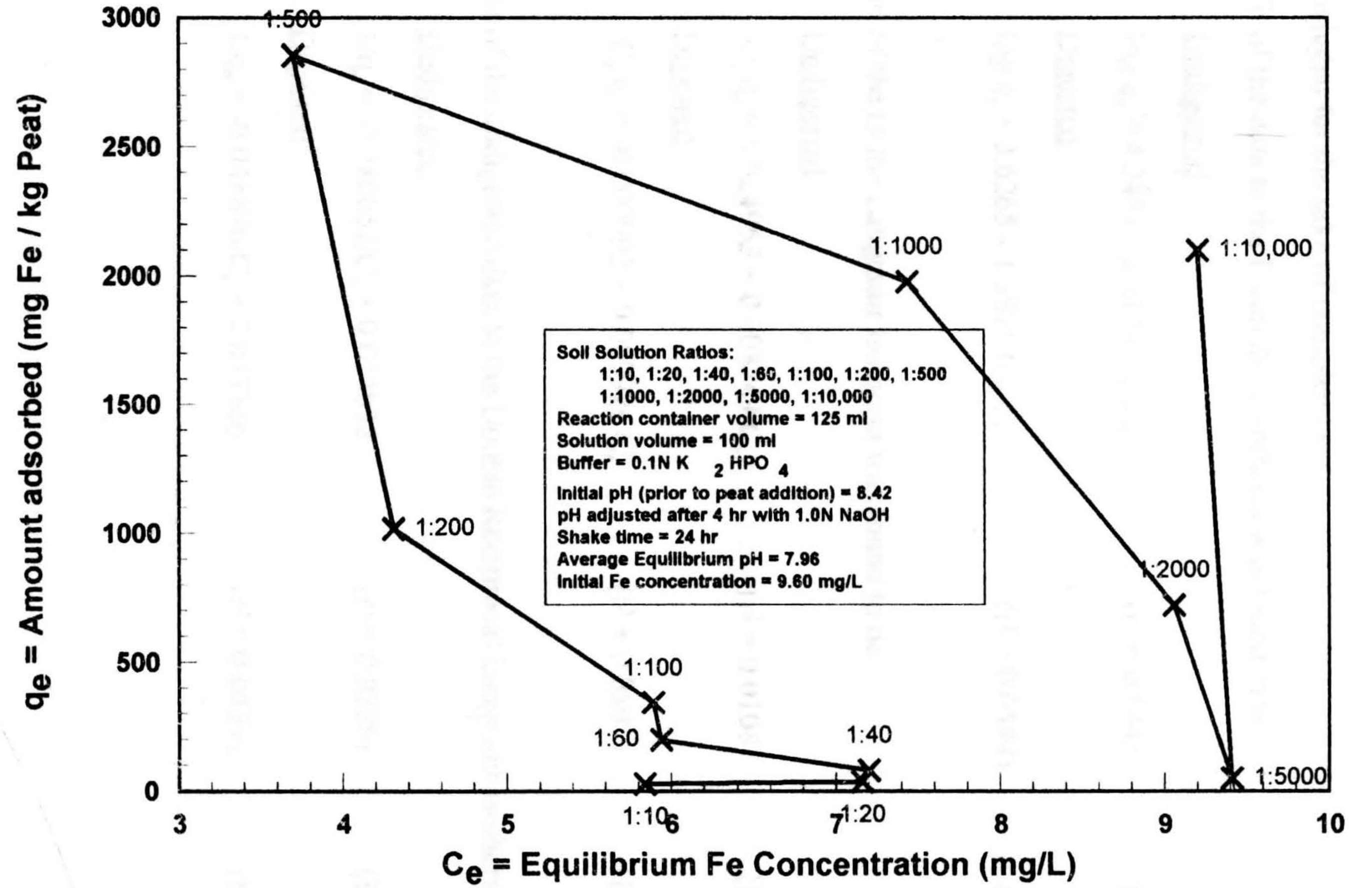


Figure 4-32. Batch Experiment #10 (Digested) - Fe/Peat with Variable Soil:Solution Ratio

4.2.10.2 Analysis of Batch Experiment #10

Regression analysis of the data obtained in Batch Experiment #10 showed that none of the adsorption isotherm equations (Freundlich, Langmuir, or Double Reciprocal Langmuir) was suitable to describe the results of this experiment. The following results are included for the sake of completeness.

The fit of the data to the Freundlich Isotherm was found to be:

Undigested

$\log q_e = 4.2477 - 2.2123 \log C_e$ ($r^2 = 0.1444$) {Eqn. 4-29}

Digested

$\log q_e = 3.6265 - 1.3875 \log C_e$ ($r^2 = 0.0599$) {Eqn. 4-30}

The fit of the to the Langmuir Isotherm was found to be:

Undigested

$C_e/q_e = 0.024963 + 0.008749\, C_e$ ($r^2 = 0.0108$) {Eqn. 4-31}

Digested

$C_e/q_e = -0.000092 + 0.009926\, C_e$ ($r^2 = 0.0501$) {Eqn. 4-32}

The fit of the undigested data to the Double Reciprocal Langmuir isotherm was:

Undigested

$1/q_e = -0.080052/C_e + 0.024032$ ($r^2 = 0.0286$) {Eqn. 4-33}

Digested

$1/q_e = -0.048896/C_e + 0.017366$ ($r^2 = 0.0433$) {Eqn. 4-34}

4.3. Column Experiment Results

4.3.1 Selection of the Adsorbate and the Adsorbent for the Column Experiment

The results of the Batch Experiments were examined and used as the basis for the selection of copper as the adsorbate and peat as the adsorbent used in the column experiment. Peat was shown to exhibit an affinity for copper adsorption throughout Batch Experiments #1 through #6. Yard waste compost also was shown to be an effective adsorbent of copper in Batch Experiment #7. However, the compost was incorporated into this study to confirm that a substrate's adsorptive capacity for metals is related to the presence of organic matter in the substrate. It is hoped that a detailed analysis of the adsorption of metals by yard waste compost will be performed as a follow-up to this study.

The results obtained from Batch Experiment #8 involving iron and peat were not consistent with the results obtained from the copper/peat experiments. While the peat exhibited some capacity to adsorb iron, it is suspected that the peat used in this study may have been near its capacity for iron adsorption at the time it was mined and processed. The relatively high background concentration of iron in the peat may possibly be due to adsorption occurring naturally as the peat developed in the bog or fen from which it came. Further study of the interactions between iron and peat is necessary.

As expected, in Batch Experiments #9 and #10 sand showed comparatively little capacity for the adsorption of either metal studied. If metal removal is a primary concern, constructed wetland systems designed with sand as the principal substrate material must rely upon mechanisms of metal removal other than adsorption to the substrate to accomplish the desired treatment.

4.3.2 General Overview of Column Experiment

The behavior of the copper-peat adsorption system was examined during the column experiment which will be categorized in two separate ways. The first of these is based on the hydraulic residence time (HRT) of the system, which can be divided into three distinct phases - I, II, and III. Phase I was conducted during the initial column startup (time = 0 to 34 hours). During this phase, the pump was set to maintain an estimated HRT of 1.4 days (33 hours) in order to flush the column and to ensure that the media was saturated. During Phase II (t = 34 to 861 hours), flow was maintained to achieve an estimated HRT of 6.7 days (160 hours), which would be a typical design value for a SF constructed wetland. To examine the ability of the system to function under extreme conditions, the hydraulic residence time was decreased to 1.3 days (31 hours) by increasing the flow rate during Phase III (t = 861 to 1060 hours).

The column experiment may also be analyzed based on the composition and pH of the influent copper solution. On this basis, the experiment may be classified into four other phases - A, B, C, and D. During Phase A (t = 0 to 78 hours), an unbuffered 10 mg/L copper solution having a pH of approximately 4.2 was prepared by diluting Copper Reference Standard with deionized water. During Phase B (t = 78 to 248 hours), the influent copper solution (pH ~ 4.7) was prepared by mixing $CuSO_4 \cdot 5H_2O$ (0.040 g/L) with deionized water, but no buffer was used. To examine the system performance at a higher pH (~ 6.6), a 0.0008N K_2HPO_4 (0.0697 g/L) buffer was introduced to the solution in Phase C (t = 248 to 1004 hours). The buffer was increased to 0.001N (0.0871 g/L) during Phase D (t = 1004 to 1060 hours) which raised the influent pH to approximately 7.0. Copper sulfate was used as the copper source in phases C and D.

During the course of the column experiment, the hydraulic residence phases (I, II, and III) can be correlated to the applied copper phases (A, B, C, and D) for ease of analysis. The experiment can be divided into six time periods based on the correlation of Phases I through III and A through D. Table 4-14 shows these periods and their pertinent operating characteristics.

Throughout the column experiment, the peat showed its ability to remove copper from solution. Over ninety percent removal of the copper was consistently achieved during all phases of the experiment. Changing the hydraulic residence time did not result

Table 4-14. Column Experiment Operating Characteristics and Results

Period	HRT - Hydaulic Residence Time (hours)	Applied Copper Phase*	Time from start of experiment (hours)	Length of Period (hours)	Average Influent pH	Average Effluent pH	Average Influent Copper Conc. (mg/L)	Average Effluent Copper Conc. (mg/L)
I-A	33	A	0 to 34	34	4.18	3.76	9.80	3.38
II-A	160	A	34 to 78	44	4.22	3.78	9.79	1.01
II-B	160	B	78 to 248	170	4.66	4.37	10.25	0.79
II-C	160	C	248 to 861	613	6.67	4.37	9.56	0.22
III-C	31	C	861 to 1004	143	6.49	4.04	28.11	0.03
III-D	31	D	1004 to 1060	56	6.95	4.09	48.66	0.19
Entire Test	—	—	0 to 1060	1060	6.14	4.20	17.66	0.59

*A - Cu Reference Std., no buffer; B - $CuSO_4$, no buffer; C - $CuSO_4$, w/0.0008N K_2HPO_4; D - $CuSO_4$, w/0.001N K_2HPO_4

in significant changes in the effluent copper concentration. The higher influent pH values of the copper solution used in Phases C and D resulted in a copper precipitate (most likely tenorite) forming in the reservoir. To mix the solution, a magnetic stirrer was placed under the reservoir and a 2" stir bar was placed in the reservoir (t ~ 410 hours). The stirrer was undersized, however, and difficulties were encountered maintaining a consistent level of copper in the influent solution.

When the column was dismantled after the conclusion of the experiment, a bright blue layer of copper precipitate approximately ¼" thick was found on the surface of the peat (at the liquid/solid interface). Since the interior of the column acted as a closed system, the precipitate was reasoned to be malachite, but no analysis was performed to support this hypothesis. Regardless of the chemical composition of the precipitate, the effects of changing the hydraulic residence time in Phase 3 on the adsorption mechanisms of the system may have been masked by the filtration of the precipitate by the peat. However, decreases in copper concentration approaching the level of 3-log removal (99.9%) were achieved through the combined mechanisms of precipitation, filtration, and adsorption.

Throughout the column experiment, the effluent showed the characteristic brownish-red to brownish-yellow color indicative of the presence of organic acids. The effluent color at the start of Phase A was a light brownish-yellow, and it deepened to a rich, tea-like brownish-red color through Phase B. For the remainder of the experiment the effluent color gradually decreased to a pale yellow color. It is not certain if this was a function of the influent pH (which was increased through Phases C and D), the phosphate buffer, or simply the result of colloidal particles gradually being flushed from the column. There was very little change in the effluent pH during the period when the color seemed to be decreasing, so the color change was apparently influenced more by a decrease in colloidal particles in the column than by the soluble organic acids. Unfortunately, no measurements of true or apparent color were conducted.

Figure 4-33 is a plot of the average daily influent and effluent pH values for the entire experiment. The average daily influent and effluent copper concentrations are plotted on Figure 4-34. A detailed presentation of the results obtained from all influent and effluent samples is given in Appendix B.

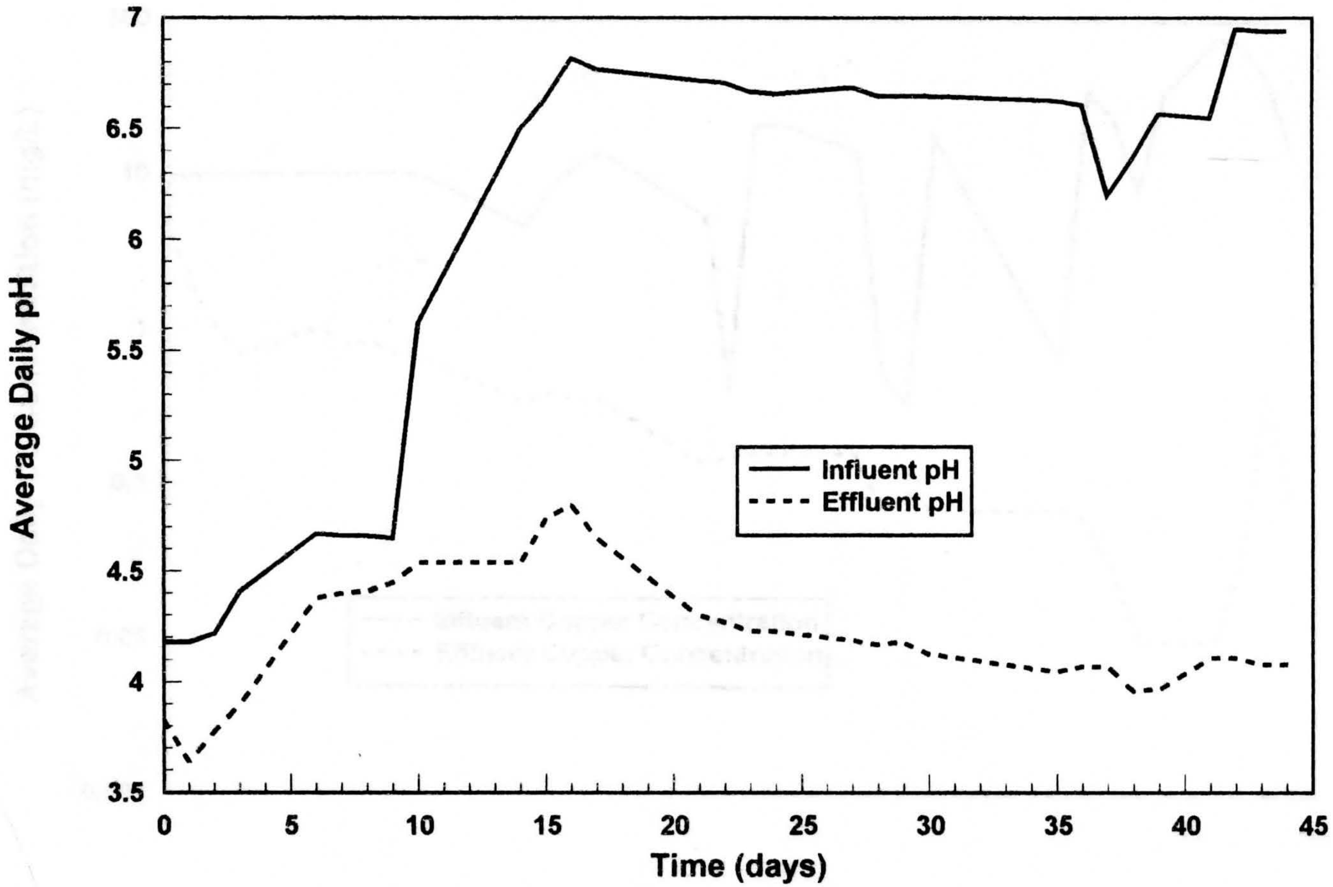


Figure 4-33. Average Daily pH of Influent and Effluent Solutions from Column Experiment

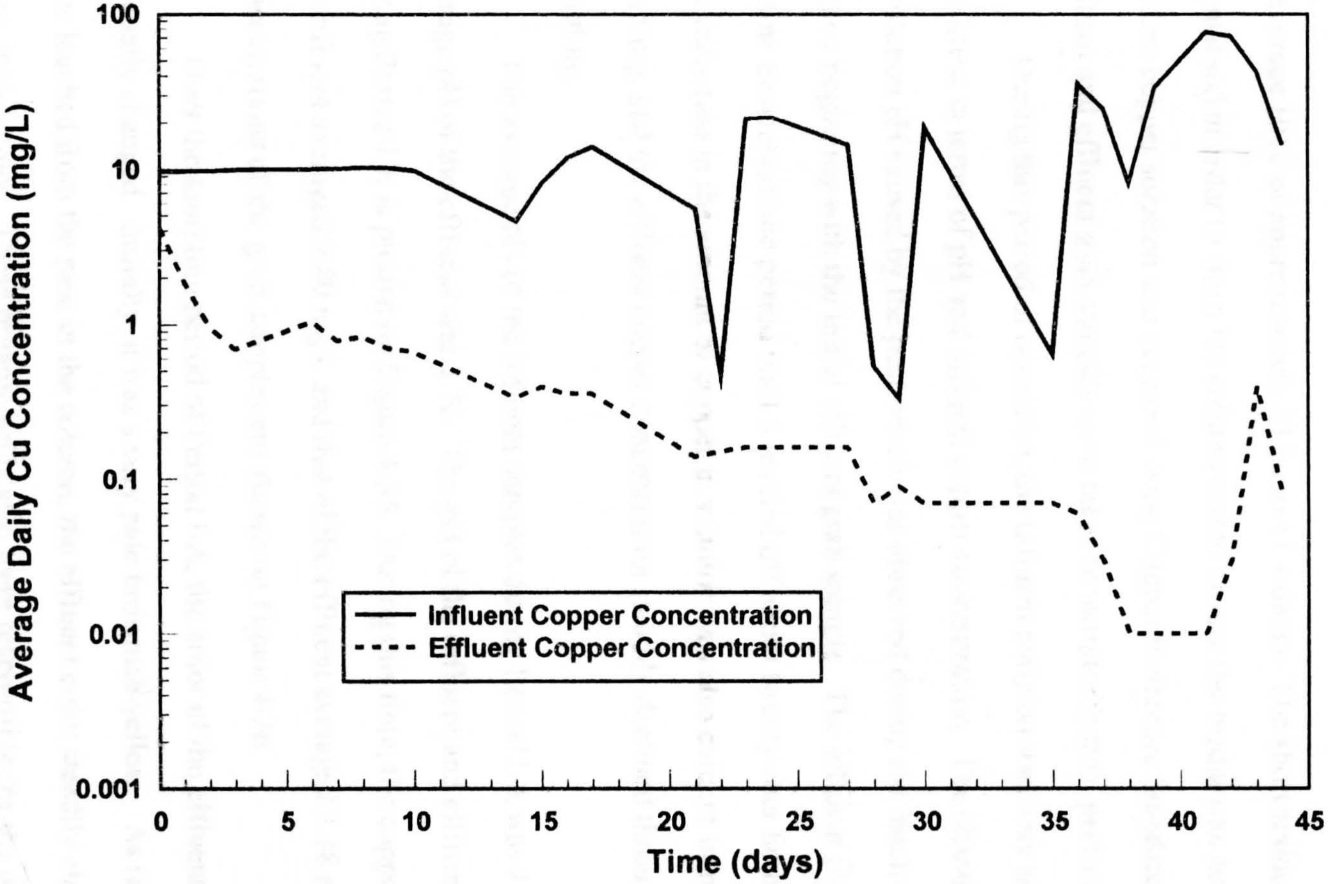


Figure 4-34. Average Daily Influent and Effluent Copper Concentration from Column Experiment

4.3.3 Results of Period I-A

Period I-A of the column experiment began after the column had been filled with peat and copper solution, as previously described, and lasted for 34 hours (t = 0 to 34 hours). The column effluent flow rate was controlled by the peristaltic pump to maintain an average HRT of approximately 33 hours (1.4 days). The short residence time was maintained in order to flush the column and to ensure the media was saturated. The influent copper solution was prepared using Copper Reference Standard and no buffer. Influent and effluent grab samples were taken to monitor system performance.

During this period of operation, the influent solution was very stable and consistent in terms of pH and influent copper concentration. The characteristic decrease in solution pH caused by the peat which was observed during the batch experiments was evident beginning with the initial effluent grab sample. The effluent pH continued to decline throughout the period until it leveled off about twenty-four hours after start-up. The reduction in the amount of copper in solution was also evident from the start of sampling, and the effluent copper concentration steadily declined throughout Period I-A sampling.

The average pH of the influent samples during Period I-A was 4.18, while the average pH of the effluent was 3.76. The pH of the influent and effluent grab samples during Period I-A is plotted on Figure 4-35. During this time, the copper concentration of the influent averaged 9.80 mg/L and that of the effluent averaged 3.38 mg/L. The copper concentrations of the grab samples are shown on Figure 4-36.

Over the sampling period of Period I-A, the color of the effluent solution gradually changed. Initially, it was a very pale brownish-yellow. As the organic acids were leached from the peat in the column, the effluent color steadily changed to a deeper, more golden color. These organic acids also were responsible for the decrease in solution pH.

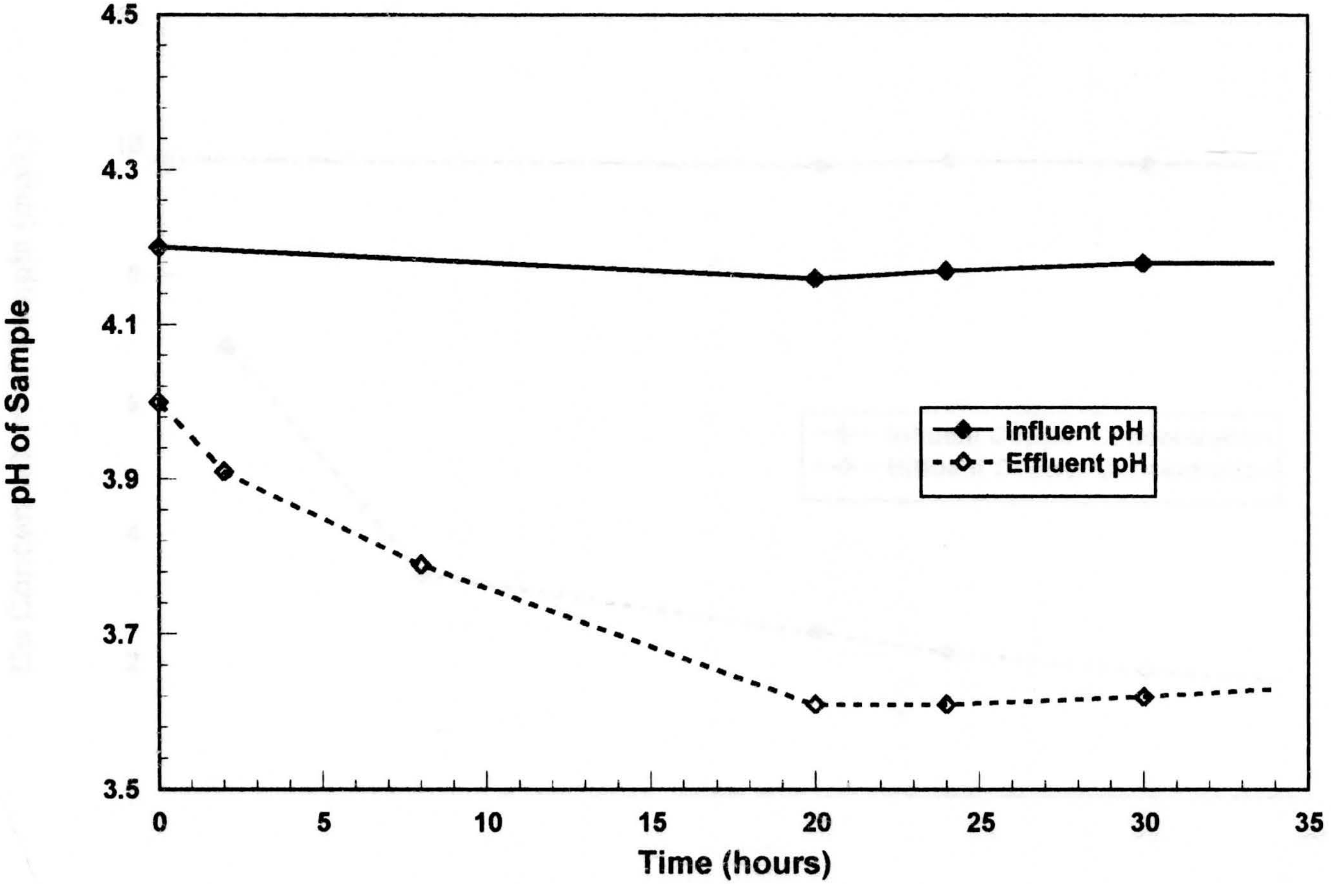


Figure 4-35. Column Experiment Phase I-A - Influent and Effluent pH

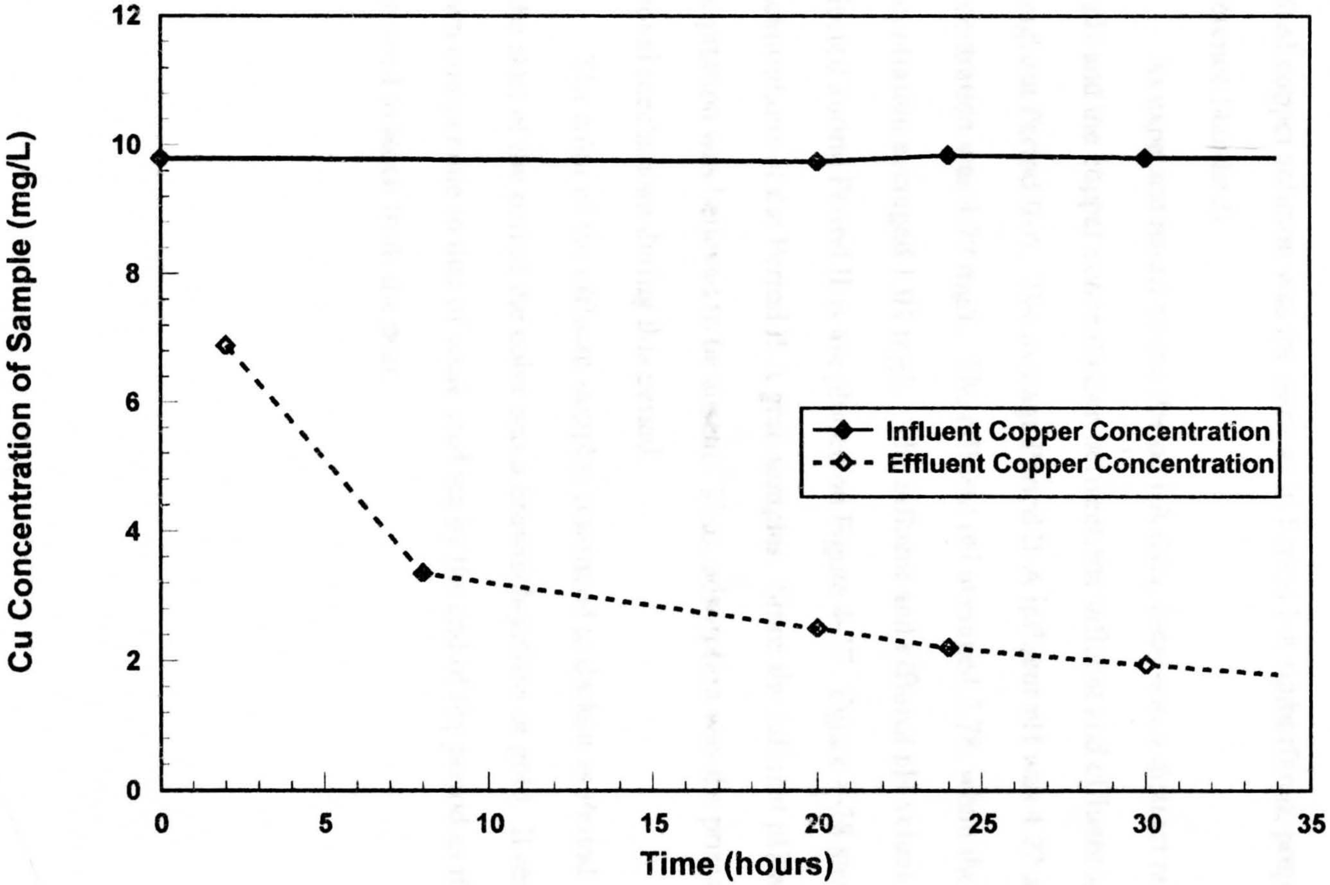


Figure 4-36. Column Experiment Phase I-A - Influent and Effluent Copper Concentration

4.3.4 Results of Period II-A

During Period II-A (t = 34 to 78 hours), the hydraulic residence time was increased to approximately 160 hours (6.7 days). This residence time falls in the range of typical design values for constructed wetlands of 4 to 15 days. During this period, the applied copper solution was the same as in Period I-A (unbuffered, prepared with Copper Reference Standard).

As expected based on the Period I-A data, there was a distinct reduction in both the pH and the copper concentration between the influent and effluent samples throughout Period II-A. The average Period II-A influent pH was 4.22 and the copper concentration was 9.79 mg/L. The effluent pH averaged 3.78, while the copper concentration averaged 1.01 mg/L. The influent and effluent pH values of the samples collected during Period II-A are plotted on Figure 4-37. Figure 4-38 shows the copper concentrations of the Period II-A grab samples. Since the influent pH was low, precipitation was believed to be absent. Thus, adsorption was the primary copper removal mechanism during this period.

The color of the effluent samples continued to darken as Period II-A progressed. At the start of the period the color was a brownish-yellow or gold. It reached a reddish-brown comparable to that of weak iced tea by the end of the period as the organics continued to leach from the peat.

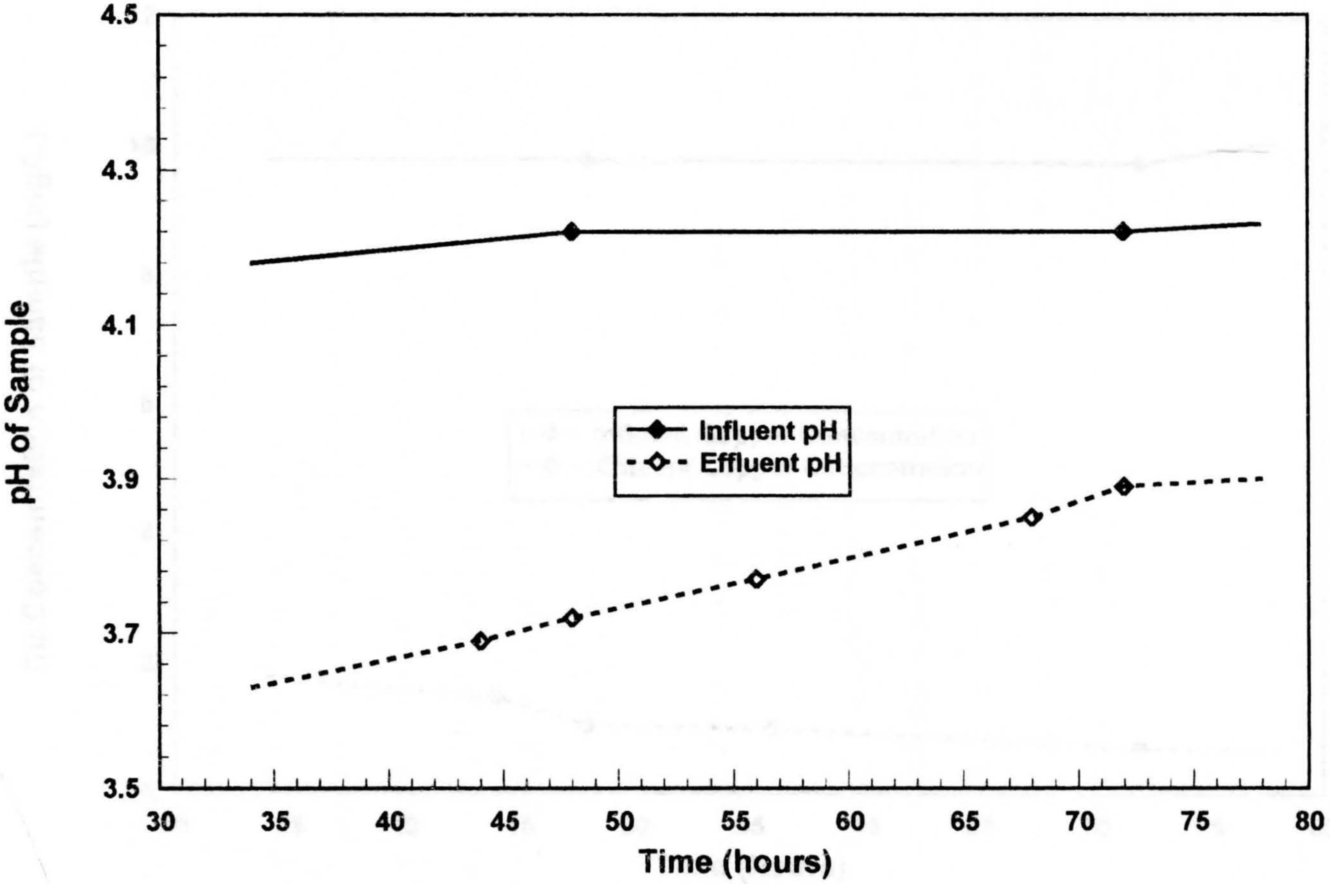


Figure 4-37. Column Experiment Phase II-A - Influent and Effluent pH

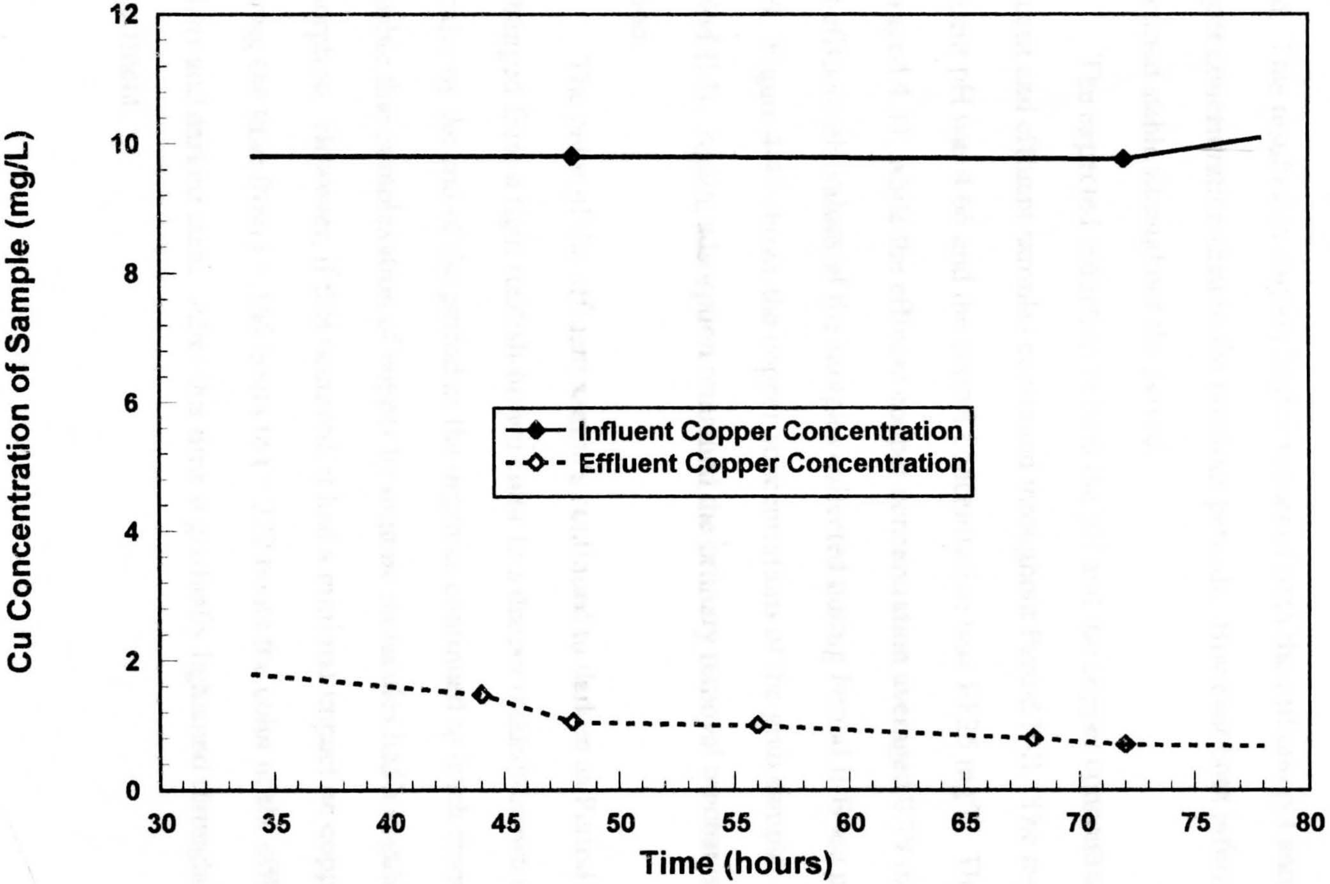


Figure 4-38. Column Experiment Phase II-A - Influent and Effluent Copper Concentration

4.3.5 Results of Period II-B

During Period II-B (t = 78 to 248 hours), the hydraulic residence time was maintained at 160 hours (6.7 days). During this period, the applied copper solution was prepared by mixing $CuSO_4 \cdot 5H_2O$ (0.040 g/L) with deionized water, but no buffer was used. This resulted in slightly higher values of both the influent pH and the influent copper concentration than in the previous periods. However both influent parameters remained stable throughout the period.

The expected reduction in both the pH and the copper concentration between the influent and effluent samples continued throughout Period II-B. The average Period II-B influent pH was 4.66 and the copper concentration was 10.25 mg/L. The effluent pH averaged 4.37, while the effluent copper concentration averaged 0.79 mg/L. The influent and effluent pH values of the samples collected during Period II-B are plotted on Figure 4-39. Figure 4-40 shows the copper concentrations of the grab samples taken during Period II-B. Again, adsorption remained the primary removal mechanism during this period.

The color of the effluent samples continued to darken as Period II-B progressed. It changed from a light reddish-brown color to a deeper reddish-brown color comparable to cider by the end of the period as the organics continued to leach from the peat. It is possible that complexation of copper by organic molecules had a negative impact on adsorption. However, if this occurred, it had a minimal impact on copper removal. During the time from t = 164 hours to t = 222 hours the color of the effluent was at its richest and darkest state. After this time it gradually lightened throughout the rest of the experiment.

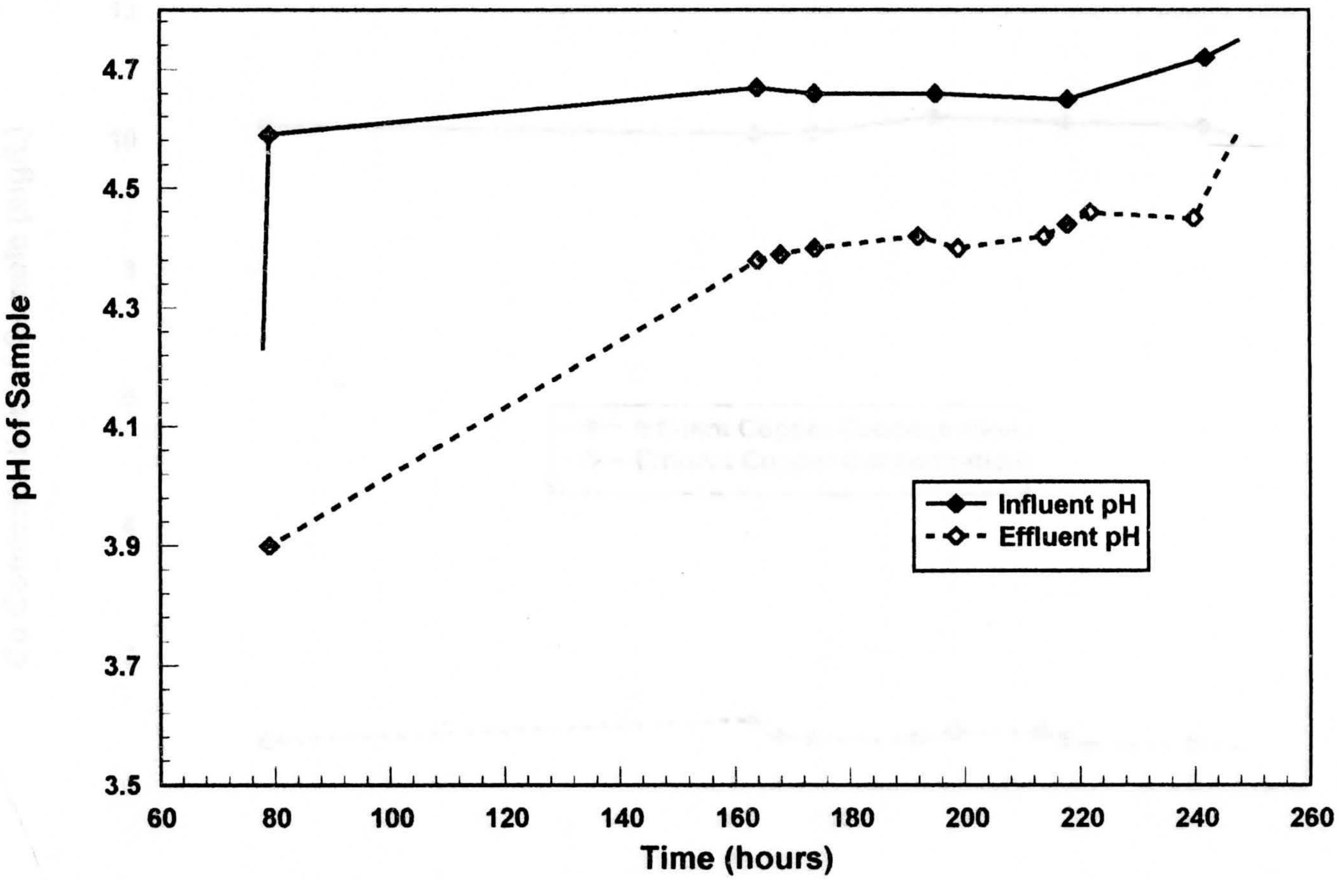


Figure 4-39. Column Experiment Phase II-B - Influent and Effluent pH

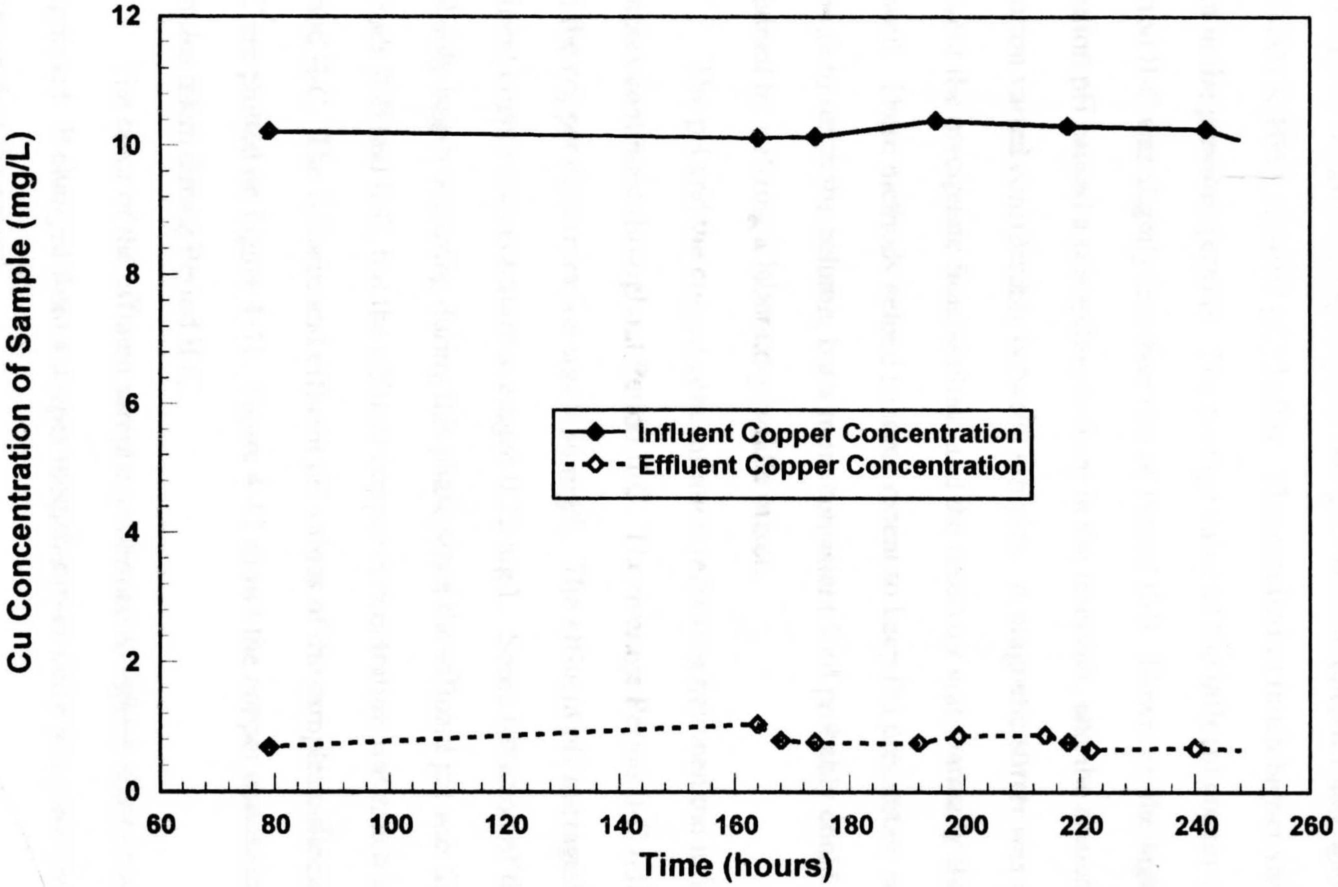


Figure 4-40. Column Experiment Phase II-B - Influent and Effluent Copper Concentration

4.3.6 Results of Period II-C

During Period II-C (t = 248 to 861 hours), the hydraulic residence time was maintained at 160 hours (6.7 days). During this period, the applied copper solution was prepared by mixing $CuSO_4 \cdot 5H_2O$ (0.040 g/L) with deionized water, and buffering with 0.0008N K_2HPO_4 (0.0697 g/L) buffer. This resulted in much higher values of influent pH than in the previous periods. The average value of the influent copper concentration for Period II-C was slightly less than that of Period II-B. However, the higher influent solution pH caused a precipitate to form in the reservoir, and the amount of copper in solution varied considerably between samples. A magnetic stirrer was utilized to help prevent the precipitate from settling, and the reservoir was manually shaken periodically as well. These methods helped to some extent to keep the precipitate suspended long enough to reach the column, but a more consistent feed probably could have been obtained by utilizing a laboratory paddle mixer.

The pH and the copper concentration reduction between the influent and effluent samples continued throughout Period II-C. The average Period II-C influent pH was 6.67 and the copper concentration was 9.56 mg/L. The effluent pH averaged 4.37, while the effluent copper concentration averaged 0.22 mg/L. Some filtration of the precipitate probably began occurring during this phase since the effluent pH was the same for Periods II-B and II-C, but the effluent copper concentration was much lower during Period II-C. The influent and effluent pH values of the samples collected during Period II-C are plotted on Figure 4-41. Figure 4-42 shows the copper concentrations of the grab samples taken during Period II-C.

The color of the effluent samples continued to lighten somewhat as Period II-C progressed. It changed from a deeper reddish-brown color to a paler yellow-brown color by the end of the period.

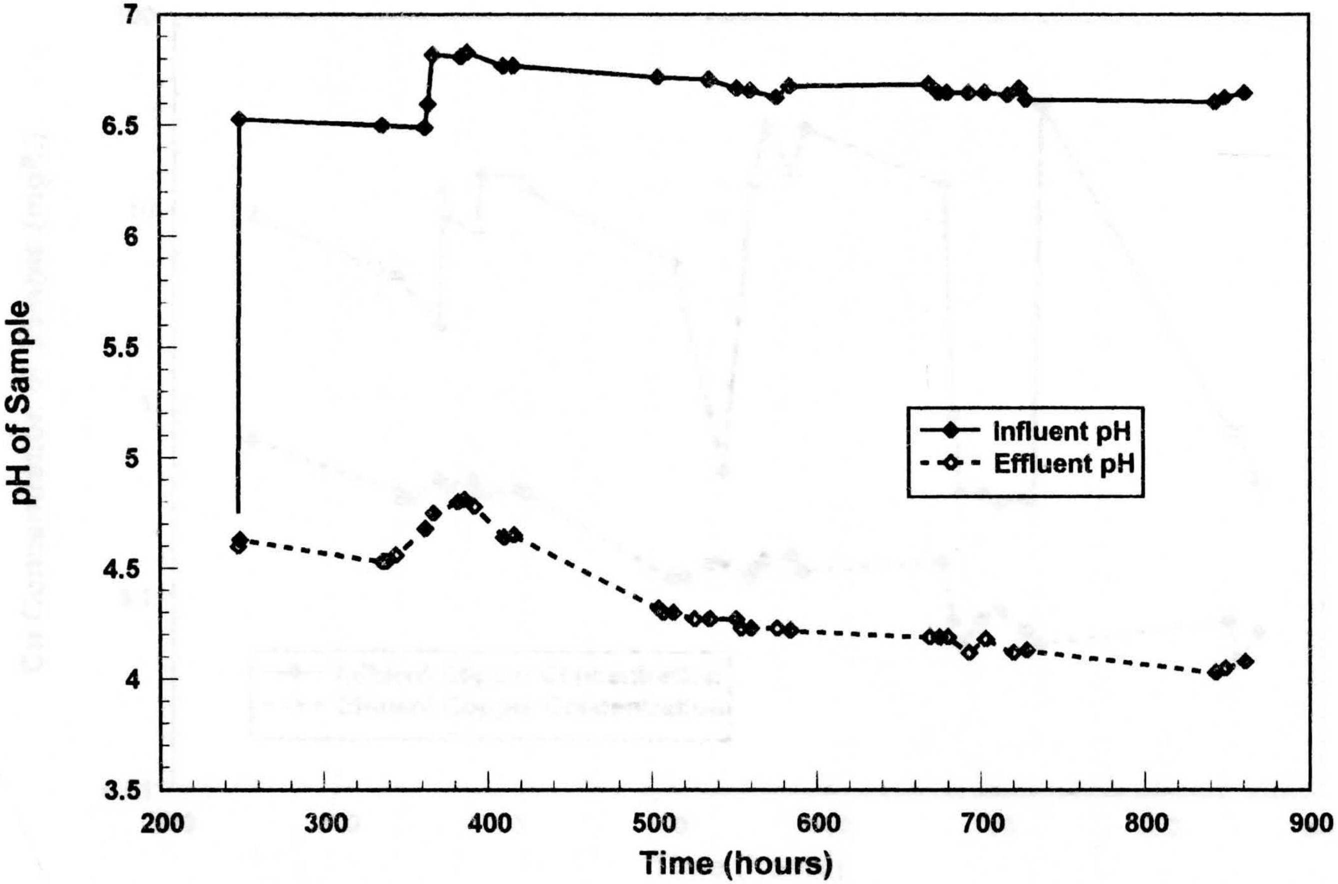


Figure 4-41. Column Experiment Phase II-C - Influent and Effluent pH

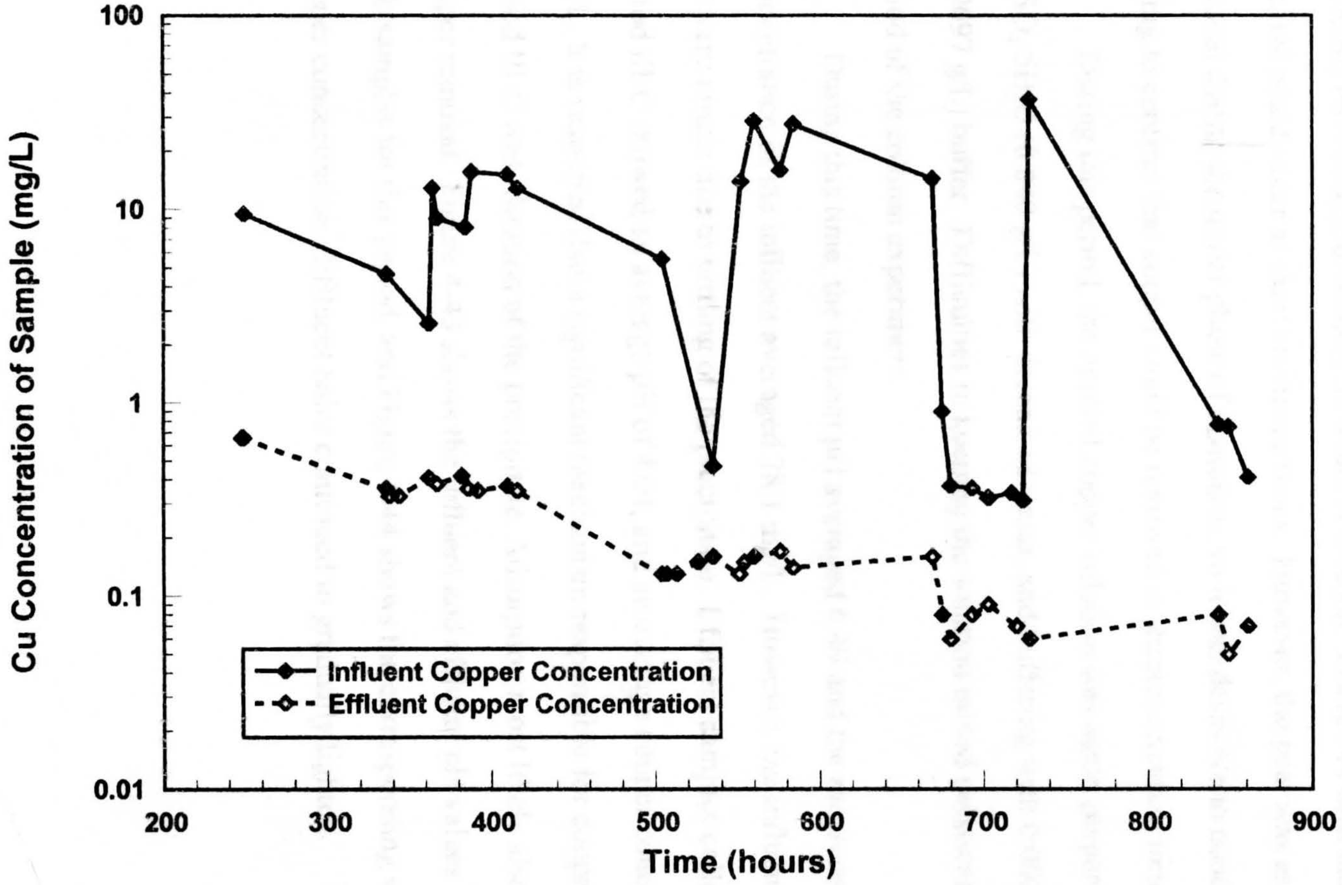


Figure 4-42. Column Experiment Phase II-C - Influent and Effluent Copper Concentration

4.3.7 Results of Period III-C

In order to examine the effectiveness of a shorter retention time, the flow was increased sufficiently during Phase III-C (t = 861 to 1004 hours) to create an hydraulic residence time of approximately 31 hours (1.3 days). Phase I-A data indicated copper removal could occur at short residence times. However, the peat was essentially virgin material during the initial phase of operation, so it was desirable to conduct further testing to confirm that copper could be removed at shorter retention times.

During this period, the applied copper solution was again prepared by mixing $CuSO_4{\cdot}5H_2O$ (0.040 g/L) with deionized water, and buffering with 0.0008N K_2HPO_4 (0.0697 g/L) buffer. Difficulties in keeping the solution mixed persisted throughout this period of the column experiment.

During this time, the influent pH averaged 6.49 and the measured copper concentration of the influent averaged 28.1 mg/L. However, the influent concentration was very erratic due to settling of the precipitate. Effluent samples collected during Period III-C showed an average pH of 4.04, and an average copper concentration of 0.03 mg/L. It is suspected that a significant mechanism responsible for copper removal during Period III-C was filtration of the precipitate. Adsorption most likely also contributed to copper removal. Figure 4-43 shows the influent and effluent pH values obtained from the grab samples for this period, and Figure 4-44 shows the corresponding values of sample copper concentration. Effluent color continued to gradually lighten.

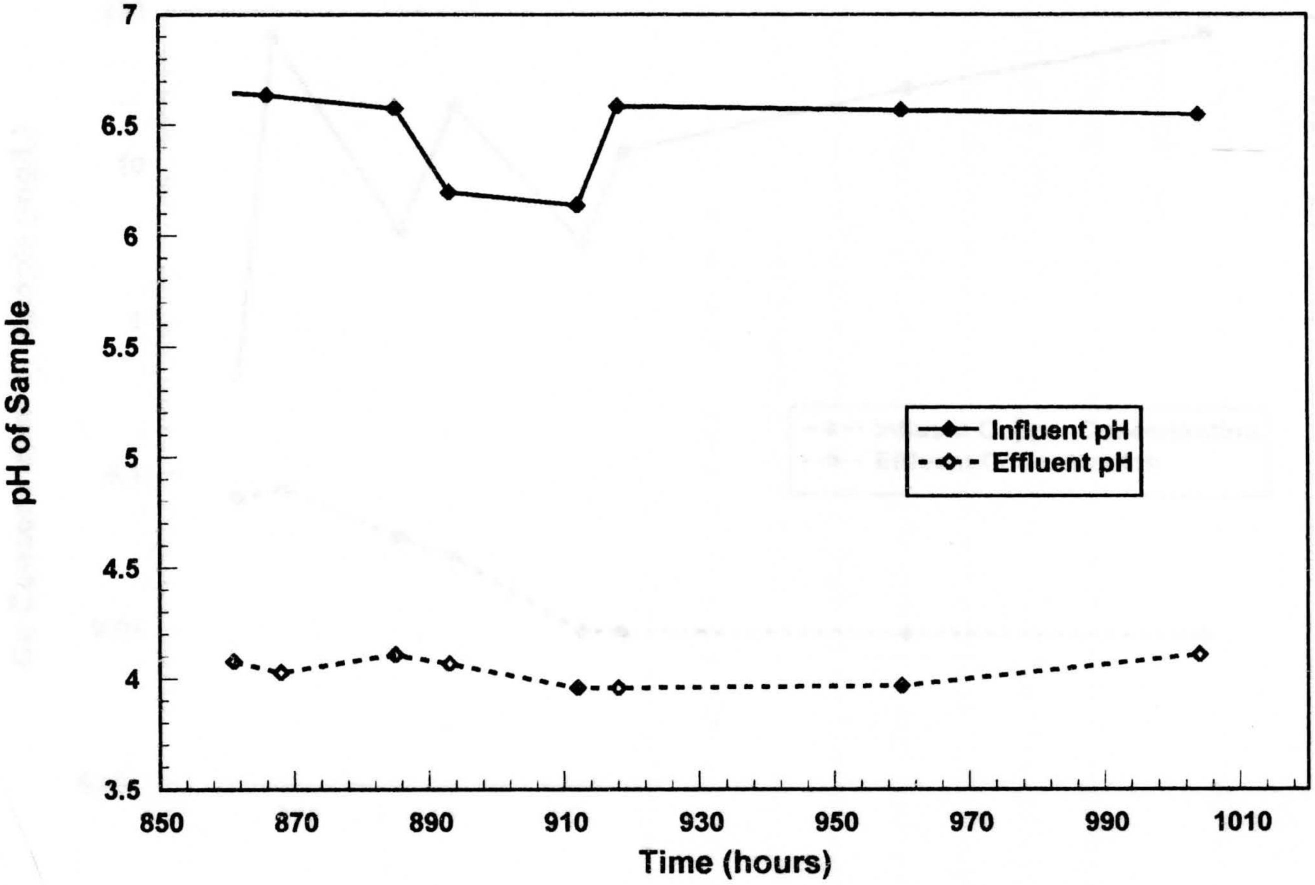


Figure 4-43. Column Experiment Phase III-C - Influent and Effluent pH

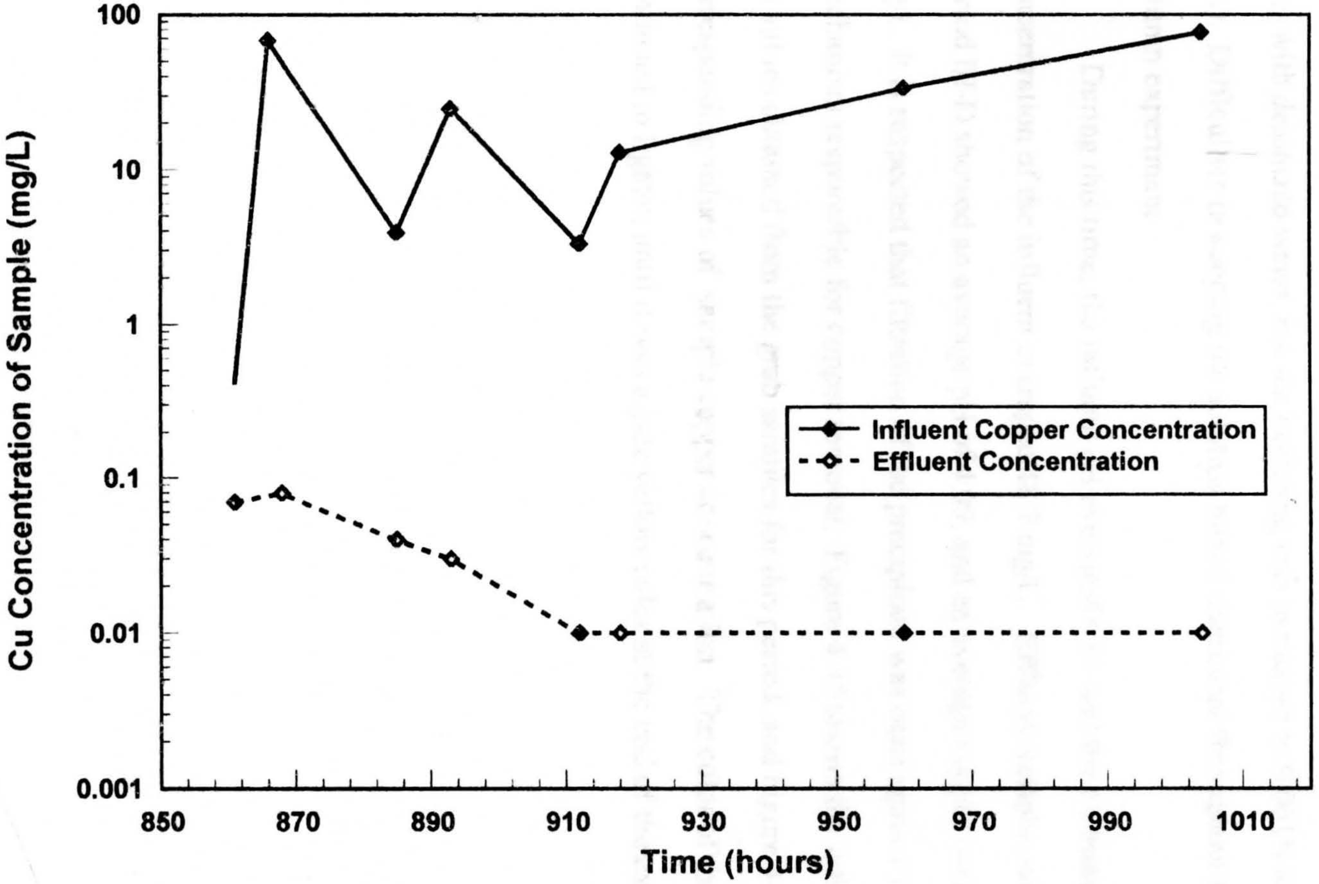


Figure 4-44. Column Experiment Phase III-C - Influent and Effluent Copper Concentration

4.3.8 Results of Period III-D

During Period III-D (t = 1004 to 1060 hours) the shorter hydraulic residence time (31 hours) was maintained, but the buffer intensity was increased slightly. During this period, the applied copper solution was again prepared by mixing $CuSO_4 \cdot 5H_2O$ (0.040 g/L) with deionized water, but the buffering was increased to 0.001N K_2HPO_4 (0.0871 g/L). Difficulties in keeping the solution mixed continued throughout this period of the column experiment.

During this time, the influent pH averaged 6.95 and the measured copper concentration of the influent averaged 48.7 mg/L. Effluent samples collected during Period III-D showed an average pH of 4.09, and an average copper concentration of 0.19 mg/L. It is suspected that filtration of the precipitate was once again a significant mechanism responsible for copper removal. Figure 4-45 shows the influent and effluent pH values obtained from the grab samples for this period, and Figure 4-46 shows the corresponding values of sample copper concentration. The color of the effluent solution continued to lighten until it was a pale yellow color at the end of the experiment.

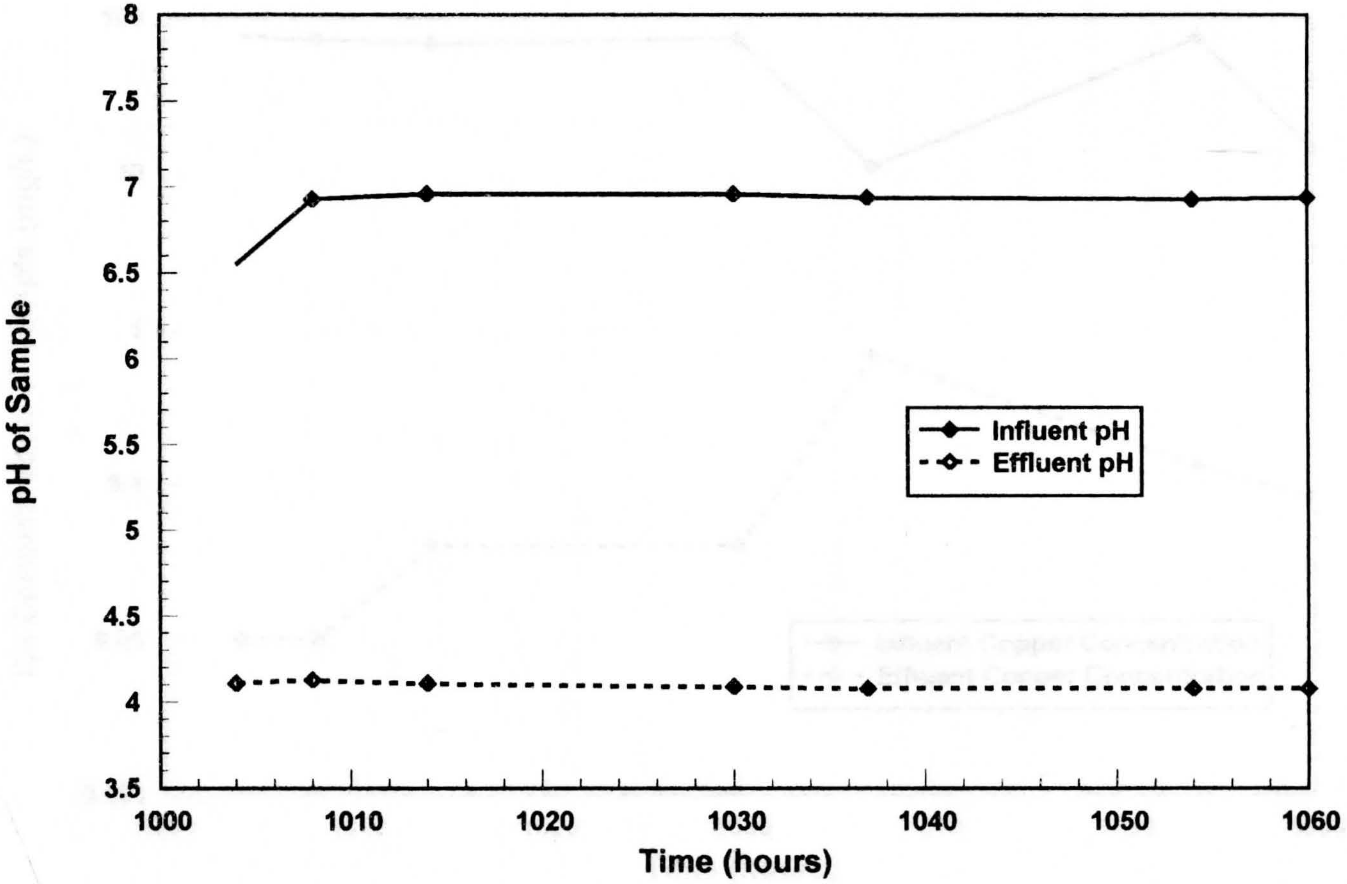


Figure 4-45. Column Experiment Phase III-D - Influent and Effluent pH

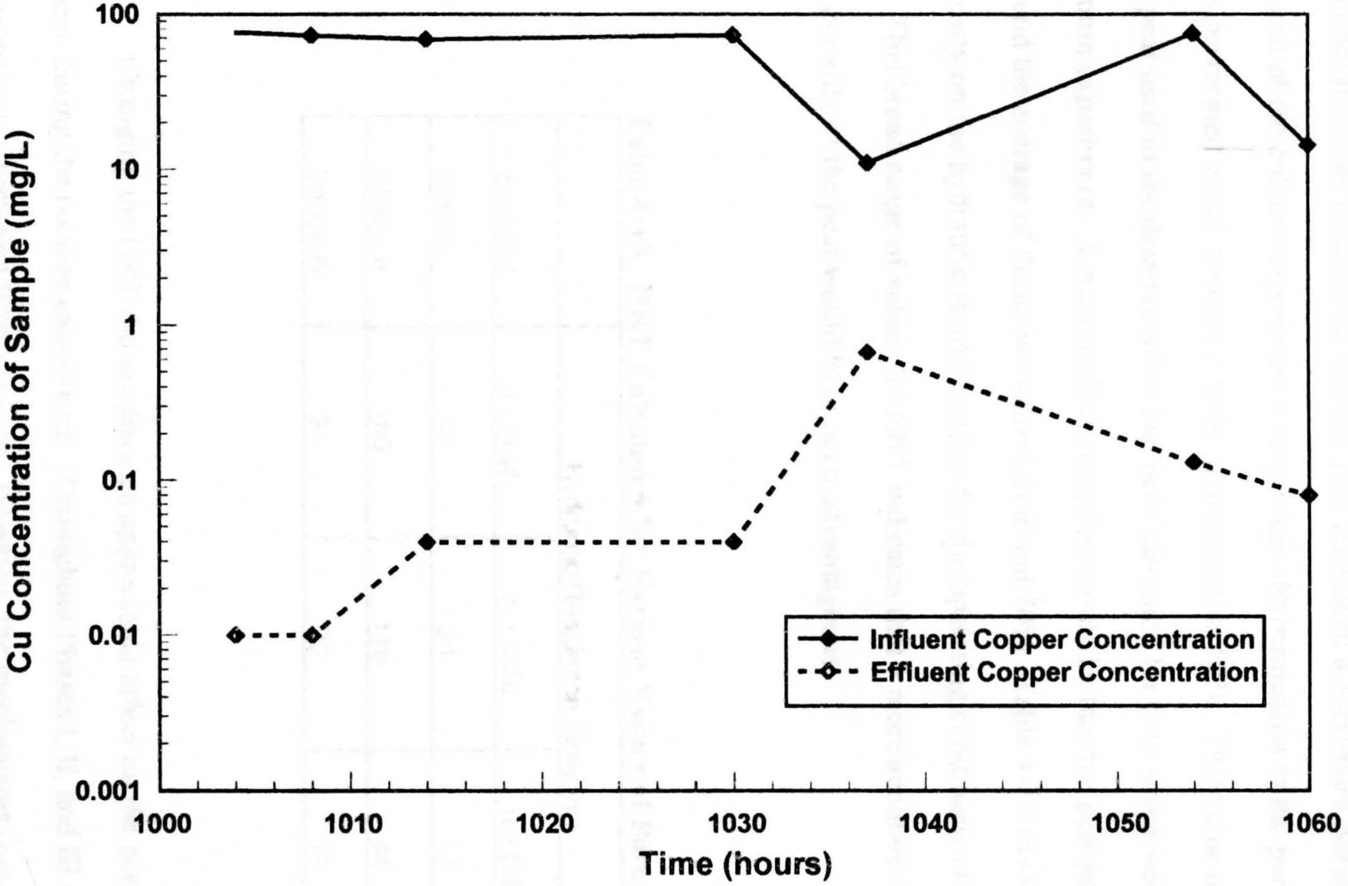


Figure 4-46. Column Experiment Phase III-D - Influent and Effluent Copper Concentration

4.3.9 Effect of Hydraulic Residence Time and pH on the Column Experiment

As previously stated, the hydraulic residence times of 33 hours for Phase I, 160 hours for Phase II, and 31 hours for Phase III were estimated values. These estimates were based on the assumption that the peat possessed a maximum porosity of 95%. At the end of the column experiment a very rough determination of the porosity of the peat was performed which showed it to be approximately 50%. This value is suspect since the peat used in the determination had been saturated for over seven weeks during the column experiment. A reasonable assumption would be that the peat porosity would be around the average of these two values, or about 70%. Table 4-15 shows the effect of porosity on the hydraulic residence time for the operating conditions of Phases I, II, and III. This broad range of values for HRT indicates that a more accurate determination of the porosity of the peat would have been advantageous.

Table 4-15. HRT Calculated for Various Values of Porosity

	Hydrualic Residence Time (hr)		
porosity	n = 0.95	n = 0.70	n = 0.50
Phase I	33	24	17
Phase II	160	118	84
Phase III	31	23	16

Changing the HRT did not have an appreciable affect on the performance of the system during the column experiment. Throughout Phases I, II, and III significant levels of copper were removed from solution. However, the mechanisms responsible for the copper removal appeared to change during these phases, and were dependent upon the influent pH. During periods I-A, II-A, and II-B the predominant mechanism responsible for the removal of copper from solution appeared to be adsorption by the peat. As the influent pH was increased through Periods II-C, III-C, and III-D filtration of the precipitate which formed appeared to contribute significantly to removal.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

5.1 Summary of Batch and Column Experiments

The overall results obtained for the removal of copper from solution during the Batch and Column Experiments are encouraging. Copper was consistently removed from solution during Batch Experiments #1 through #6, as well as during the entire Column Experiment.

The results of Batch Experiments #1 through #6 which utilized copper as the adsorbate and peat as the adsorbent led to the following conclusions:

- The adsorption of copper by peat in Batch Experiments using variable soil:solution ratios generally followed the Freundlich Isotherm as reported in the literature.
- Batch Experiment #6 was the first (and only) test to yield an adsorption isotherm resembling those typically encountered. The Double Reciprocal Langmuir Isotherm Equation was found to fit the data slightly better than the Langmuir and Freundlich Isotherm Equations, although any of these equations could be used to describe the data.
- The following isotherm constants were determined from the results of Batch Experiment #6: Freundlich Isotherm - $K_f = 7{,}928$ and $n = 2.0319$; Langmuir Isotherm - $Q = 27{,}710$ mg/kg and $b = 0.5654$ L/mg; Double Reciprocal Langmuir Isotherm - $Q = 30{,}442$ mg/kg and $b = 0.6148$ L/mg.
- The colloidal humic material inherent to the peat played a significant role in the adsorption of copper as shown in Batch Experiment #4 by comparing the undigested and digested results.
- The peat consistently reduced the pH of solution, most likely due to the organic acids leached from the peat.
- The recommended mixing time of twenty-four hours for samples to reach equilibrium was confirmed.

- Once the equilibrium copper concentration neared or exceeded 5 mg/L in the variable soil:solution ratio Batch Experiments #3 and #4, adsorption appeared to increase dramatically. However, this is attributed to copper precipitating at higher equilibrium pH (≥8.6). Less peat was added to these samples (1:5000 and 1:10,000 ratios), resulting in higher pH values and higher soluble copper concentrations.

Copper was also shown to be effectively adsorbed by yard waste compost in Batch Experiment #7. However, sand was shown to adsorb only a minimal amount of copper in Batch Experiment #8. The organic content of both the peat and yard waste compost is much greater than that of the sand. Thus, the presence of organic matter in the substrate material is a primary design concern if adsorption is expected to be the primary metal removal mechanism in the constructed wetland system.

The Batch Experiments involving iron were not nearly as encouraging as the copper experiments. However, only a limited amount of work was performed using iron as an adsorbate, so the results obtained are inconclusive. As expected, sand showed little adsorption capacity for iron -- again most likely due to the minimal organic content of the sand. Batch Experiment #10 involving iron and peat did not generate any usable data due to the complex interaction of many variables.

Throughout the Batch Experiments, a number of phenomena were observed which could not be satisfactorily explained. These included variations in the amount of copper adsorbed by the reaction vessels, the behavior of samples using small amounts of peat (1:5000 and 1:10,000 ratios), and the adsorption of iron by peat.

The Column Experiment involving copper and peat generated results consistent with the Batch Experiments. During the forty-four day period of operation, the following observations were made:

- The peat system consistently reduced the pH 2 to 3 units between the influent and the effluent. This was due to the organic acids leached from the peat.
- The brown coloration of the column effluent was also due to the organic acids in the peat. However, the color imparted to the effluent gradually lessened over the course of the Column Experiment.
- Copper removal of at least 95% (log removal = 1.3) was consistently achieved.
- Increasing influent pH caused copper to precipitate, but the precipitate was easily filtered by the peat.
- Combining the mechanisms of precipitation, filtration, and adsorption resulted in 3-log removal of copper from solution.

5.2 Conclusion and Scope of Future Work

The overall results of the Column Experiment, combined with the results of the Batch Experiments, show that peat possesses a definite ability to adsorb copper from solution at concentrations typically found in both acid mine drainage and landfill leachate, as well as at much higher values. While the results are promising, a number of items need additional examination. To gain further insight into the behavior of the copper/peat system, Batch Experiments that utilize another buffering system should be conducted, as well as some using no buffer. These experiments may help to quantify the effect, if any, of the phosphate buffer on the system. Also, the porosity of the peat should be established, and additional Column Experiments should be performed in which the hydraulic residence time is better determined. Column effluent should also be closely monitored for color, as well as total organic carbon (TOC). These tests would be good indicators of the effect of the organic acids leached from the peat.

Further bench-scale study of the interaction of metals with various substrate materials is necessary to develop a greater understanding of the processes occurring which influence the removal of metals in the wetland environment. Additional study is needed regarding the optimal removal mechanisms of many of the heavy metals (As, Cd, Cu, Fe, Mn, Ni, Pb, Zn) by the various substrate materials utilized as constructed wetland substrate (peat, yard waste compost, mushroom compost, limestone, gravels, sand, etc.). Individually, each of these substrates should be examined for their ability to remove specific metals. Also, two or more substrates may be combined to overcome individual limitations. An example which is readily apparent would be combining limestone and peat to neutralize the tendency of the peat to reduce the pH.

After additional information is collected regarding other substrates and metals, more bench-scale, or even pilot-scale testing, incorporating actual mine drainage, landfill leachate, or an appropriate simulated mixture, should be conducted over a relatively large time period. These tests should be indicative of actual system performance and show if the system exhibits the preferential removal of certain contaminants (e.g., competition between metal ions for adsorption sites). Additional tests should also incorporate typical wetland plants to further determine the role of vegetation in the removal of metals.

The preceding list of proposed work is by no means all-inclusive, but is intended to show that we know only a little, and there is much to be discovered yet. Constructed wetlands have been used for over a quarter of a century to treat various types of wastewater, but their effectiveness may be greatly enhanced though the investigation of the naturally occurring processes.

Aljoe, W.W., "Hydrologic and Water Quality Characteristics of a Partially-Flooded, Abandoned Underground Coal Mine" in International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, Volume 2 of 4: Mine Drainage (Proceedings of a conference held in Pittsburgh, PA on April 24-29, 1994), US Department of the Interior Bureau of Mines Special Publication SP 06B-94, pp. 178-187.

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, Boca Raton, 1993, pp. 59-68.

Brodie, G.A., "Staged, Aerobic Constructed Wetlands to Treat Acid Drainage: Case History of Fabius Impoundment 1 and Overview of the Tennessee Valley Authority's Program" in Constructed Wetlands for Water Quality Improvement, Moshiri, G.A., ed., CRC Press, Boca Raton, 1993, pp. 157-165.

Busch, D.H., *et al.*, Chemistry, 2nd ed., Allyn and Bacon, Inc., Boston, 1978.

Corbitt, R.A., and Bowen, P.T., "Constructed Wetlands for Wastewater Treatment" in Applied Wetlands Science and Technology, Kent, D.M., ed., CRC Press, Boca Raton, 1994, pp. 221-241.

Couillard, D., "The Use of Peat in Wastewater Treatment" in Water Resources, Elsevier Science, Ltd., Great Britain, 1994, Vol. 28, No.6, pp. 1261-1274.

Crum, H., A Focus of Peatlands and Peat Mosses, University of Michigan Press, Ann Arbor, 1988.

Dietz, J.M., *et al.*, "Evaluation of Acidic Mine Drainage Treatment in Constructed Wetland Systems" in International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, Volume 1 of 4: Mine Drainage (Proceedings of a conference held in Pittsburgh, PA on April 24-29, 1994), US Department of the Interior Bureau of Mines Special Publication SP 06B-94, pp. 70-79.

Eger, P., *et al.*, "Metal Removal in Wetland Treatment Systems" in International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, Volume 1 of 4: Mine Drainage (Proceedings of a conference held in Pittsburgh, PA on April 24-29, 1994), US Department of the Interior Bureau of Mines Special Publication SP 06B-94, pp. 80-88.

Eger, P. *et al.*, "The Use of Constructed Wetland Treatment to Remove Trace Metals from Mine Drainage" in Constructed Wetlands for Water Quality Improvement, Moshiri, G.A., ed., CRC Press, Boca Raton, 1993, pp. 171-178.

Faulkner, S.P., and Richardson, C.J., "Physical and Chemical Characteristics of Freshwater Wetland Soils" in Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural, Hammer, D.A., ed., Lewis Publishers, Chelsea, MI, 1989, pp. 41-72.

Frostman, T.M., " A Peat/Wetland Treatment Approach to Acidic Mine Drainage Abatement" in Constructed Wetlands for Water Quality Improvement, Moshiri, G.A., ed., CRC Press, Boca Raton, 1993, pp. 197-200.

Fuchsman, C.H., Peat, Industrial Chemistry and Technology, Academic Press, Inc., New York, 1980.

Fyson, A., *et al.*, "Arsenic and Nickel Removal by Wetland Sediments" in International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, Volume 1 of 4: Mine Drainage (Proceedings of a conference held in Pittsburgh, PA on April 24-29, 1994), US Department of the Interior Bureau of Mines Special Publication SP 06B-94, pp. 109-118.

Guntenspergen, G.R., "Wetland Vegetation" in Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural, Hammer, D.A., ed., Lewis Publishers, Chelsea, MI, 1989, pp. 73-88.

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, Chelsea, MI, 1989, pp. 5-20.

Holtz, R.D., and Kovacs, W.D., An Introduction to Geotechnical Engineering, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1981.

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

Knight, R.L., *et al.*, "Wetlands for Wastewater Treatment: Performance Database" in Constructed Wetlands for Water Quality Improvement, Moshiri, G.A., ed., CRC Press, Boca Raton, 1993, pp. 35-58.

LaGrega, M.D., *et al.*, Hazardous Waste Management, McGraw-Hill, Inc., New York, 1994.

McIlroy, L.M., *et al.*, "Partitioning of Heavy Metals to Suspended Solids of the Flint River, Michigan" in *Environmental Toxicology and Chemistry*, Vol. 5, 1986, pp. 609-623.

Sawyer, C.N., *et al.*, Chemistry for Environmental Engineering, 4th ed., McGraw-Hill, Inc., New York, 1994

Shuckrow, *et al.*, "Hazardous-Waste Leachate Management" in Hazardous Waste Management Engineering, Martin, E.J, and Johnson, J.H., Jr., eds., Van Nostrand Reinhold Company, New York, 1987, pp. 441-467.

Snoeyink, V.L., and Jenkins, David, Water Chemistry, John Wiley & Sons, Inc., New York, 1980.

Standard Methods for the Examination of Water and Wastewater, 16th edition, prepared and published jointly by American Public Health Association, American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1985

Stark, L.R., *et al.*, "Iron Retention and Vegetative Cover at the SIMCO Constructed Wetland: An Appraisal Through Year Eight of Operation" in International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, Volume 1 of 4: Mine Drainage (Proceedings of a conference held in Pittsburgh, PA on April 24-29, 1994), US Department of the Interior Bureau of Mines Special Publication SP 06B-94, pp. 89-98.

Staubitz, *et al.*, "Potential Use of Constructed Wetlands to Treat Landfill Leachate" in Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural, Hammer, D.A., ed., Lewis Publishers, Chelsea, MI, 1989, pp. 735-742.

Steiner G.R., and Freeman, R.J., Jr., "Configuration and Substrate Design Considerations for Constructed Wetlands Wastewater Treatment" in Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural, Hammer, D.A., ed., Lewis Publishers, Chelsea, MI, 1989, pp. 363-378.

Steiner G.R., and Watson, J.T., General Design, Construction, and Operation Guidelines: Constructed Wetlands Wastewater Treatment Systems for Small Users Including Individual Residences, 2nd ed., TVA/WM--93/10, Tennessee Valley Authority Water Management Resource Group, Chattanooga, 1993.

Stumm, W., and Morgan, J.J., Aquatic Chemistry: An Introduction Emphasizing Chemical Equlibria in Natural Waters, 2nd ed., John Wiley & Sons, Inc., New York, 1981.

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, Boca Raton, 1993, pp. 23-34.

Tchobanoglous, G. & Burton, Wastewater Engineering: Treatment, Disposal, and Reuse, Metcalf & Eddy - 3rd ed., McGraw-Hill, Inc., 1991.

Tchobanoglous, G. and Schroeder, E.D., Water Quality: Characteristics, Modeling, Modification, Addison-Wesley Publishing Company, Inc., Reading, MA, 1985.

Tchobanoglous, G., *et al.*, Integrated Solid Waste Management: Engineering Principles, and Management Issues, McGraw-Hill, Inc., 1993.

United States Environmental Protection Agency (US EPA), Subsurface Flow Constructed Wetlands for Wastewater Treatment: A Technology Assessment, EPA 832-R-93-008, US EPA, Washington, D.C., July 1993.

United States Environmental Protection Agency (US EPA), Technical Resource Document: Batch-Type Procedures for Estimating Soil Adsorption of Chemicals, EPA 530/SW-87/006-F, US EPA, Washington, D.C., April 1992.

United States Environmental Protection Agency (US EPA), Water Quality Standards for Wetlands: National Guidance, EPA 440/S-90-011, US EPA, Washington, D.C., July 1990.

United States Environmental Protection Agency (US EPA), Design Manual: Constructed Wetlands and Aquatic Plant Systems for Municipal Wastewater Treatment, EPA 625/1-88/022, US EPA, Cincinnati, Oh, 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, Washington, D.C., October, 1987.

Watson, J.T., and Hobson, J.A., "Hydraulic Design Considerations and Control Structures for Constructed Wetlands for Wastewater Treatment" in Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural, Hammer, D.A., ed., Lewis Publishers, Chelsea, MI, 1989, pp. 379-392.

Watson, J.T., *et al.*, " Performance Expectations and Loading Rates for Constructed Wetlands" in Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural, Hammer, D.A., ed., Lewis Publishers, Chelsea, MI, 1989, pp. 319-351.

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

Wildeman T.R., and Laudon, L.S., "Use of Wetlands for Treatment of Environmental Problems in Mining: Non-Coal-Mining Applications" in Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural, Hammer, D.A., ed., Lewis Publishers, Chelsea, MI, 1989, pp. 221-232.

Witthar, S.R., "Wetland Water Treatment Systems" in Constructed Wetlands for Water Quality Improvement, Moshiri, G.A., ed., CRC Press, Boca Raton, 1993, pp. 147-156.

BATCH EXPERIMENT NUMBER: 1 (not digested)

ADSORBATE: Copper

ADSORBENT: Peat

Sample ID	C, Equilibrium Cu Conc.	q, Amount Adsorbed	Freundlich		Langmuir		Double Reciprocal Langmuir	
			log(C)	log(q)	C	C/q	1/C	1/q
1:10	0.05	96	-1.301	1.982	0.05	0.000521	20.00	0.010417
1:20	0.08	192	-1.097	2.283	0.08	0.000417	12.50	0.005208
1:25	0.09	239	-1.046	2.378	0.09	0.000377	11.11	0.004184
1:40	0.09	383	-1.046	2.583	0.09	0.000235	11.11	0.002611
1:50	0.10	478	-1.000	2.679	0.10	0.000209	10.00	0.002092
1:60	0.11	573	-0.959	2.758	0.11	0.000192	9.09	0.001745

Fit to Freundlich Isotherm

K(f) = 75,963

n = 0.4411

Regression Output:

Constant		4.880600
Std Err of Y Est		0.105371
R Squared		0.893449
No. of Observations		6
Degrees of Freedom		4
X Coefficient(s)	2.267169	
Std Err of Coef.	0.391469	

Fit to Langmuir Isotherm

Q = -170

b = -7.0501

Regression Output:

Constant		0.000836
Std Err of Y Est		0.000060
R Squared		0.835455
No. of Observations		6
Degrees of Freedom		4
X Coefficient(s)	-0.005891	
Std Err of Coef.	0.001307	

Fit to Langmuir Double Reciprocal Isotherm

Q = -180

b = -6.8760

Regression Output:

Constant		-0.005546
Std Err of Y Est		0.000690
R Squared		0.963734
No. of Observations		6
Degrees of Freedom		4
X Coefficient(s)	0.000807	
Std Err of Coef.	0.000078	

BATCH EXPERIMENT NUMBER: 2 (not digested)

ADSORBATE: Copper

ADSORBENT: Peat

			Freundlich		Langmuir		Double Reciprocal Langmuir	
Sample ID	C, Equilibrium Cu Conc.	q, Amount Adsorbed	log(C)	log(q)	C	C/q	1/C	1/q
1:100	0.12	945	-0.921	2.975	0.12	0.000127	8.33	0.001058
1:200	0.14	1,886	-0.854	3.276	0.14	0.000074	7.14	0.00053
1:400	0.15	3,768	-0.824	3.576	0.15	0.00004	6.67	0.000265
1:500	0.15	4,710	-0.824	3.673	0.15	0.000032	6.67	0.000212
1:600	0.15	5,652	-0.824	3.752	0.15	0.000027	6.67	0.000177
1:1000	0.17	9,400	-0.770	3.973	0.17	0.000018	5.88	0.000106

Fit to Freundlich Isotherm	**Regression Output:**		
	Constant		9.351029
	Std Err of Y Est		0.102714
	R Squared		0.934089
	No. of Observations		6
K(f) = 2.24E+09	Degrees of Freedom		4
n = 0.1438	X Coefficient(s)	6.953940	
	Std Err of Coef.	0.923603	

Fit to Langmuir Isotherm	**Regression Output:**		
	Constant		0.000397
	Std Err of Y Est		0.000017
	R Squared		0.869009
	No. of Observations		6
Q = -426	Degrees of Freedom		4
b = -5.9103	X Coefficient(s)	-0.002349	
	Std Err of Coef.	0.000456	

Fit to Langmuir Double Reciprocal Isotherm	**Regression Output:**		
	Constant		-0.002524
	Std Err of Y Est		0.000108
	R Squared		0.926971
	No. of Observations		6
Q = -396	Degrees of Freedom		4
b = -5.9672	X Coefficient(s)	0.000423	
	Std Err of Coef.	0.000059	

BATCH EXPERIMENT NUMBER: 3 (not digested)

ADSORBATE: Copper

ADSORBENT: Peat

Sample ID	C, Equilibrium Cu Conc.	q. Amount Adsorbed	Freundlich		Langmuir		Double Reciprocal Langmuir	
			log(C)	log(q)	C	C/q	1/C	1/q
1:10	0.12	90	-0.921	1.954	0.12	0.001333	8.33	0.011111
1:20	0.19	178	-0.721	2.250	0.19	0.001067	5.26	0.005618
1:40	0.25	354	-0.602	2.549	0.25	0.000706	4.00	0.002825
1:60	0.25	531	-0.602	2.725	0.25	0.000471	4.00	0.001883
1:100	0.33	878	-0.481	2.943	0.33	0.000376	3.03	0.001139
1:200	0.36	1,750	-0.444	3.243	0.36	0.000206	2.78	0.000571
1:500	0.48	4,315	-0.319	3.635	0.48	0.000111	2.08	0.000232
1:1000	0.71	8,400	-0.149	3.924	0.71	0.000085	1.41	0.000119
1:2000	2.88	12,460	0.459	4.096	2.88	0.000231	0.35	0.00008
1:5000	5.24	19,350	0.719	4.287	5.24	0.000271	0.19	0.000052
1:10,000	5.40	37,100	0.732	4.569	5.40	0.000146	0.19	0.000027

Fit to Freundlich Isotherm	**Regression Output:**		
	Constant		3.584103
	Std Err of Y Est		0.332886
	R Squared		0.869730
	No. of Observations		11
K(f) = 3,838	Degrees of Freedom		9
n = 0.7164	X Coefficient(s)	1.395773	
	Std Err of Coef.	0.180063	

Fit to Langmuir Isotherm	**Regression Output:**		
	Constant		0.000578
	Std Err of Y Est		0.000397
	R Squared		0.172709
	No. of Observations		11
Q = -11,938	Degrees of Freedom		9
b = -0.1449	X Coefficient(s)	-0.000084	
	Std Err of Coef.	0.000061	

Fit to Langmuir Double Reciprocal Isotherm	**Regression Output:**		
	Constant		-0.001519
	Std Err of Y Est		0.001369
	R Squared		0.856214
	No. of Observations		11
Q = -658	Degrees of Freedom		9
b = -1.1897	X Coefficient(s)	0.001277	
	Std Err of Coef.	0.000174	

BATCH EXPERIMENT NUMBER: 4 (not digested)

ADSORBATE: Copper

ADSORBENT: Peat

			Freundlich		Langmuir		Double Reciprocal Langmuir	
Sample ID	C, Equilibrium Cu Conc.	q, Amount Adsorbed	log(C)	log(q)	C	C/q	1/C	1/q
1:10	0.09	90	-1.046	1.954	0.09	0.001	11.11	0.011111
1:20	0.15	178	-0.824	2.250	0.15	0.000843	6.67	0.005618
1:40	0.29	350	-0.538	2.544	0.29	0.000829	3.45	0.002857
1:60	0.29	529	-0.538	2.723	0.29	0.000548	3.45	0.00189
1:100	0.29	891	-0.538	2.950	0.29	0.000325	3.45	0.001122
1:200	0.31	1,789	-0.509	3.253	0.31	0.000173	3.23	0.000559
1:500	0.31	4,490	-0.509	3.652	0.31	0.000069	3.23	0.000223
1:1000	0.52	8,770	-0.284	3.943	0.52	0.000059	1.92	0.000114
1:2000	1.80	14,980	0.255	4.176	1.80	0.00012	0.56	0.000067
1:5000	4.91	21,900	0.691	4.340	4.91	0.000224	0.20	0.000046
1:10,000	5.11	41,800	0.708	4.621	5.11	0.000122	0.20	0.000024

Fit to Freundlich Isotherm	**Regression Output:**		
	Constant		3.707874
	Std Err of Y Est		0.398164
	R Squared		0.823248
	No. of Observations		11
K(f) = 5,104	Degrees of Freedom		9
n = 0.7144	X Coefficient(s)	1.399683	
	Std Err of Coef.	0.216185	

Fit to Langmuir Isotherm	**Regression Output:**		
	Constant		0.000490
	Std Err of Y Est		0.000337
	R Squared		0.170951
	No. of Observations		11
Q = -13,123	Degrees of Freedom		9
b = -0.1556	X Coefficient(s)	-0.000076	
	Std Err of Coef.	0.000056	

Fit to Langmuir Double Reciprocal Isotherm	**Regression Output:**		
	Constant		-0.001342
	Std Err of Y Est		0.001133
	R Squared		0.901782
	No. of Observations		11
Q = -745	Degrees of Freedom		9
b = -1.3090	X Coefficient(s)	0.001025	
	Std Err of Coef.	0.000113	

BATCH EXPERIMENT NUMBER: 4 (digested)

ADSORBATE: Copper

ADSORBENT: Peat

Sample ID	C, Equilibrium Cu Conc.	q, Amount Adsorbed	Freundlich		Langmuir		Double Reciprocal Langmuir	
			log(C)	log(q)	C	C/q	1/C	1/q
1:10	0.15	89	-0.824	1.949	0.15	0.001685	6.67	0.011236
1:20	0.22	176	-0.658	2.246	0.22	0.00125	4.55	0.005682
1:40	0.33	348	-0.481	2.542	0.33	0.000948	3.03	0.002874
1:60	0.33	527	-0.481	2.722	0.33	0.000626	3.03	0.001898
1:100	0.36	883	-0.444	2.946	0.36	0.000408	2.78	0.001133
1:200	0.40	1,770	-0.398	3.248	0.40	0.000226	2.50	0.000565
1:500	0.44	4,425	-0.357	3.646	0.44	0.000099	2.27	0.000226
1:1000	0.55	8,740	-0.260	3.942	0.55	0.000063	1.82	0.000114
1:2000	2.19	14,200	0.340	4.152	2.19	0.000154	0.46	0.00007
1:5000	5.93	16,800	0.773	4.225	5.93	0.000353	0.17	0.00006
1:10,000	5.97	33,200	0.776	4.521	5.97	0.00018	0.17	0.00003

Fit to Freundlich Isotherm

K(f) = 3,460
n = 0.7209

Regression Output:

Constant 3.539120
Std Err of Y Est 0.430210
R Squared 0.780138
No. of Observations 11
Degrees of Freedom 9
X Coefficient(s) 1.387082
Std Err of Coef. 0.245454

Fit to Langmuir Isotherm

Q = -11,750
b = -0.1260

Regression Output:

Constant 0.000675
Std Err of Y Est 0.000524
R Squared 0.129508
No. of Observations 11
Degrees of Freedom 9
X Coefficient(s) -0.000085
Std Err of Coef. 0.000074

Fit to Langmuir Double Reciprocal Isotherm

Q = -539
b = -1.1489

Regression Output:

Constant -0.001855
Std Err of Y Est 0.001557
R Squared 0.818545
No. of Observations 11
Degrees of Freedom 9
X Coefficient(s) 0.001614
Std Err of Coef. 0.000253

BATCH EXPERIMENT NUMBER: 6 **(digested)**

ADSORBATE: Copper

ADSORBENT: Peat

			Freundlich		Langmuir		Double Reciprocal Langmuir	
Sample ID	C, Equilibrium Cu Conc.	q, Amount Adsorbed	log(C)	log(q)	C	C/q	1/C	1/q
2 mg/L	0.11	1,850	-0.959	3.267	0.11	0.000059	9.09	0.000541
5 mg/L	0.24	4,850	-0.620	3.686	0.24	0.000049	4.17	0.000206
10 mg/L	0.72	9,310	-0.143	3.969	0.72	0.000077	1.39	0.000107
20 mg/L	4.42	15,400	0.645	4.188	4.42	0.000287	0.23	0.000065
30 mg/L	7.36	22,610	0.867	4.354	7.36	0.000326	0.14	0.000044
40 mg/L	14.86	25,440	1.172	4.406	14.86	0.000584	0.07	0.000039

Fit to Freundlich Isotherm	**Regression Output:**		
	Constant		3.899188
	Std Err of Y Est		0.122774
	R Squared		0.937131
	No. of Observations		6
K(f) = 7,928	Degrees of Freedom		4
n = 2.0319	X Coefficient(s)	0.492160	
	Std Err of Coef.	0.063737	

Fit to Langmuir Isotherm	**Regression Output:**		
	Constant		0.000064
	Std Err of Y Est		0.000036
	R Squared		0.977196
	No. of Observations		6
Q = 27,710	Degrees of Freedom		4
b = 0.5654	X Coefficient(s)	0.000036	
	Std Err of Coef.	0.000003	

Fit to Langmuir Double Reciprocal Isotherm	**Regression Output:**		
	Constant		0.000033
	Std Err of Y Est		0.000029
	R Squared		0.982099
	No. of Observations		6
Q = 30,442	Degrees of Freedom		4
b = 0.6148	X Coefficient(s)	0.000053	
	Std Err of Coef.	0.000004	

BATCH EXPERIMENT NUMBER: 7 (not digested)

ADSORBATE: Copper

ADSORBENT: Yard Waste Compost

Sample ID	C, Equilibrium Cu Conc.	q, Amount Adsorbed	Freundlich		Langmuir		Double Reciprocal Langmuir	
			log(C)	log(q)	C	C/q	1/C	1/q
2 mg/L	0.14	1,780	-0.854	3.250	0.14	0.000079	7.14	0.000562
5 mg/L	0.25	4,440	-0.602	3.647	0.25	0.000056	4.00	0.000225
10 mg/L	0.50	7,910	-0.301	3.898	0.50	0.000063	2.00	0.000126
20 mg/L	1.34	16,070	0.127	4.206	1.34	0.000083	0.75	0.000062
30 mg/L	1.95	23,190	0.290	4.365	1.95	0.000084	0.51	0.000043
40 mg/L	2.62	32,240	0.418	4.508	2.62	0.000081	0.38	0.000031

Fit to Freundlich Isotherm	**Regression Output:**		
	Constant		4.120356
	Std Err of Y Est		0.067326
	R Squared		0.983931
	No. of Observations		6
K(f) = 13,193	Degrees of Freedom		4
n = 1.0887	X Coefficient(s)	0.918527	
	Std Err of Coef.	0.058691	

Fit to Langmuir Isotherm	**Regression Output:**		
	Constant		0.000066
	Std Err of Y Est		0.000010
	R Squared		0.427841
	No. of Observations		6
Q = 131,061	Degrees of Freedom		4
b = 0.1159	X Coefficient(s)	0.000008	
	Std Err of Coef.	0.000004	

Fit to Langmuir Double Reciprocal Isotherm	**Regression Output:**		
	Constant		-0.000009
	Std Err of Y Est		0.000040
	R Squared		0.969253
	No. of Observations		6
Q = -106,810	Degrees of Freedom		4
b = -0.1251	X Coefficient(s)	0.000075	
	Std Err of Coef.	0.000007	

BATCH EXPERIMENT NUMBER: 8 (not digested)

ADSORBATE: Copper

ADSORBENT: Sand

			Freundlich		Langmuir		Double Reciprocal Langmuir	
Sample ID	C, Equilibrium Cu Conc.	q, Amount Adsorbed	log(C)	log(q)	C	C/q	1/C	1/q
1:2	2.88	13	0.459	1.114	2.88	0.221538	0.347	0.076923
1:3	5.35	12	0.728	1.079	5.35	0.445833	0.187	0.083333
1:5	5.99	17	0.777	1.230	5.99	0.352353	0.167	0.058824
1:10	6.90	25	0.839	1.398	6.90	0.276	0.145	0.04
1:25	7.31	51	0.864	1.708	7.31	0.143333	0.137	0.019608
1:50	7.35	101	0.866	2.004	7.35	0.072772	0.136	0.009901

Fit to Freundlich Isotherm	**Regression Output:**		
	Constant		0.225733
	Std Err of Y Est		0.304074
	R Squared		0.448275
	No. of Observations		6
K(f) = 1.682	Degrees of Freedom		4
n = 0.6316	X Coefficient(s)	1.583292	
	Std Err of Coef.	0.878254	

Fit to Langmuir Isotherm	**Regression Output:**		
	Constant		0.414314
	Std Err of Y Est		0.143468
	R Squared		0.115435
	No. of Observations		6
Q = -37	Degrees of Freedom		4
b = -0.0657	X Coefficient(s)	-0.027223	
	Std Err of Coef.	0.037680	

Fit to Langmuir Double Reciprocal Isotherm	**Regression Output:**		
	Constant		0.002170
	Std Err of Y Est		0.025122
	R Squared		0.441946
	No. of Observations		6
Q = 461	Degrees of Freedom		4
b = 0.0088	X Coefficient(s)	0.246295	
	Std Err of Coef.	0.138382	

BATCH EXPERIMENT NUMBER: 9 (not digested)

ADSORBATE: Iron

ADSORBENT: Sand

			Freundlich		Langmuir		Double Reciprocal Langmuir	
Sample ID	C, Equilibrium Fe Conc.	q, Amount Adsorbed	log(C)	log(q)	C	C/q	1/C	1/q
1:2	5.14	9.6	0.711	0.982	5.14	0.535417	0.195	0.104167
1:3	5.45	13.5	0.736	1.130	5.45	0.403704	0.183	0.074074
1:5	7.23	13.6	0.859	1.134	7.23	0.531618	0.138	0.073529
1:10	9.60	3.5	0.982	0.544	9.60	2.742857	0.104	0.285714
1:25	9.81	3.5	0.992	0.544	9.81	2.802857	0.102	0.285714
1:50	9.81	7.0	0.992	0.845	9.81	1.401429	0.102	0.142857
1:100	9.83	12.0	0.993	1.079	9.83	0.819167	0.102	0.083333
1:200	9.90	10.0	0.996	1.000	9.90	0.990000	0.101	0.100000

Fit to Freundlich Isotherm	**Regression Output:**		
	Constant		1.806324
	Std Err of Y Est		0.227080
	R Squared		0.249832
	No. of Observations		8
K(f) = 64.02	Degrees of Freedom		6
n = -1.0095	X Coefficient(s)	-0.990597	
	Std Err of Coef.	0.700771	

Fit to Langmuir Isotherm	**Regression Output:**		
	Constant		-1.157133
	Std Err of Y Est		0.823112
	R Squared		0.388950
	No. of Observations		8
Q = 3.427	Degrees of Freedom		6
b = -0.2522	X Coefficient(s)	0.291809	
	Std Err of Coef.	0.149319	

Fit to Langmuir Double Reciprocal Isotherm	**Regression Output:**		
	Constant		0.278606
	Std Err of Y Est		0.086720
	R Squared		0.211504
	No. of Observations		8
Q = 3.589	Degrees of Freedom		6
b = -0.2651	X Coefficient(s)	-1.050949	
	Std Err of Coef.	0.828412	

BATCH EXPERIMENT NUMBER: 10 (not digested)

ADSORBATE: Iron

ADSORBENT: Peat

Sample ID	C, Equilibrium Fe Conc.	q, Amount Adsorbed	Freundlich		Langmuir		Double Reciprocal Langmuir	
			log(C)	log(q)	C	C/q	1/C	1/q
1:10	7.19	14	0.857	1.146	7.19	0.513571	0.139	0.071429
1:20	6.95	42	0.842	1.623	6.95	0.165476	0.144	0.023810
1:40	6.89	93	0.838	1.968	6.89	0.074086	0.145	0.010753
1:60	6.17	186	0.790	2.270	6.17	0.033172	0.162	0.005376
1:100	6.14	319	0.788	2.504	6.14	0.019248	0.163	0.003135
1:200	4.74	931	0.676	2.969	4.74	0.005091	0.211	0.001074
1:500	4.05	2,681	0.607	3.428	4.05	0.001511	0.247	0.000373
1:1000	7.80	1,620	0.892	3.210	7.80	0.004815	0.128	0.000617
1:2000	9.16	520	0.962	2.716	9.16	0.017615	0.109	0.001923
1:5000	9.35	350	0.971	2.544	9.35	0.026714	0.107	0.002857
1:10,000	9.41	100	0.974	2.000	9.41	0.094100	0.106	0.010000

Fit to Freundlich Isotherm	**Regression Output:**		
	Constant		4.247693
	Std Err of Y Est		0.668907
	R Squared		0.144393
	No. of Observations		11
K(f) = 17,689	Degrees of Freedom		9
n = -0.4520	X Coefficient(s)	-2.212309	
	Std Err of Coef.	1.795098	

Fit to Langmuir Isotherm	**Regression Output:**		
	Constant		0.024936
	Std Err of Y Est		0.157271
	R Squared		0.010836
	No. of Observations		11
Q = 114	Degrees of Freedom		9
b = 0.3509	X Coefficient(s)	0.008749	
	Std Err of Coef.	0.027863	

Fit to Langmuir Double Reciprocal Isotherm	**Regression Output:**		
	Constant		0.024032
	Std Err of Y Est		0.021714
	R Squared		0.028601
	No. of Observations		11
Q = 42	Degrees of Freedom		9
b = -0.3002	X Coefficient(s)	-0.080052	
	Std Err of Coef.	0.155511	

BATCH EXPERIMENT NUMBER: 10 (digested)

ADSORBATE: Iron

ADSORBENT: Peat

Sample ID	C, Equilibrium Fe Conc.	q, Amount Adsorbed	Freundlich		Langmuir		Double Reciprocal Langmuir	
			log(C)	log(q)	C	C/q	1/C	1/q
1:10	5.84	29	0.766	1.462	5.84	0.201379	0.171	0.034483
1:20	7.16	37	0.855	1.568	7.16	0.193514	0.140	0.027027
1:40	7.20	81	0.857	1.908	7.20	0.088889	0.139	0.012346
1:60	5.94	200	0.774	2.301	5.94	0.029700	0.168	0.005000
1:100	5.89	344	0.770	2.537	5.89	0.017122	0.170	0.002907
1:200	4.31	1,018	0.634	3.008	4.31	0.004234	0.232	0.000982
1:500	3.70	2,856	0.568	3.456	3.70	0.001296	0.270	0.000350
1:1000	7.44	1,980	0.872	3.297	7.44	0.003758	0.134	0.000505
1:2000	9.06	720	0.957	2.857	9.06	0.012583	0.110	0.001389
1:5000	9.41	50	0.974	1.699	9.41	0.188200	0.106	0.020000
1:10,000	9.21	2,100	0.964	3.322	9.21	0.004386	0.109	0.000476

Fit to Freundlich Isotherm	**Regression Output:**		
	Constant		3.626528
	Std Err of Y Est		0.763901
	R Squared		0.059871
	No. of Observations		11
K(f) = 4,232	Degrees of Freedom		9
n = -0.7207	X Coefficient(s)	-1.387538	
	Std Err of Coef.	1.832780	

Fit to Langmuir Isotherm	**Regression Output:**		
	Constant		-0.000092
	Std Err of Y Est		0.087322
	R Squared		0.050076
	No. of Observations		11
Q = 101	Degrees of Freedom		9
b = -107.8511	X Coefficient(s)	0.009926	
	Std Err of Coef.	0.014411	

Fit to Langmuir Double Reciprocal Isotherm	**Regression Output:**		
	Constant		0.017366
	Std Err of Y Est		0.012618
	R Squared		0.043317
	No. of Observations		11
Q = 58	Degrees of Freedom		9
b = -0.3552	X Coefficient(s)	-0.048896	
	Std Err of Coef.	0.076595	

Day	Sample Time from start of run (hours)	Hydraulic Retention Phase	Applied Copper Phase	Influent Sample pH	Effluent Sample pH	Average Daily Influent pH	Average Daily Effluent pH
0						4.18	3.83
	0	I	A	4.20	4.00		
	2	I	A		3.91		
	8	I	A		3.79		
	20	I	A	4.16	3.61		
1						4.18	3.64
	24	I	A	4.17	3.61		
	30	I	A	4.18	3.62		
	44	II	A		3.69		
2						4.22	3.78
	48	II	A	4.22	3.72		
	56	II	A		3.77		
	68	II	A		3.85		
3						4.41	3.90
	72	II	A	4.22	3.89		
	79	II	B	4.59	3.90		
6						4.67	4.38
	164	II	B	4.67	4.38		
7						4.66	4.40
	168	II	B		4.39		
	174	II	B	4.66	4.40		
8						4.66	4.41
	192	II	B		4.42		
	195	II	B	4.66			
	199	II	B		4.40		
	214	II	B		4.42		
9						4.65	4.45
	218	II	B	4.65	4.44		
	222				4.46		
10						5.63	4.54
	240	II	B		4.45		
	242	II	B	4.72			
	249	II	C	6.53	4.63		
14						6.50	4.54
	336	II	C	6.50	4.53		
	338	II	C		4.53		
	344	II	C		4.56		
15						6.64	4.74
	362	II	C	6.49	4.68		
	364	II	C	6.60			
	367	II	C	6.82	4.75		
	382	II	C		4.80		
16						6.82	4.80
	384	II	C	6.81			
	386	II	C		4.81		

Day	Sample Time from start of run (hours)	Hydraulic Retention Phase	Applied Copper Phase	Influent Sample pH	Effluent Sample pH	Average Daily Influent pH	Average Daily Effluent pH
	388	II	C	6.83			
	392	II	C		4.78		
17						6.77	4.65
	410	II	C	6.77	4.64		
	416	II	C	6.77	4.65		
21						6.72	4.30
	504	II	C	6.72	4.32		
	507	II	C		4.30		
	513	II	C		4.30		
	526	II	C		4.27		
22						6.71	4.27
	535	II	C	6.71	4.27		
	551	II	C		4.27		
23						6.67	4.23
	552	II	C	6.67			
	554	II	C		4.23		
	560	II	C	6.66	4.23		
24						6.66	4.23
	576	II	C	6.63	4.23		
	584	II	C	6.68	4.22		
27						6.69	4.19
	669	II	C	6.69	4.19		
28						6.65	4.17
	675	II	C	6.65	4.19		
	680	II	C	6.65	4.19		
	693	II	C	6.65	4.12		
29						6.65	4.18
	703	II	C	6.65	4.18		
	717	II	C	6.64			
30						6.65	4.13
	720	II	C		4.12		
	724	II	C	6.67			
	728	II	C	6.62	4.13		
35						6.63	4.05
	843	II	C	6.61	4.03		
	849	II	C	6.63	4.05		
	861	III	C	6.65	4.08		
36						6.61	4.07
	866	III	C	6.64			
	868	III	C		4.03		
	885	III	C	6.58	4.11		
37						6.20	4.07
	893	III	C	6.20	4.07		
38						6.37	3.96
	912	III	C	6.14	3.96		

Day	Sample Time from start of run (hours)	Hydraulic Retention Phase	Applied Copper Phase	Influent Sample pH	Effluent Sample pH	Average Daily Influent pH	Average Daily Effluent pH
	918	III	C	6.59	3.96		
39						6.57	3.97
	960	III	C	6.57	3.97		
41						6.55	4.11
	1004	III	C	6.55	4.11		
42						6.95	4.11
	1008	III	D	6.93	4.13		
	1014	III	D	6.96	4.11		
	1030	III	D	6.96	4.09		
43						6.94	4.08
	1037	III	D	6.94	4.08		
	1054			6.93	4.08		
44						6.94	4.08
	1060	III	D	6.94	4.08		
			Average Phase I	4.18	3.76		
			Average Phase II	6.14	4.31		
			Average Phase III	6.68	4.06		
			Average Phase A	4.19	3.77		
			Average Phase B	4.66	4.37		
			Average Phase C	6.62	4.30		
			Average Phase D	6.95	4.09		
			Average Phase I-A	4.18	3.76		
			Average Phase II-A	4.22	3.78		
			Average Phase II-B	4.66	4.37		
			Average Phase II-C	6.67	4.37		
			Average Phase III-C	6.49	4.04		
			Average Phase III-D	6.95	4.09		
			Overall Average	6.14	4.20		

Day	Sample Time from start of run (hours)	Hydraulic Retention Phase	Applied Copper Phase	Influent Sample Copper Content (mg/L)	Effluent Sample Copper Content (mg/L)	Average Daily Influent Copper (mg/L)	Average Daily Effluent Copper (mg/L)
0						9.78	4.25
	0	I	A	9.80			
	2	I	A		6.89		
	8	I	A		3.36		
	20	I	A	9.75	2.51		
1						9.83	1.88
	24	I	A	9.85	2.21		
	30	I	A	9.81	1.95		
	44	II	A		1.48		
2						9.81	0.96
	48	II	A	9.81	1.06		
	56	II	A		1.01		
	68	II	A		0.81		
3						10.00	0.70
	72	II	A	9.77	0.71		
	79	II	B	10.23	0.69		
6						10.13	1.05
	164	II	B	10.13	1.05		
7						10.15	0.79
	168	II	B		0.80		
	174	II	B	10.15	0.77		
8						10.40	0.84
	192	II	B		0.76		
	195	II	B	10.40			
	199	II	B		0.87		
	214	II	B		0.88		
9						10.32	0.71
	218	II	B	10.32	0.77		
	222				0.65		
10						9.88	0.67
	240	II	B		0.68		
	242	II	B	10.27			
	249	II	C	9.49	0.66		
14						4.66	0.34
	336	II	C	4.66	0.36		
	338	II	C		0.33		
	344	II	C		0.33		
15						8.20	0.40
	362	II	C	2.60	0.41		
	364	II	C	12.98			
	367	II	C	9.02	0.38		
	382	II	C		0.42		
16						11.95	0.36
	384	II	C	8.12			
	386	II	C		0.36		

Day	Sample Time from start of run (hours)	Hydraulic Retention Phase	Applied Copper Phase	Influent Sample Copper Content (mg/L)	Effluent Sample Copper Content (mg/L)	Average Daily Influent Copper (mg/L)	Average Daily Effluent Copper (mg/L)
	388	II	C	15.77			
	392	II	C		0.35		
17						14.08	0.36
	410	II	C	15.25	0.37		
	416	II	C	12.90	0.35		
21						5.58	0.14
	504	II	C	5.58	0.13		
	507	II	C		0.13		
	513	II	C		0.13		
	526	II	C		0.15		
22						0.47	0.15
	535	II	C	0.47	0.16		
	551	II	C		0.13		
23						21.36	0.16
	552	II	C	14.02			
	554	II	C		0.15		
	560	II	C	28.70	0.16		
24						21.81	0.16
	576	II	C	16.05	0.17		
	584	II	C	27.57	0.14		
27						14.46	0.16
	669	II	C	14.46	0.16		
28						0.54	0.07
	675	II	C	0.90	0.08		
	680	II	C	0.37	0.06		
	693	II	C	0.36	0.08		
29						0.33	0.09
	703	II	C	0.32	0.09		
	717	II	C	0.34			
30						18.81	0.07
	720	II	C		0.07		
	724	II	C	0.31			
	728	II	C	37.30	0.06		
35						0.64	0.07
	843	II	C	0.77	0.08		
	849	II	C	0.75	0.05		
	861	III	C	0.41	0.07		
36						36.21	0.06
	866	III	C	68.50			
	868	III	C		0.08		
	885	III	C	3.92	0.04		
37						24.95	0.03
	893	III	C	24.95	0.03		
38						8.12	0.01
	912	III	C	3.32	0.01		

Day	Sample Time from start of run (hours)	Hydraulic Retention Phase	Applied Copper Phase	Influent Sample Copper Content (mg/L)	Effluent Sample Copper Content (mg/L)	Average Daily Influent Copper (mg/L)	Average Daily Effluent Copper (mg/L)
	918	III	C	12.92	0.01		
39						33.95	0.01
	960	III	C	33.95	0.01		
41						76.90	0.01
	1004	III	C	76.90	0.01		
42						72.00	0.03
	1008	III	D	73.20	0.01		
	1014	III	D	69.20	0.04		
	1030	III	D	73.60	0.04		
43						43.03	0.40
	1037	III	D	11.06	0.67		
	1054			75.00	0.13		
44						14.42	0.08
	1060	III	D	14.42	0.08		
			Average Phase I	9.80	3.38		
			Average Phase II	9.98	0.44		
			Average Phase III	38.67	0.09		
			Average Phase A	9.80	2.20		
			Average Phase B	10.25	0.79		
			Average Phase C	14.06	0.18		
			Average Phase D	48.66	0.19		
			Average Phase I-A	9.80	3.38		
			Average Phase II-A	9.79	1.01		
			Average Phase II-B	10.25	0.79		
			Average Phase II-C	9.56	0.22		
			Average Phase III-C	28.11	0.03		
			Average Phase III-D	48.66	0.19		
			Overall Average	17.66	0.59		