ADSORPTION OF HEAVY METALS FROM WASTE STREAMS BY PEAT

by

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ABSTRACT

Adsorption of heavy metal ions (e.g. copper, nickel and lead) onto sphagnum moss peat was investigated. The influence of pH, concentration, temperature, nature of solute, number of solutes simultaneously present, peat dose and reaction time on batch adsorption equilibria and kinetics tests were examined.

Batch adsorption of copper and nickel onto peat was pH dependent, the optimum range being 4.0 to 5.0 for copper and 4.0 to 7.0 for nickel. Langmuir and Freundlich isotherms showed a single relationship between initial metal concentration, metal removal, and initial pH. The latter was found to control efficiency of metal removal.

The use of peat in removal of lead from aqueous solution was studied in batch experiments. Investigations included the effect of pH and temperature of adsorption. The adsorption equilibria data followed Langmuir and Freundlich models. Efficiency of lead removal depended very little on the reaction temperatures (12 to 37°C) and initial pH values (4.0 to 6.0). The results suggested that the adsorption process is endothermic for lead-peat adsorption.

Kinetic data suggested involvement of a chemical rate-limiting step, and a predictive relationship was derived relating metal removal to peat dose. In comparison with other metals, nickel removal is poor, and possible reasons are discussed. Kinetic results also indicated that pore diffusion is not the only rate determining step in peat metal adsorption.

A rate equation is described for the study of the kinetics of adsorption of aqueous divalent metal ions onto sphagnum moss peat for a range of conditions. An empirical model was devised for predicting percentage metal ion adsorbed. The model showed a high coefficient of correlation, indicating its reasonableness.

The last section describes the results of an examination into the simultaneous adsorption by peat of several metals. Initially copper and nickel from both single- and bi-solute systems were tested. In general, pore diffusion appeared to be the rate-controlling step. The effects of competitive adsorption in batch systems for copper and nickel

system was also studied in various ratios of metal concentration. A mathematical model was used successfully and shown to be predictive for various ratio of metal ions concentration in competitive adsorption. The dose effect on the uptake of metals on moss peat was also studied for bi-solute adsorption systems. The best interpretation which could be placed on the data was that the behaviour of nickel was unusual. The results also showed that the kinetics of adsorption were best described by a second-order expression rather than a first-order model. For metal ions which are of different size but are divalent metal ions, we used lead(II) and copper(II) as well as lead(II) and nickel(II) systems. The effects of competitive adsorption in batch systems indicated that copper had a greater effect on lead adsorption than did nickel. However, lead had a greater effect on nickel than copper.

A copper, lead and nickel triple-solute system was also tested. The adsorption of any single metal such as copper, lead and nickel was hindered by the presence of the other metals. The competitive effect appears to have affected the three ions in the order nickel > lead > copper with nickel affected most; the adsorption capacity for each solute from the mixed solution was 15.9, 57.4 and 71.5% of that of a single-solute system for copper, lead and nickel, respectively. The kinetic results showed that the heavy metals are adsorbed fairly rapidly, and that there is a relatively good fit between experimental data and the second order model for copper, lead and nickel.

Correction list

4.2. Pseudo Second-Order Reaction Model

Original in the thesis	Corrected
$\frac{-d(P)_t}{dt} = 2K[(P)_0 - (P)_t]^2$	$\frac{d(P)_t}{dt} = K[(P)_0 - (P)_t]^2$
$\frac{-d(HP)_t}{dt} = 2K[(HP)_0 - (HP)_t]^2$	$\frac{d(HP)_t}{dt} = K[(HP)_0 - (HP)_t]^2$
$\frac{-d(q_e - q_t)}{dt} = 2K(q_e - q_t)^2,$ (4.2-1)	$\frac{d(q_t)}{dt} = K(q_e - q_t)^2,$ (4.2-1)
$\frac{-d(q_e - q_t)}{(q_e - q_t)^2} = 2Kdt$	$\frac{-d(q_e - q_t)}{(q_e - q_t)^2} = Kdt$
$\int_0^{q_t} \frac{-d(q_e - q_t)}{(q_e - q_t)^2} = \int_0 2Kt$	$\int_0^{q_t} \frac{-d(q_e - q_t)}{(q_e - q_t)^2} = \int_0 Kt$
$\frac{1}{q_e - q_t} = \frac{1}{q_e} + 2Kt,$ (4.2-2)	$\frac{1}{q_e - q_t} = \frac{1}{q_e} + Kt,$ (4.2-2)
$q_t = \frac{t}{\frac{1}{2Kq_e^2} + \frac{t}{q_e}},$ (4.2-3)	$q_t = \frac{t}{\frac{1}{Kq_e^2} + \frac{t}{q_e}},$ (4.2-3)
$\frac{t}{q_t} = \frac{1}{2Kq_e^2} + \frac{1}{q_e}t.$ (4.2-4)	$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{1}{q_e}t.$ (4.2-4)
$h = 2Kq_e^2$	$h = Kq_e^2$

To my dear late father and to my dear mother

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Scientific Papers Published

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Presented at: *Challenges and Opportunities in Science: First Symposium of Chinese Institute of Engineers in UK*, Cambridge, April, (1995).

Title: Kinetic Studies of Competitive Heavy Metal Adsorption by Sphagnum Moss Peat
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Title: Removal of Lead Ions From Wastewater Using Sphagnum Moss Peat
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Title: The Study of Kinetics of Adsorption of Aqueous Divalent Metal Ions Solution onto Sphagnum Moss Peat
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Related to MPhil Thesis (Sheffield University):

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Title: The Synthesis and Crystal Structure of A Cerium(III) Complex of 2,6-Bis[2-Formylphenoxymethyl]Pyridine
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Published: *Inorganica Chimica Acta*, (1995), **232**, 227-230.

Title: The Structures of Dimeric Lead(II) Complex of a 15-Membered Pyridyl-Derived N_3O_3- and of the Hydrobromide Salt of a Related 17-Membered Macrocycle
Author: N.A. Bailey, D.E. Fenton, J.G. Ford, Y.S. Ho, S.J. Kitchen, P.B. Leeson, P.A. Tasker and M.G. Williams
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LIST OF ABBREVIATIONS

[A] and [B]	concentration of the components A and B
A	cross sectional area of solute, (Å^2)
a and b	constants of k_b/C_0 equation
A_1 and A_2	constants of C_e/m_s equation, (l/mg) and (l^2/mgg)
A_c	constant of Clausius-Clapeyron equation
b_1 and b_2	constants of R/C_0 equation
C	dimensionless liquid-phase concentration
C_e	equilibrium concentration, (mg/l)
C_t	concentration of metal ions at any time t, (mg/l)
C_0	initial concentration of metal ions, (mg/l)
d_p	geometric mean size of adsorbent particles, (μm)
[H$^+$]	proton concentration, (M)
h	initial adsorption rate, (mg/gmin)
k_a^A and k_a^B	rate constants of adsorption of the components A and B
k_{-a}^A and k_{-a}^B	rate constants of adsorption that are proportional to the number of impacts of molecules on the unoccupied parts of the surface of the components A and B
K	adsorption rate constant
k	Langmuir constant, (l/mg)
K′	apparent conditional stability constant, (l/mg)
K_1 and K_2	constants for bi-solute of Freundlich type
k_1 and k_2	Langmuir constants of solutes 1 and 2, (l/mg)
K_A and K_B	adsorption constants for bi-solute of A and B
k_b	binding kinetic constant
K_D	distribution coefficient
k_d	rate constant for low concentration
K_F	Freundlich constant

K_i	reaction constant between protons and the surface of peat
K_R	equilibrium parameter for adsorption
k_r	reverse reaction constant
K_t	constant of R/t equation
M	molecular weight of solute
(M)	concentration of free metal in solution, (mg/l)
$(M)_e$	equilibrium residual free metal concentration in solution, (mg/l)
$(M)_{in}$	initial free metal concentration, (mg/l)
m_1	constant of R/t equation
m_s	peat dose, (g/l)
N	Avogadro number, 6.02×10^{23}
n	constant of ϕ/C_0 equation
1/n	Freundlich constant
(P)	concentration of peat binding sites, (mg/l)
$(P)_0$ and $(HP)_0$	total active sites of peat
$(P)_t$ and $(HP)_t$	active sites of peat at time t
(PM)	concentration of metal bound to peat, (mg/l)
(PM) and $(PM)_{lim}$	variable and equilibrium bound metal concentration, (mg/l)
pH_0	pH of solution at equilibrium for $C_0 = 0$ mg/l
pH_{200}	pH of solution at equilibrium for $C_0 = 200$ mg/l
pH_{fin}	equilibrium pH of solution
pH_{in}	initial pH of solution
Q	dimensionless solid-phase concentration
q_1 and q_2	amounts of 1 and 2 adsorbed per unit weight of adsorbent at equilibrium concentration C_1 and C_2 in a solution containing two solutes
$q_{e,1}$ and $q_{e,2}$	amounts of solutes 1 and 2 adsorbed per unit weight of adsorbent at equilibrium concentrations $C_{e,1}$ and $C_{e,2}$

$q_{e,Cu}$	amount of Cu adsorbed per unit weight of adsorbent at equilibrium concentration $C_{e,Cu}$ in a bi-solute (copper/nickel) system
$q_{e,Ni}$	amount of Ni adsorbed per unit weight of adsorbent at equilibrium concentration $C_{e,Ni}$ in a bi-solute (copper/nickel) system
q_e	amount of metal adsorbed at equilibrium, (mg/g)
q_i	amount of i adsorbed per unit weight of adsorbent at equilibrium concentration C_i in a solution containing n solutes
q_m	infinity adsorption capacity, (mg/g); when peat dose approaches zero
q_s	adsorption density at the equilibrium solute concentration C_s
q_t	amount of divalent metal ion on the surface of adsorbent at any time, t, (mg/g)
R	percentage of metal ion removal, (%)
R_0	maximum percentage of metal ion removal at equilibrium, (%), when peat dose is infinity
r^2	correlation coefficient
R_e	percentage of metal ion removal at equilibrium, (%)
R_t	percentage of metal ion removal at any time, (%)
S	specific surface area, (m^2/g)
S_1	constant of R_e/m_s equation, (g/%l)
S_2	constant of q_e/m_s equation, (l/mg)
t	contact time, (min.)
T	temperature, (°C)
X_{Cu}	mole ratio of concentration of copper
$X_{m,1}$ and $X_{m,2}$	maximum adsorption capacities of solutes 1 and 2 corresponding to complete monolayer coverage, (mg/g)
$X_{m,Cu}$	monolayer adsorption capacity for copper system, (mg/g)
$X_{m,Ni}$	monolayer adsorption capacity for nickel system, (mg/g)

X_m	maximum adsorption capacity corresponding to complete monolayer coverage, (mg/g)
X_{Ni}	mole ratio of concentration of nickel
Y_h	coefficient for higher competitive metal ion
Y_l	coefficient for lower competitive metal ion
v_a^A and v_a^B	rates of adsorption of the components A and B
v_{-a}^A and v_{-a}^B	rates of adsorption that are proportional to the number of impacts of molecules on the unoccupied parts of the surface of the components A and B
α, β, and γ	constant of R/pH_{in} equation
ϕ	initial rate parameter
θ_A	fraction of the surface occupied by molecules of solute A
θ_B	fraction of the surface occupied by molecules of solute B
ΔH	enthalpy change, (KJ/mol)

CHAPTER ONE

INTRODUCTION

1.1. WATER POLLUTION

"Water, Water, everywhere, nor any drop to drink." So goes the ancient sailor's lament as he sees himself surrounded by water which he cannot consume. A modern parallel occurs when sufficient water is available but is so polluted or brackish that its uses are restricted (Sundstrom and Klei, 1979).

Even in the Stone Age, water pollution was from man's own waste. The philosophy has often been that when "washed away" the material is no further trouble. The Middle Ages were the great period of artistic metalwork and when man started to make tools, there was environmental contamination by metal ions, increasing in extent during the centuries (Montgomery, 1972). Since the Industrial Revolution, the development of industry has progressed. Pollution problems were rapidly created and then steadily increased over the longer term. From World War II there has been a tremendous growth in the manufacture and the use of synthetic chemicals (Manahan, 1991). Many of these chemicals, for example, insecticides and herbicides, appear in the environment as runoff from agricultural land. Industrial waste too, is discharged into surface water. Today there are still many problems although the control of environmental pollution has been investigated and legislated on for a long time.

Water is essential to life, and as some water pollution can have serious health consequences, particularly if the pollution leads to pathogenic materials, considerable effort is put into waste water treatment (Fergusson, 1982). There are a number of possible sources of wastewaters. These include domestic sewage, industrial wastewaters, agricultural runoff, and storm water urban runoff. In fact, it is not easy to classify water pollution and their sources. However, one attempt is given in **Table 1.1-1**. The first four groupings are the major ones. The most complex pollution is from industrial wastewaters which include many chemical contaminants and heavy metals (Fergusson, 1982).

TABLE 1.1-1: Types of Water Pollutants (Information From Fergusson, 1982).

Type of Pollutant	Sources	Effects
Oxygen Demanding Sewage	Urban Environment, Domestic, Industrial Food Processing, and Commercial	Oxygen Levels in Water, Water Quality, Eutrophication
Disease Causing		
Chemical Carcinogens Pathogens	Urban Environment, Uncontrolled Wastes, Sewage	Health Effects
Organic Chemicals		
Trace Amounts Pesticides Polychlorinated Biphenyls Petroleum Wastes Detergents	Urban Environment, Rural, Agriculture, Oil Spills, Sewage, Industrial, Commercial, Cleaning Oil Tankers and Use of Seawater as Ballast	Health, Environmental Destruction, Eutrophication, Wild Life, Aquatic Life
Inorganic Chemicals and Minerals		
Trace Elements Metal-Organic Acid-Bases	Urban Environment, Industry, Mining, Commercial, Leaching Refuse Dumps	Health, Metal Transport, Water Quality, Aquatic Life
Sediments	Leaching, Wind, Dumping Solid Waste	Water Quality, Wildlife, Aquatic Life
Radioactive Materials	Nuclear Power Stations, Waste Disposal, Nuclear Explosions, Mining	Health
Thermal	Power Stations, Urban Environment	Aquatic Life

1.1.1. Characteristics of Wastewater

Contaminants in wastewaters are usually a complex mixture of organic and inorganic compounds. It is usually impractical, if not nearly impossible, to obtain a complete chemical analysis of most wastewaters. An important aspect of water pollution from industry is that it cannot be characterised solely by one or two non-specific criteria such as BOD, suspended solids, coliform count, or heavy metal concentration. Depending on the type of industry a wide variety of hazardous substances may be dissolved, suspended, or adsorbed on suspended particles in effluents. This is especially true of the chemical industry because of the large number of different substances which are handled (Moore and Moore, 1976). Wastewaters are, therefore, not easily characterised. Most heavy metals found in wastewater are in the inorganic form. However, in some industries such as textiles and dyeing, heavy metals are in the organic form. Treatment technology is different for these two forms. Organic contaminants can probably be catalogued to be oxygen consuming organics that can be decomposed by adding soluble oxygen to the wastewater or toxic organic compounds such as phenol, aromatics, polychlorinated biphenyls, pesticide and petroleum pollutants.

A number of empirical methods for the evaluation of the concentration of contaminants in wastewaters have been devised, the application of which does not require knowledge of the chemical composition of the specific wastewater under consideration. The most common methods for the analysis of organic contaminants are BOD and COD. Biochemical oxygen demand (BOD) is used as a measure of the quantity of oxygen required for the oxidation of biodegradable organic matter present in the water sample by aerobic biochemical action (Ramalho, 1983). Chemical oxygen demand (COD) corresponds to the amount of oxygen required to oxidise the organic fraction of the sample which is susceptible to permanganate or dichromate oxidation in an acid solution (Ramalho, 1983). However, analytical methods for organic contaminants are classified into two groups (Ramalho, 1983):

Group 1. Oxygen-demand parameter methods

1. Theoretical oxygen demand (ThOD)
2. Chemical oxygen demand (COD):
    - standard dichromate oxidation method
    - permanganate oxidation test
    - rapid COD tests
    - instrumental COD methods
3. Biochemical oxygen demand (BOD):
    - dilution methods
    - manometric methods
4. Total oxygen demand (TOD)

Group 2. Carbon-content parameter methods

1. Theoretical organic carbon (ThOC)
2. Total organic carbon (TOC):
    - wet oxidation method
    - carbon analyser determinations

1.1.2. Heavy Metal Pollution

Heavy metals in the environment are of concern to man due to their high toxicity potential. The addition of metal ions to a natural water system is a ubiquitous process, involving all avenues of human endeavour, ranging from large industrial enterprises to activities in the home (Fergusson, 1982). Heavy metal is the classification that is generally applied to those metals of particular concern in the treatment of industrial wastewaters: copper, silver, zinc, cadmium, mercury, lead, chromium, iron, and nickel. Other metals that may be considered part of this category are tin, arsenic, selenium, molybdenum, cobalt, manganese, and aluminium. In addition to industry, metals get into water from weathering of rocks and soils, atmospheric fallout, agricultural activity, domestic sewage, runoff from streets and highways and land clearing. Unlike many organic wastes, heavy metals cannot be degraded biologically, by burning or by decomposition into harmless products. Ideally heavy metals removed from wastewater should be recycled for industrial use or disposed of in a way that presents little or no threat to humans or the environment (Huang *et al.*, 1991). The research reported in this volume therefore concentrates on three of the more serious metal pollutants, which occur particularly often; namely copper, nickel, and lead.

One of the most important sources of heavy metal pollution in surface water is the direct or indirect discharge of effluents from the electroplating industry. Acidic electrolytes are mainly employed for the plating of copper, nickel, zinc, and chromium. Alkaline electrolytes, containing the metal as cyanide complexes, are used for the deposition of copper, zinc, cadmium, gold, silver, and brass. Many of the processes in the electroplating industry such as pickling, dipping, and polishing generally use strongly acidic media and contain appreciable concentrations of metals, the concentration varying according to the age and condition of the pickle and dip and, in a manually operated plant, to the skill of the operator (Lowe, 1970). The volume of effluent discharged will vary according to the number of different processes in use and the work output of the plants. After plating, some metal ions remain in the film of liquid on the particle, which then is rinsed. **Table 1.1.2-1** shows the concentration of the more common metals in drag-out rinses (Farkas and Mitchell, 1985).

TABLE 1.1.2-1: The Concentration of the More Common Metals in Drag-Out Rinses (Information From Farkas and Mitchell, 1985).

Metal	Concentration (mg/l)
Cu	500-950
Pb	100-250
Ni	50-350
Au	10-50
Ag	20-100

More than 90% of the wastewater discharged from a plating shop comes from rinsing of work pieces with the occasional discharges of process solution, spillage or cleaning of process devices. The characteristics of electroplating wastewater are a function of the types of plating processes, rinsing methods and plating practices. The characteristics of the plating wastewater vary from one factory to another even though both might be engaged in the same plating processes.

Cyanide has been detected in the combined wastewater discharged from copper and zinc plating factories. The sources of cyanide detected in the wastewater should be derived from the washing of the drag-out solution still attached on the surface of the plated items. Depending upon the type of plating processes, heavy metals such as copper, nickel, zinc, aluminium, and silver were also detected in the wastewater. In summary, the combined plating wastewater generally contained cyanide, hexavalent chromium and heavy metals.

1.2. SOURCES OF POLLUTION BY COPPER, NICKEL, AND LEAD

There are many routes by which metals can enter the air, water and soil as a result of man's activities. The sources of metals in air and water are presented in the following sections.

Atmospheric emissions of trace elements such as copper, nickel, and lead from major anthropogenic sources in Europe were estimated on the basis of emission factors and statistical data on the consumption of raw materials and the production of industrial goods in 1982. The estimates are presented in **Table 1.2-1** (Pacyna *et al.*, 1991).

TABLE 1.2-1: European Emissions of Trace Elements Such as Copper, Nickel, and Lead From Various Anthropogenic Sources in 1982 (t/y) (Information From Pacyna *et al.*, 1991).

Source	Cu	Ni	Pb
Conventional Thermal Power Plants	1,377	4,580	1,301
Industrial, Commercial, Residential Boilers	2,038	7,467	1,606
Fuel-Wood Combustion	1,500	375	420
Gasoline Combustion	-	1,330	68,337
Mining	192	1,640	824
Primary Non-Ferrous Metal Production			
Copper	7,850	140	3,992
Zinc	440	-	4,029
Lead	120	-	3,642
Secondary Non-Ferrous Metal Production			
Copper	61	-	407
Lead	-	-	273
Iron and Steel Manufacturing	1,710	340	3,900
Refuse Incineration	260	10	536
Phosphate Fertiliser Production	77	77	-
Cement Production	-	-	613
Total	15,600	16,000	89,750

1.2.1. Sources of Copper

Production of non-ferrous metals represents 38% of anthropogenic emissions. About 21% originates from wood combustion, followed by iron and steel production, waste incineration, industrial applications and coal combustion (Moore and Ramamoorthy, 1984). The most important natural discharge of copper to the atmosphere is windblown dust. Discharges of mine tailings and fly-ash are the major source of solid copper waste. Other sources of solid wastes include fertiliser production and municipal and industrial sewage (Moore and Ramamoorthy, 1984). The largest emissions of atmospheric As, Cd, Cu, In, and Zn come from the pyrometallurgical processes employed in the production of lead, copper, and zinc (Pacyna *et al.*, 1991).

A principal source of copper in industrial waste streams is metal cleaning and plating baths, and rinses, as brass, boiler pipe, cooking utensils, fertilisers, and from copper metal working, which requires periodic oxide removal by immersing the metal in strong acid baths. Solution adhering to the cleaned metal surface, referred to as drag-out, is rinsed from the metal and contaminates the waste rinse water. Similarly, plated metal parts are also rinsed and produce waste water. Copper concentration in the plating bath depends upon the bath type, and may range from 3,000-50,000 mg/l (Patterson, 1975). Therefore, copper is frequently found in water and wastewater in significant quantities. Process wastewater concentrations are summarised in **Table 1.2.1-1**.

1.2.2. Sources of Nickel

Oil and gasoline combustion is the largest single source, followed by production of non-ferrous metals, waste incineration, wood combustion, industrial application, and iron and steel production (Moore and Ramamoorthy, 1984). The most important natural discharge of nickel to the atmosphere is windblown dust.

Emissions of airborne nickel vary widely both from nickel-producing and nickel-using industries. Combustion of fossil fuels to produce electricity and heat is the main source for anthropogenic emissions of Be, Co, Hg, Mo, Ni, Sb, Se, Sn, and V, and incidentally combustion processes are also an important source of atmospheric As, Cr, Cu, Mn, and Zn (Pacyna *et al.*, 1991). Although the world consumption of oil is much less than that of coal, the higher nickel content of this fossil fuel has led a number of authors to attribute ambient nickel concentrations mainly to emissions produced by its use (Gatz, 1975). Another significant use of nickel is in the electroplating industry. Nickel is a significant component of copper, lead, zinc, and asbestos deposits and, since much processing of this material involves dry physical manipulation though blasting and crushing, significant amounts of dust are produced as a by-product. Indeed, in such situations , nickel is likely to be present in small, but significant concentrations.

TABLE 1.2.1-1: Concentrations of Copper in Industrial Process Wastewaters (Information From Patterson, 1975).

Source	Copper Concentration (mg/l) Range	Copper Concentration (mg/l) Average
Plating Rinse	0-120	-
Plating	2.0-88	-
Appliance Manufacturing		
Spent Acids	0.6-11.0	-
Alkaline Wastes	0-1.0	-
Automobile Heater Production	24-33	28
Silver Plating		
Silver Bearing	3-900	12
Acid Wastes	30-590	135
Alkaline Wastes	3.2-19	6.1
Brass Plating		
Pickling Bath Wastes	4.0-23	-
Bright Dip Wastes	7.0-44	-
Plating Wastes	2.8-7.8	4.5
Pickling Wastes	0.4-2.2	1.0
Brass Dip	2-6	-
Brass Mill Rinse	4.4-8.5	-
Brass Mill Rinse		
Tube Mill	74	-
Rod And Wire Mill	888	-
Brass Mill Bichromate Pickle		
Tube Mill	13.1	-
Rod and Wire Mill	27.4	-
Rolling Mill	12.2	-
Copper Rinse	13-74	-
Brass Mill Rinse	4.5	-
Brass and Copper Wire Mill	75-124	-
Brass and Copper Pickle	6-9	-
Brass and Copper Bright Dip	20-35	-
Copper Mill Rinse	19-74	-
Copper Tube Mill	-	70
Copper Wire Mill	-	800
Copper Ore Extraction	0.28-0.33	-
Gold Ore Extraction	20	-
Acid Mine Drainage	0.12-128	-

Nickel is an important metal and is frequently used in metal industries, particularly in plating operations. Nickel concentrations reported for a variety of wastewater source are summarised in **Table 1.2.2-1**. Wastewaters resulting from pickling and plating of nickel and nickel alloys pose far more problems in treatment than is the case for other plating metals such as copper.

TABLE 1.2.2-1: Concentrations of Nickel in Industrial Process Wastewaters (Information From Patterson, 1975).

Source	Nickel Concentration (mg/l)	
	Range	Average
Tableware Plating		
Silver Bearing Waste	0-30	5
Acid Waste	10-130	33
Alkaline Waste	0.4-3.2	1.9
Metal Finishing		
Mixed Wastes	17-51	-
Acid Wastes	12-48	-
Alkaline Wastes	2-21	-
Small Parts Fabrication	179-184	181
Combined Degreasing, Pickling and Ni Dipping of Sheet Steel	3-5	-
Brass Pickling	-	3
Business Machine Manufacture		
Plating Wastes	5-35	11
Pickling Wastes	6-32	17
Plating Plants		
4 Different Plants	2-205	-
Rinse Waters	2-900	-
Large Plants	-	25
5 Different Plants	5-58	24
Large Plating Plant	88 (Single Waste Stream)	-
	46 (Combined Flow)	-
Automatic Plating of Zinc Base	45-55	-
Castings	30-40	-
Automatic Plating Of Plastics	15-25	-
Manual Barrel and Rack		
Other		
Mine Drainage	0.19-0.51	-
Acid Mine Drainage	0.46-3.4	-
Gold Ore Extraction	-	6.5

1.2.3. Sources of Lead

The automotive combustion of lead-containing gasoline represents 61% of anthropogenic emissions (Moore and Ramamoorthy, 1984). Other major anthropogenic inputs include non-ferrous metal production, iron and steel production, and coal combustion. The most important natural discharge of lead to the atmosphere is windblown dust (Moore and Ramamoorthy, 1984).

At one time, up to the early part of the present century, smelting and refining were probably a major source of lead released to the atmosphere. Today, lead in the atmosphere comes mainly from vehicles burning leaded petrol. The lead industry is also important as a source of lead in air, but on a more local scale than vehicle emissions. The concentration of lead in the atmosphere varies with population, traffic density, though traffic speed and weather conditions also make a difference. Currently lesser amounts of lead are released in smelting ores containing lead and in burning fossil fuels. During combustion, most lead becomes concentrated in the ash. In commercial combustion, such as a power station, however, most ash is entrained as fly ash and the amount reaching the atmosphere is highly dependent upon the control devices in use (Harrison and Laxen, 1981).

Lead is deposited from the atmosphere directly onto water surfaces. Water is also contaminated by effluents arising from industrial and natural sources, in particular through lead mineralization. It is one of the most widely used non-ferrous metals in industry. The concentration of lead in polluted source waters lies typically in the range 1-100 mg/l (**Table 1.2.3-1**). The concentrations are, however, frequently reduced during treatment, prior to discharge to the receiving waters (Harrison and Laxen, 1981).

TABLE 1.2.3-1: Concentrations of Lead in Industrial Process Wastewaters (Information From Harrison and Laxen, 1981).

Source	Lead Concentration (mg/l)
Battery Manufacture	
Particulate	5-48
Soluble	0.5-25
Tetraethyl lead Manufacture	
Organic	127-145
Inorganic	66-85
Plating	2-140
Plating	0-30
Television Tube Manufacture	400
Mine Drainage	0.02-2.5
Multi-Product Dyestuffs	3
Mining Process Water	0.018-0.098
Steelworks	
Soluble	<0.05-9.5
Particulate	0.016-49
Tetraethyl lead Manufacture	45

1.3. TOXIC EFFECTS OF METALS

Elements in every group of the periodic table have been found to be stimulatory to animals. The distribution of metals with inherent carcinogenicity in the periodic table is shown in **Figure 1.3-1**. Most metals in the fourth period are carcinogenic. It can be assumed that the carcinogenicity is related to the electronic structure of these transition and inner transitional metals (Luckey and Venugopal, 1977).

Toxicity is the ability of a chemical molecule or substance to produce injury once it reaches a susceptible site in or an organism. This research considers some of the more important trace elements, and those most commonly encountered in the environment.

🕯 H																	2 He
💧 Li	☠💧 Be											5 B	🕯 C	🕯 N	🕯 O	◈ F	10 Ne
🕯 Na	*🕯 Mg											💣 Al	*☹◈ Si	15 P	🕯 S	🕯 Cl	18 Ar
🕯 K	🕯 Ca	☹ Sc	☹ Ti	◈ V	☠🕯 Cr	☹🕯 Mn	*💣🕯 Fe	☠🕯 Co	*☠◈ Ni	💣🕯 Cu	☠🕯 Zn	☹💧 Ga	💧 Ge	☹💧 As	☠🕯 Se	35 Br	36 Kr
37 Rb	38 Sr	☹ Y	*☠ Zr	* Nb	🕯 Mo	☢ Tc	44 Ru	☹ Rh	☹ Pd	*💣 Ag	☠💧 Cd	💧 In	*☠◈ Sn	💧 Sb	*💧 Te	🕯 I	54 Xe
55 Cs	💧 Ba	57 La	72 Hf	* Ta	74 W	75 Re	💧 Os	77 Ir	78 Pt	* Au	*💧 Hg	💧 Tl	☠💧 Pb	💧 Bi	☢ Po	☢ At	☢ Rn
☢ Fr	☢ Ra	☢ Ac															

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
☢ Th	☢ Pa	☢ U	☢ Np	☢ Pu	☢ Am	☢ Cm	☢ Bk	☢ Cf	☢ Es	☢ Fm	☢ Md	☢ No	☢ Lr

☹ Suspected Carcinogenic	☠ Proven Carcinogen
💣 Special Complexes are Carcinogenic	☢ Radioactive
💧 Well Established Toxicity	🕯 Essential
◈ Probably Required	* Non-Specific Oncogen

Figure 1.3-1: Biological activity of the elements (Information from Luckey and Venugopal, 1977; and Fergusson, 1982).

1.3.1. Toxic Effects of Copper

Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess. Excess copper accumulates in the liver: the most toxic form of copper is thought to be Cu^+. Its toxicity is highly pH dependent and it has been reported to be more toxic to fish at lower pH values (Sharma *et al.*, 1992). In some respect the intake of essential elements is more critical than for toxic elements. However, epidemiological evidence, such as a high incidence of cancer among coppersmiths, suggests a primary carcinogenic role for copper (Luckey and Venugopal, 1977). The cocarcinogenic character of copper is accepted. A higher incidence of stomach cancer in humans has been found in regions where the Zn:Cu ratio in the soil exceeded certain limits (Luckey and Venugopal, 1977).

1.3.2. Toxic Effects of Nickel

Nickel, like many other heavy metals, is toxic mainly because of its role as an antagonist of essential metals (Nieboer *et al.*, 1984), and it is also one of the few metals whose carcinogenicity has been verified in mammals (Reith and Broegger, 1984). Costa and Mollenhauer (1980) found that the biological effects of particulate nickel compounds, whether cytoxicity or carcinogenicity, are lessened by phagocytosis of the metal compound. Acute toxicity arises from competitive interaction with five major essential elements, calcium, cobalt, iron, and zinc (Moore and Ramamoorthy, 1984). Although water soluble nickel salts have not been shown to initiate carcinogenesis in rodents, the soluble nickel salts are evidently effective as cancer-initiators in conjunction with hydrocarbons and nitrosoamines; the combination is clearly synergistic (Sunderman, 1987).

1.3.3. Toxic Effects of Lead

Lead is a typical toxic heavy metal with cumulative and nondegradative characteristics. Lead is fairly widespread in our consumer society, it is probably the most serious toxic metal. Evidence of harmful effects in adults is rarely seen at blood lead levels below 80μg/100ml. Human exposure to lead occurs though air, water and food. The passage of lead into and between these media involves many complex environmental pathways. There is a long history of human exposure to abnormally elevated levels of lead in food and drink due to practices such as cooking in lead-lined or lead-glazed pots and the supply of water through lead pipes (Manahan, 1991). Also, lead occurs in water in the +II oxidation state and arises from a number of industrial and mining sources

(Manahan, 1991). Lead powder is not carcinogenic either by inhalation or implantation. Tetraethyl lead is not known to cause cancer directly, but the breakdown products can cause cancer (Luckey and Venugopal, 1977). In fact, some historians believe that the use of the lead containers for food and drink poisoned ancient Rome's ruling class and accelerated its downfall. Although lead is a non-essential element, it is present in all tissues and organs of all mammals. The large affinity of lead for thiol- and phosphate-containing ligands inhibits the biosynthesis of heme and thereby affects membrane permeability of kidney, liver and brain cells. This results in either reduced functioning or complete breakdown of these tissues because lead is a cumulative poison (Förstner and Wittmann, 1981). Since the most drastic and obvious effects are on children, great control has been on products likely to give them large doses of lead, but much less is known about the results of extended low-level exposure of either children or adults. The earliest symptoms are rather vague and so it has been suggested that those at risk should be regularly monitored since there is a fairly straightforward test using a blood enzyme which is very sensitive to lead poisoning and shows changed activity before there are any obvious clinical signs (Tearle, 1973).

1.4. TREATMENT OF COPPER, NICKEL, AND LEAD

A number of specialised processes have been developed for the removal of metals from waste discharges. These unit operation include: chemical precipitation, ion exchange, cementation, evaporation, reverse osmosis, solvent extraction, complexation, electrochemical operations, biological operations, adsorption. Many of them have not yet been successfully implemented on a full scale basis for metal treatment. Precipitation is only widely practised where product recovery from the waste stream is not sought.

1.4.1. Chemical Precipitation

The processes most frequently employed for the removal of toxic metal ions comprise chemical precipitation or co-precipitation techniques, often involving such processes as hydroxide precipitation, sulphide precipitation, and carbonate precipitation, perhaps with combined chemical treatment. Adjusting the effluent pH can cause the precipitation of the metals that are subsequently removed by sedimentation or filtration. Often a flocculating or coagulating agent is added to improve the sedimentation characteristics of the precipitate. However, some complexing agents (NH_3, CN^-, and organics) can prevent precipitation thus severely reducing treatment efficiency. A number of processes have been considered in recent years for toxic metal removal. Generally, hydroxide precipitation involves sodium hydroxide, or the significantly cheaper potassium hydroxide. In the presence of high sulphate, considerable calcium sulphate precipitate may form, and the recovery value of the copper sludge may dictate the use of a move expensive base to obtain a purer sludge. Lead has a solubility minimum at about pH 10 with respect to the hydroxide and pH 8-10 with respect to carbonate species. In the precipitation processes, lead is normally precipitated as the carbonate, $PbCO_3$ or hydroxide, $Pb(OH)_2$. In forming insoluble lead hydroxide, lime is the treatment chemical of choice, although caustic has been used. Solubility of lead carbonate is dependent upon both treatment pH and carbonate concentration. For a fixed carbonate dosage, a broad range of pH 8.0-9.2 provides consistent treatment (Hem and Durum, 1973). The formation and precipitation of nickel hydroxide is generally the basis for destructive treatment of nickel bearing waste. Precipitation with carbonate is most commonly associated with recovery system. Nickel forms insoluble nickel hydroxide upon addition of lime.

Typical chemical precipitation processes are reported by Nilsson (1971), who presented work on chemcal treatment of wastewater by aluminium sulphate and calcium hydroxide chemical treatment of the waste water to reduce Pb(II), Cu(II), Cr(III), Hg(II), Cd(II), and As(V) to low levels by both precipitants. Zn(II), Ni(II), and Co(II) are precipitated only at pH ≤ 9.5, while Cu(II) and Pb(II) precipitation was greatly inhibited by the presence of nitrilotriacetate at pH ≤ 9. Further practical applications of chemical precipitation are given by Larsen *et al.* (1973), who reported a two-stage process of chemical addition to mine drainage waters was successful in removing heavy metals such as iron, copper, manganese, aluminium, zinc, lead, nickel, arsenic, and cadmium, while Maruyama *et al.* (1975) reported that removal of copper(II), nickel(II), and lead(II) were higher than 90% using a low and high lime system. Further application of precipitation includes reports by Patterson *et al.* (1977) on carbonate precipitation for heavy metals, Semmens and Martin (1980) on removal of lead, silver, and cadmium by clinoptilolite from solution, Bhattacharyya *et al.* (1981) on both laboratory-scale and full-scale sulphide precipitation, and Kim (1981) on sulphide precipitation using a calcium sulphide slurry for cleanup of Cd, Cu, Pb, Ag, and Zn from wastewaters.

Lime is the most frequently employed base, primarily due to its lower cost relative to sodium hydroxide or soda ash (sodium carbonate). However, when strong acid wastewaters are to be treated, such as waste plating or pickling solutions containing sulphuric acid, lime neutralisation yields large volumes of calcium sulphate sludge. Metals normally removed by hydroxide or carbonate precipitation will remain soluble if strong complexing ligands are present. This point is especially important to environmental engineers because they often depend on precipitation and predicting its effects on metal removal from solution.

1.4.2. Ion Exchange

Ion exchange is well known as a technique for water softening and is an effective means of removing heavy metals from wastewaters. It is also more properly a concentration than final treatment technique. Soluble metals exchange rapidly with cations, such as hydrogen, sodium or calcium, saturating an ion exchange resin. During treatment, the ion-exchange resin exchanges its ions for those in the wastewater. When the resins are saturated, the exhausted resin must be regenerated by another chemical to remove the metal ions from the resin bed. The regenerate brine is smaller in volume and higher in concentration than the original wastewater, but these high-metal solutions must then be adequately treated of or recovered (Lanouette, 1977). Ion exchange is capable of achieving very high levels of copper removal, particularly from dilute wastes. Recovery of nickel can be accomplished by ion exchange and has been used for some time. Recovery of nickel from process waste streams is more attractive than for some other metals, due to the high value of nickel. Successful ion exchange treatment has also been reported for copper by cation exchange, and both inorganic and organic lead (Liebig, *et al.*, 1943; and Nozaki and Hatotani, 1967). An effluent level of 0.002 mg/l was achieved for treated tap water. The organic lead compounds were removed effectively on a strongly acid cation exchange resin and almost completely converted to inorganic lead compounds, which could be treated as described above. Overall lead removals to less than 1 mg/l residual were expected for the final plant effluent, after installation of the organic lead wastewaters treatment sequence.

Linstedt *et al.* (1971) used lime coagulation, sedimentation, sand filtration, and activated carbon adsorption prior to ion exchange for conditioning the wastewater in order to reduce interfence of organics by complexing cations or competing directly with anionic trace metals, thus fouling the exchange column and interfering with regeneration.

Yeats (1977) reported that ion-exchange selectively removes heavy metals from mixed plating wastes. The concentrations of copper, nickel, and lead in final treated effluents were lower than 0.05 mg/l.

Further work by Hertzenberg and Sherry (1980) on lead and cadmium ion exchange by the synthetic zeolite Na-A showed that the zeolite is very selective for these ions. This selectivity is greater in nitrate solution than in acetate solution. The divalent ion that have been observed to displace Na^+ in zeolite A are to date Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and Eu^{2+}. In this connection, Wiers *et al.* (1982) pointed out that ion-exchanges with Pb^{2+}, Cd^{2+}, and Cu^{2+}, Pb^{2+}, and Cd^{2+} were reversible, whereas Cu^{2+} exchange was not, probably due to $Cu(OH)_2$ precipitation upon or within the zeolite.

Cullen and Siviour (1982) extracted Cu, Ni, Cr, Cd, Pb, Zn, Hg, Co, Ag, Fe, Mn, V, Ge, Ga, Al, Sb, and U using ion-exchange media produced by contacting brown coal, peat, or wood sawdust with a solution of calcium hydroxide.

Ion exchange is particularly applicable to waste streams which cannot be treated effectively by other means or where the metals can be recovered and reused. Ion exchange is also an attractive process for the removal of small amounts of impurities from dilute wastewaters, or the concentration and recovery of expensive chemicals from segregated concentrated wastewaters.

1.4.3. Evaporation

As a unit operation, the primary use of evaporation treatment has been for product recovery. However, there has been limited use to drive off the water as vapour and thus concentrate wastewater residues to dryness for zero discharge, but this is confined to dry sunny climates, where no energy input other than sunlight is required to cause evaporation. Recovery of copper is often more attractive than some other metals such as zinc, due to its higher value.

There are basically two types of evaporative recovery processes commonly in use: the vacuum evaporator and atmospheric evaporator. Evaporation is a well-established industrial process for recovering plating chemicals and water from plating waste effluents. Commercial units for handling zinc, copper, nickel, chromium, and other metal plating baths have been operating successfully and economically (Patterson and Minear, 1975).

1.4.4. Reverse Osmosis

Reverse osmosis consists of semipermeable membrane which acts as molecular sieves permitting soluble compounds having various molecular size ranges to pass through their pores (Dean *et al.*, 1972). Essentially, reverse osmosis uses a pressure differential across the semipermeable membrance to separate a solution into a concentrated and a more dilute solution. The system is primarily a concentration technique and is most effective if the concentrate can be reused. It has been utilised in several plating industry installations for chemical recovery, wherein small units of under 300 gal/h capacity have been installed to recover plating bath chemicals and make closed-loop operation of a plating line possible (Patterson and Minear, 1975). However membrane-treatment of industrial wastewaters is limited to a few applications where the membrane's properties and environmental resistance match the particular application (Sternberg, 1987).

The system works at pressures up to 600 psi and has been used effectively in the plating industry for recovery and reuse of nickel in plating-bath waters (Lanouette, 1977). This technique is widely used in treating industrial wastes and can be employed for desalination of seawater. Successful operation and performance of ultrafiltration and reverse osmosis pilot units on mixed industrial waste, has led to the purchase of full-scale units (Lopez and Johnston, 1977).

1.4.5. Cementation

Cementation is a metal-replacement process in which a solution containing the dissolved metallic ion comes in contact with a more active metal such as iron. Cementation is thus the recovery of an ionised metal from solution by spontaneous electrochemical reduction to the elemental metallic state with subsequent oxidation of a sacrificial metal. This process is particularly applicable as a means of removing copper and silver from solution (Lanouette, 1977). It is an interesting, and apparently effective method of treating copper wastewaters. The reaction for copper and iron is:

$$Cu^{++} + Fe^{0} \rightarrow Cu^{0} + Fe^{++}$$

The result is to replace copper with iron in solution; the copper plates onto the solid iron surface. This reaction has been used for many years in the mining industry to recover copper from sulphuric acid leachates. Patterson and Jancuk (1977) studied cementation treatment of copper in wastewater. They found copper cementation was a first-order reaction with respect to the removal copper from wastewater. As a further example, zinc dust will precipitate gold and silver from cyanide solutions, a widely used cementation process that has interesting potential for recovering certain small amounts of metals, such as cadmium, mercury, and lead from industrial wastes (Dean *et al.*, 1972).

Nozaki and Hatotani (1967) also have described treatment of wastewaters from a tetraethyl lead manufacturing process. The two major categories of waste were inorganic lead wastewaters and organic lead wastewaters. After sedimentation in a holding basin to recover solid lead and lead oxide, the inorganic lead waste fraction (66.1 mg/l) was effectively treated by coagulation with ferric and ferrous sulphate. The effluent contained trace to 1.4 mg/l of inorganic lead, and most of the influent organic lead.

1.4.6. Electrochemical Operations

Electrolysis is primarily a recovery technique, normally yielding an effluent which requires subsequent treatment by precipitation or other means. Direct electrolytic recovery of copper from concentrated waste streams is often both technically and economically feasible. The process may require a preconcentration step, such as ion exchange or evaporation. Recovery of copper or zinc from plating baths normally presents no problem, but the presence of other metal contaminants may interfere by simultaneous or preferential plating at the electrode. For copper cyanide baths, copper recovery by electrolysis can be accomplished in conjunction with cyanide destruction within the cell.

1.4.7. Adsorption

Chemical contaminants at low concentrations are difficult to remove from aqueous solutions. Chemical precipitation, reverse osmosis, and any other methods become inefficient when contaminants are present in trace concentrations. The process of adsorption is one of the few alternatives available for such situations (Huang *et al.*, 1991). A number of adsorbent materials have been studied for their capacity to remove heavy metals, including: activated carbon, activated alumina, ion exchangers, tree bark, straw, peanut husks, peat moss, crushed coal, and insoluble starch xanthate. Some of these materials, such as ion exchange resins are effective but expensive; other adsorbents such as coal and straw are inexpensive and poor adsorbants. Activated alumina is effective in removing heavy metals, but is readily soluble under extreme pH conditions (Huang *et al.*, 1989).

Kinniburgh *et al.* (1976) reported adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminium. They found that the selectivity sequence for the Fe gel was: Pb > Cu > Zn > Ni > Cd > Co > Sr > Mg, whereas the sequence for the Al gel was: Cu > Pb > Zn > Ni > Co > Cd > Mg > Sr. Adsorption occurred even when the extent of cation hydrolysis was much less than 1%, and invariably occurred at a pH lower than that for hydroxide precipitation.

Activated carbon has been recognised as a highly effective adsorbent for the treatment of heavy metals in water and wastewaters. It was found that among all brands of activated carbon, only the L-carbon shows a good removal capacity for heavy metals (Corapcioglu and Huang, 1987; and Huang and Blankenship, 1984). Granular carbon is usually preferred to powdered carbon, as the former, although more expensive can be regenerated and reused. Adsorption capacity usually increases as the pH decreases, whilst the efficiency increases as the metal concentration increases (Lanouette, 1977). Wilczak and Keinath (1993) presented kinetics of sorption and desorption of copper(II) and lead(II) on activated carbon. The sorption of copper(II) and lead (II) on activated carbon was noted to consist of a rapid initial uptake step followed by a slow approach to equilibrium extending over a period of several weeks.

Reed and Arunachalam (1994) used granular activated carbon columns for lead removal from wastewater. Column pH and influent characteristics appeared to be the critical parameters influencing granular activated carbon column performance.

1.4.8. Complexation

Complexation of heavy metals by inorganic and organic ligands is important for two reasons. The first is that the biological availability and toxicity of heavy metals are dependant on the chemical form of the metal. The second reason is that soluble complex formation competes with precipitation (Crosser and Allen, 1977).

Holcombe *et al.* (1987) presented methods for removal of copper and iron from chemical cleaning wastes generated during the cleaning of steam tubes in utility boilers. Cleaning may be accomplished using one of several solutions, including: inhibited hydrochloric acid, ammonium bromate, ethylenediamine tetraacetic acid (EDTA), citrate, and hydroxyacetic-formic acid. The raw wastes were treated by conventional lime and caustic precipitation and by co-ponding with coal fly ash.

1.4.9. Other processes

There are various other processes which have been used to remove metals from aqueous wastes. For instance, Kim *et al.* (1978) reported removal of heavy metals via ozonation, and Ray and Ramesy (1987) studied removal of heavy metals in wastewater in a clay soil matrix using electro-osmosis. The results of this study indicated that Randall clay possesses a high sorption capacity for heavy metals like Cd, Cu, and Pb. Preliminary data indicated that clay permeability could be improved by electro-osmosis.

Removal of heavy metals from a fatty acid wastewater with a completely mixed anaerobic filter has been studied (Chian and DeWalle, 1977). The process was effective in removing heavy metals from a concentrated acidic waste stream. The removals of soluble metals such as Cu, Ni, and Pb were between 83.7% and 88.1%.

Squires (1992) studied removal of heavy metals from industrial effluent by crossflow microfiltration. It is shown that industrial effluents containing mixed heavy metals are very effectively treated by this process. Moreover, it can successfully treat effluent containing mixed metals. However, removal of antimony from mixed metal wastewaters was affected by the concentration of sodium sulphate in the wastewater.

Stones (1977) investigated fate of metals during sewage treatment. For convenience, the average results have been presented on a comparative basis (**Tables 1.4.9-1** to **1.4.9-6**).

TABLE 1.4.9-1: The Effect of Tank Treatment on the Metallic Constituents of Sewage (Information From Stones, 1977).

Metal	Tank Influent, (mg/l)	Tank Effluent, (mg/l)	Reduction, (%)
Copper	0.56	0.31	44.6
Nickel	0.19	0.15	21.1
Lead	0.62	0.37	40.3

TABLE 1.4.9-2: The Effect of Biological Activity During Sedimentation on the Metallic Constituents of Sewage (Information From Stones, 1977).

Metal	Unsettled sewage	Supernatant Liquors After 18 Hours Settlement		% of Deposited Metal Resulting From Biological Activity
		Unsterilised	Sterilised	
Copper	0.68	0.26	0.38	28.6
Nickel	0.27	0.22	0.22	-
Lead	0.60	0.29	0.34	16.1

TABLE 1.4.9-3: The Effect of Chemical Precipitation on the Metallic Constituents of Sewage (Information From Stones, 1977).

Metal	Unsettled Sewage	Supernatant Liquors After 18 Hours Settlement							
		No precipn.		400 mg/l CaO		400 mg/l H_2SO_4		400 mg/l $Al_2(SO_4)_3 18H_2O$	
	mg/l	mg/l	%	mg/l	%	mg/l	%	mg/l	%
Copper	0.68	0.29	57.4	0.12	82.4	0.27	60.3	0.07	89.7
Nickel	0.21	0.17	19.1	0.10	52.4	0.21	Nil	0.17	19.1
Lead	0.71	0.33	53.3	0.04	94.4	0.46	35.2	0.03	95.8

TABLE 1.4.9-4: The Effect of Biological Filtration on the Metallic Constituents of Sewage (Information From Stones, 1977).

Metal	Filter feed, (mg/l)	Settled filter effluent, (mg/l)	Reduction, (%)
Copper	0.32	0.13	59.4
Nickel	0.15	0.08	46.7
Lead	0.37	0.11	70.3

TABLE 1.4.9-5: The Proportion of The Metallic Constituents Contained in the Humus Solids After Biological Filtration (Information From Stones, 1977).

Metal	Unsettled Filter Effluent (mg/l)	Paper Filtrate (mg/l)	% of Metal In Humus Solids
Copper	0.26	0.09	65.4
Nickel	0.09	0.07	22.2
Lead	0.26	0.05	80.8

TABLE 1.4.9-6: The Effect of Activated Sludge Treatment on the Metallic Constituents of Sewage (Information From Stones, 1977).

Metal	Feed to Aeration Plants	Settled Effluents From Aeration Plants					
		Diffused Air		Simplex		Bioaeration	
	mg/l	mg/l	%	mg/l	%	mg/l	%
Copper	0.68	0.29	57.4	0.12	82.4	0.27	60.3
Nickel	0.21	0.17	19.1	0.10	52.4	0.21	Nil
Lead	0.71	0.33	53.3	0.04	94.4	0.46	35.2

1.5. PEAT

Peat soils cover huge areas of the USSR, Canada, Finland and other countries. A comparison of these areas has been reported by Hargitai in 1983. **Table 1.5-1** shows comparisons of countries with the largest peat territories. The data show the percentage of total area in countries with the largest peat areas, and takes into account both the absolute size of the peat territories and also their areas as a percentage of the whole country.

Peat has long been valued for a number of uses, particularly as a fuel, for agricultural and horticultural amendment, and as a raw feed stock for a variety of chemicals. During the last three decades, peat has been the subject of studies which have focused on environmental pollution control. It has also been demonstrated to be effective in the removal of oil, heavy metals, pesticides, nutrients, and trace organics.

TABLE 1.5-1: A Comparison of the Most Important Peat Areas World-Wide (Information From Hargitai, 1983).

Country	Peat Areas (1000 ha)	Peat Areas as % of Total Area
Finland	10,000	32.0
Sweden	5,500	15.0
Norway	3,000	9.2
Soviet Union	71,500	3.2
Great Britain	1,582	6.6
Ireland	1,100	17.0
Poland	1,500	4.8
Iceland	1,000	9.7
Germ. Fed. Rep.	1,125	4.5
Canada	10,000	1.0
U.S.A.	7,500	1.0
Cuba	450	3.9
Japan	200	0.6
New Zealand	167	1.5
Denmark	100	2.3
Hungary	100	1.1
Italy	120	0.4
Indonesia	1,466	2.1
France	120	-
Uruguay	-	0.6
Germ. Dem. Rep.	489	4.5

1.5.1. Properties of Peat

Peat is generally dark brown in colour, of spongy consistency and is partially fossilised plant matter that is formed in wet areas under partially anaerobic conditions, where the rate of accumulation of plant matter is greater than that of decomposition as a result of incomplete decomposition of the plant. Peat is a complex material containing mainly organic residues such as lignin (**Figure 1.5.1-1**), chelating (**Figure 1.5.1-2**)

(Souci, 1938), and cork-like tissues which are the main constituents of plants. Other substances include resins, waxes, proteins, dyes (Walmsley, 1977).

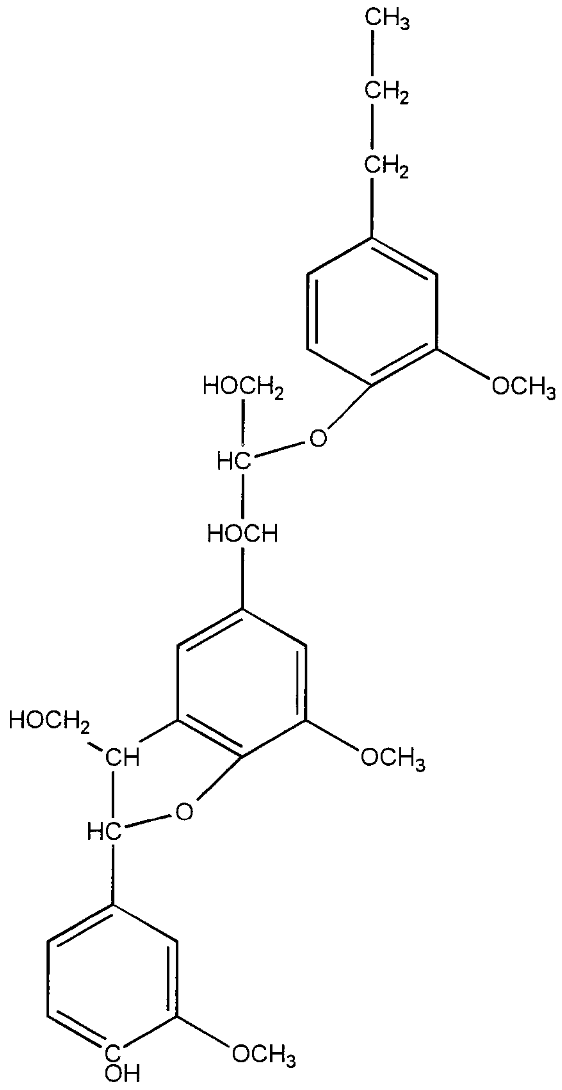


Figure 1.5.1-1: The structure of lignin.

The physical and chemical properties of the peat depend mainly upon the nature of the plants from which it has originated, the properties of the water in which the plants were growing, and the moisture relations during and following its formation and accumulation (Stanek, 1977).

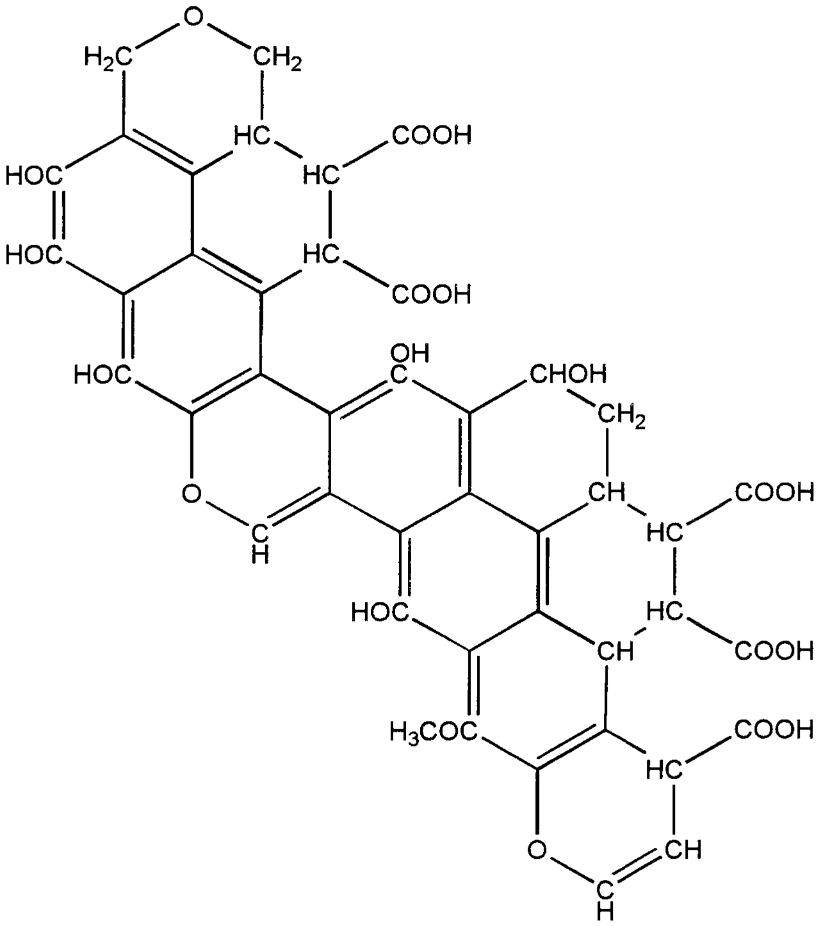


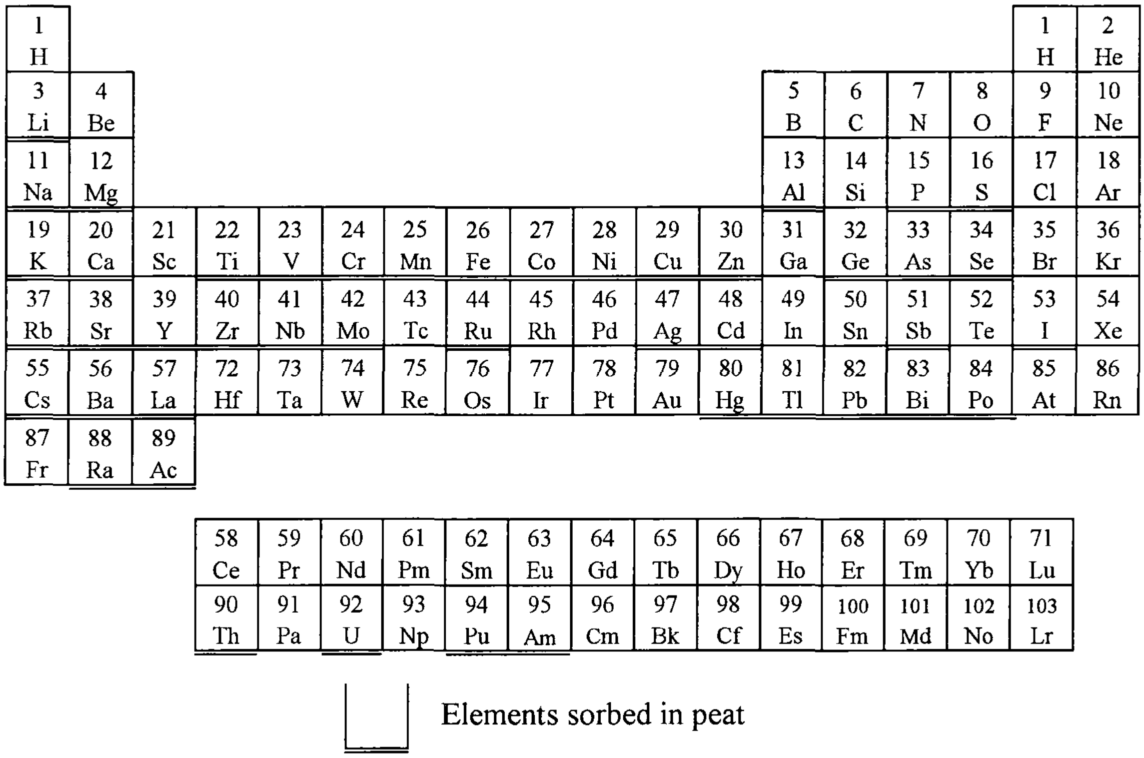
Figure 1.5.1-2: Chelating structure of peat.

Chemical adsorption can occur by the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids phenolic hydroxides and ethers as chemical bonding (Adler and Lundquist, 1963). Because of the fairly polar character of peat, the specific adsorption for dissolved solids such as transition metals and polar organic molecules is very high. According to Asplund *et al.* (1972) peat has a capacious specific surface area (> 200 m^2/g) and is extremely porous (95%). Therefore, peat is a greatly polar and porous material. Also, Poots and McKay (1979) have reported the specific surface area of a peat moss using dye solutions. The specific surface areas are not only dependent on the chemical nature of the solute and adsorbent but also the molecular dimensions of the solute. A value of 27 m^2/g was obtained for nitrogen, 11.8 m^2/g for acid dye, and 100 m^2/g for basic dye (Poots and McKay, 1979). It shows the presence of negatively charged molecules associated with the polar functional groups of peat as well as to the exchange adsorption occurring with hydrogen ions. The natural capacity of peat to retain cations is related to the pH of solution. At pH values above 8.5, peat itself is not stable. At low pH, below 3.0, most metals will be leached from peat. Between these values, it is known that peat can adsorb most metals in a fairly efficient way (Coupal and Lalancette, 1976). The peat particles are surface-active and have a high cation-exchange capacity (90-150 me/100 g dry matter) (Stewart, 1977). Szalay (1969) reported that a great number of cationic elements are sorbed, and that electrochemically equivalent quantities are sorbed from cations of different valencies by given peat preparations. The periodic table shown in **Figure 1.5.1-3** illustrates the elements that can be sorbed in peat (Szalay, 1969; Parkash and Brown, 1976; Coupal and Lalancette, 1976; Illarionovich *et al.*, 1976; Pakarinen *et al.*, 1980; Rock *et al.*, 1984; Smith *et al.*, 1984; McLellan and Rock, 1988; Sheppard *et al.*, 1989; Trujillo *et al.*, 1991; James *et al.*, 1992; and Green *et al.*, 1994).

Today the peat industry is well established in many countries and employs, directly or indirectly, specialists in such diverse fields as engineering, agriculture, forestry, horticulture, geobotany, anthropology, chemistry, and medicine (Stewart, 1977).

1.5.2. Use of Peat as a Fuel

The traditional use of peat has been fuel. By draining, cutting, and drying the peat during the summer, a winter's supply of fuel was obtained. As a fuel, peat is characterised by a high volatile content, low sulphur and ash contents, low bulk density, and high oxygen content. The character, traditional uses of peat, and availability of peat have, more recently, led to its utilisation as a fuel for generation of electricity for industry (Lang, 1984) in many countries such as Russia, Finland, Ireland, and Canada. In the seventies, the oil crisis and the continuous price increase of fuels, especially oil, caused a very rapid increase in the utilisation of peat. **Table 1.5.2-1** shows a comparison of the statistics on peat industry and peatland areas used for peat production in late 1970's (Kivinen, 1980).



1 H																1 H	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 1.5.1-3: Periodic table illustrating the elements sorbed by peat (Information from Szalay, 1969 With Additional Data From Parkash and Brown, 1976; Coupal and Lalancette, 1976; Illarionovich *et al.*, 1976; Pakarinen *et al.*, 1980; Rock *et al.*, 1984; Smith *et al.*, 1984; McLellan and Rock, 1988; Sheppard *et al.*, 1989; Trujillo *et al.*, 1991; James *et al.*, 1992; and Green *et al.*, 1994).

TABLE 1.5.2-1: A Comparison of the Statistics on Peat Industry and Peatland Areas Used for Peat Production in Late 1970's (Information From Kivinen, 1980).

Country	Annual Production Garden Peat ($10^3 m^3$/yr.)	Annual Production Fuel Peat (10^3tons/yr.)	Area Used for Peat Production (1000 ha)
Soviet Union	300,000	100,000	4,350
Germ. Fed. Rep.	6,000	250	38
China	4,000	800	n.d.
U.S.A.	1,600	0	n.d.
Great Britain	1,500	50	3
Ireland	1,133	5,572	53
Canada	1,125	0	8
Poland	850	0	5
Czechoslovakia	800	0	2.4
Sweden	800	0	10
Finland	685	1,500	20
Germ. Dem. Rep.	500	0	0.4
Denmark	324	0	n.d.
France	300	50	n.d.
Norway	250	0.8	2
New Zealand	30	0	0.5
Switzerland	4	0	n.d.
Israel	2	0	0.1

1.5.3. Use of Peat in Agriculture and Horticulture

Peat can also be considered as being fairly important in agriculture and horticulture. Its nitrogen content gives peat its outstanding value from the point of view of agricultural chemistry (Hargitai, 1983), because nitrogen is one of the principal elements in plant nutrition. This value not only depends on the fact that peat in general has a considerable amount of total nitrogen and the special forms in which the nitrogen is to be found in peat, but also because of its properties which make it an ideal additive to mineral soils for growing plants are: (a) it increases the water storage capacity of soils with coarse texture; (b) it provides ventilation in soil with fine textures; (c) it improves the nutrient-holding capacity of all soil types (Stewart, 1977). However, it must be realised that the use of this resource for agricultural purposes is essentially one-way, for once peat is drained, it loses the hydrological balance which is responsible for its formation. It is a non-renewable resource and man must be made to realise that its use for such purposes is strictly short-term (Stewart, 1977). Peatlands have been commonly used for agriculture and horticulture and in some areas, reclamation for this purpose is still important. Peat is distributed extensively throughout the world. **Table 1.5.3-1** illustrates a comparison of agricultural use of peatlands.

TABLE 1.5.3-1: A Comparison of Agricultural Use of Peatlands (Information From Kivinen, 1980).

Country	Peatland Used for Agriculture		Annual Rate of Reclamation (ha/yr.)
	Total 1000 ha	% of Total Peatland Area	
Poland	960	71	4,500
Germ. Fed. Rep.	900	81	0
Great Britain	750	68	10,000
Finland	700	7	<100
Germ. Dem. Rep.	480	87	8,000
Soviet Union	364	<1	38,000
U.S.A./Minnesota	266	9	1,000
Sweden	200	3	1,000
Norway	150	5	3,000
China	116	3	5,800
Ireland	116	10	500
New Zealand	75	50	1,000
Denmark	60	50	1,000
Canada	41	<1	n.d.
Switzerland	33	61	0
Czechoslovakia	10	29	300
Israel	6	100	0

1.5.4. Use of Peat in Pollution Control

During the last three decades, the value of peat has been recognised as an agent for water pollution control. During this period, peat-based systems have been advocated as potential solutions to a wide range of problems from municipal and industrial wastewaters. Indeed, even earlier, Moore (1954) reported on the ability of peat to adsorb uranium from solution. A maximum of 98.0 percent uranium was removed from aqueous solution by peat as an effective extracting agent. Still earlier, Ottemeyer (1930) has reported that peat was an efficient adsorbent in treating textile effluents. The first full-scale peat system for water pollution control was constructed in 1978, and has consistently produced high-quality effluent. Peat on site wastewater treatment systems are now in operation in Maine, Alaska, Canada, and Ireland, treating wastewater and protecting groundwater on sites not appropriate for conventionally designed treatment system (Brooks, 1991).

The search for new commercial uses of peat has been rewarding in the area of pollution control. For the reason of cheaper pollution control methods, Harrison Western Environmental Services Inc. of Lakewood, Colorado has developed such a process, called membrane-media extraction, which uses peat moss "capsules" to be effective at reducing concentrations of arsenic, cadmium, lead, nickel, selenium, and other metals from electroplating rinsewater, pulp and paper mill discharge, municipal wastewater, and acid mine drainage (Green *et al.*, 1994). The performance and cost of the membrane-media extraction system compared to the existing chemical precipitation unit at the ASARCO plant is illustrated in **Table 1.5.4-1** and **Table 1.5.4-2**.

TABLE 1.5.4-1: Cost Comparison of Wastewater Treatment Systems at Asarco's Globe Plant (Information From Green *et al.*, 1994).

	Existing Chemical Precipitation System	Retrofitted Membrane-Media System
Capital Costs ($)	1,000,000 (1986 dollars)	300,000 (1993 dollars)
Operating Costs ($/1,000 treated gal)		
Reagents	9.88	1.74
Direct Labour	10.00	3.33
Sludge Disposal	20.80	3.12
Treatment of Membrane-Media Water Streams by Precipitation System	NA	2.99
Total Direct Operating Costs	40.68	11.18

TABLE 1.5.4-2: Performance of Chemical Precipitation Versus the Retrofitted Membrane-Media System at Asarco's Globe Plant (Information From Green *et al.*, 1994).

Property	Influent Wastewater	Treated Water	
		Existing Chemical Precipitation System	Retrofitted Membrane-Media System
Total Dissolved Solids (ppm)	3,000-10,000	>3,000	<1,000
Temperature (°F)	50-70	50-70	50-70
pH	4.0	Approx. 7.5	Approx. 7.0
Concentration (mg/l)			
Arsenic	10.1	0.024	0.008
Cadmium	14.5	0.10	0.02
Iron	0.986	0.100	0.100
Lead	3.07	<0.050	0.050
Manganese	3.33	0.120	0.050
Nickel	0.069	0.025	0.050
Selenium	0.056	<0.01	<0.010
Zinc	35.5	0.35	0.010

Oil Removal

Research has long been focused on determining the ability of peat to act as biosorbent and to reduce the organic constituents of wastewaters. Different types of oils, ranging from bunker fuel to gasoline, have been shown to be absorbable by peat. D'Hennezel and Coupal (1972) reported that peatmoss has much stronger affinity for oil than straw which is currently used in cleaning-up oil spills. They found that peatmoss absorbs up to eight times its weight of oil. Viraraghavan *et al.* (1987) used horticultural peat to remove oil from oil-waters. It has been found that the oil binding capacity of peat was 7.5 to 7.8 times its weight. The percentage removal of oil from oily water ranged from 30 to 95% depending on the type of emulsion studied and column studies have showed that the removal of oil from oil-water emulsions was 90%. Viraraghavan and Mathacan (1988 and 1989) investigated treatment of oil-water emulsions with peat, and concluded that the oil binding capacity of the peat was 7.5 to 7.8 times its dry weight. The equilibrium time between peat and various oil-water emulsions ranged from two to three hours, and in a 300 mm deep peat column, the average percentage of oil removal during an eight hours cycle ranged from 99 to 34% depending upon the flow rate and the type of emulsion investigated. Unfortunately, peat has a tendency to break down into small particles when stored for long periods of time so that its application to an oil slick then becomes difficult and messy. To obviate this difficulty, peat could be formed into granules.

Organic Pesticides Removal

The removal of stable insecticides has been investigated by Eye (1968) who reported that peat has great adsorption capacity for dieldrin. In 1979, Brown *et al.* used a peat column process to remove dieldrin from aqueous solution. The peat column removed 88% of the dieldrin. However, when dyehouse effluent containing dieldrin was passed through the peat column, the removal of dieldrin was reduced to 57%.

Cloutier *et al.* (1985) investigated the possibility of utilising peat as an adsorbent for the removal of the herbicide 2,4-D from contaminated wastewaters. Removals for the pesticide 2,4-D of the order 90% were obtained under optimum conditions. The adsorption of 2,4-D in peat is described by the Freundlich isotherm and the column tests were correlated by the Bohart-Adams equation.

A filtering unit using peat, moss, and manure was designed by Toller and Flaim (1988) to filter out a variety of commonly-used pesticides in apple orchards. Average removal efficiencies were > 99% for iodine, copper oxychloride, azinphos methyl, triadimefon, bitertanol, dithianon, fenarimol, chlorpyrifos ethyl, cyhexatin, benzomate, dinocap, and benomyl. Removal efficiency for vamidothion averaged 61% and removal for sulphur was 73%. In addition, MacCarthy (1991) found that cationic pesticides and basic pesticides (which become cationic at low pH), paraquat, diquat, and amitrole for example, were efficiently removed from aqueous solution by H_2SO_4-treated peat.

Dye Removal

The utilisation of peat as a medium for the treatment of dye effluent has been recognised for some time. Poots *et al.* (1976, 1978) studied the adsorption of Telon Blue (Acid Blue 25), Astrazon Blue (Basic Blue 69), and Methylene Blue on peat moss. Adsorption parameters for the Langmuir and Freundlich isotherms were determined. For a particle size range of 150-250 μm, a value of 16.3 mg/g was obtained for monolayer coverage of Acid Blue, a value of 185 mg/g for Basic Blue and 96.1 mg/g for Methylene Blue; and a value of 9.0 m^2/g for specific surface areas of Acid Blue and a value of 104 m^2/g for Basic Blue. Analysis of the contact time data indicated that intraparticle diffusion is not rate controlling, and this together with the failure of the Bed-Depth-Service-Time (BDST) model to explain the fixed bed result, indicate that the mechanisms involved in acid dye removal by peat are complex. Allen *et al.* (1988) investigated adsorption rates of Acid Blue 25 onto peat in a batch adsorption system that is a two-resistance mass transfer model based on film resistance and homogeneous solid-phase diffusion.

Allen (1987) has reported that peat has considerable capacity to remove cationic dyes to a greater extent than anionic forms. Basic dye adsorption of Basic Blue 3 and

Basic Blue 69 for instance, is predominantly a chemisorption process involving attraction of the cationic groups to the anionic groups.

Allen *et al.* (1988) also studied the adsorption of basic dyes such as Astrazon Blue BG (Basic Blue 3), Astrazon Yellow 7 GL (Basic Yellow 21), and Maxilon Red BL-N (Basic Red 22) onto sphagnum moss peat from single component and multi-component solutions. The results indicated that the presence of two or more dyes in solution could and would have an effect on the amount of the dyes adsorbed. However the presence of one or more additional solute species reduced the individual dye adsorption capacity. The different dye ions would experience different physical and electrical forces according to their structure, molecular size, and functional groups. Hence, competition to take available sites cannot be considered alone. The results conform closely with the Freundlich, Langmuir, and Redlich-Peterson isotherms. The adsorption capacities were found as 390 mg/g for Basic Blue, 300 mg/g for Basic Yellow, and 240 mg/g for Basic Red.

Allen *et al.* (1989) demonstrated adsorption of a basic dye (Basic Yellow 21) from aqueous solution on to sphagnum peat moss. The results indicated that the adsorption process was related to a possible pore size distribution by three intraparticle rate parameters. It is possible to describe the adsorption process by three stages occurring in series; that is macropore diffusion, transitional pore diffusion, and micropore diffusion.

McKay and Allen (1991) studied adsorption capacity of Astrazon Blue BG (Basic Blue 3), Telon Bule ANL (Acid Blue 25), and Maxilon Red BL-N (Basic Red 22) onto sphagnum peat moss in batch systems and in fixed beds. The results indicated that two resistance models involving external mass transport and pore diffusion as well as external mass transport and solid diffusion correlated excellently with experimental data. An economic model comparing costs of removing dyestuff from wastewaters shows peat to be potentially an attractive adsorbent.

Removal of Other Organics

The sorption of a variety of other organics has been reported. Tinh *et al.* (1971) investigated the removal of alkyl benzene sulphonate (ABS) and beef extract from solution using peat moss as an adsorbent. In the case of ABS, the percentage reduction varied from 72 to 95% that depending on initial concentration of ABS; in the case of beef extract, there is a COD reduction of around 27%. They concluded that there are industrial situations in which a peat moss based process could be useful for industries such as pulp, paper, and mining.

Mueller (1972) found peat effective in the removal of phenol and in one experiment the phenol content was reduced from 40 to 5 mg/l, in another from 0.22 to 0.14 mg/l.

Studies by Soniassy (1974) showed that peat could adsorb odorous gases such as dimethylamine, ammonia, and hydrogen sulphide; for these respective gases, peat moss showed breakthrough times of 8, 6, and 3 min., compared with 35, 29, and 22 min. for activated carbon. The results indicated that peat moss possessed 30 to 38% of the adsorptive capacity of activated charcoal and that the effective life of peat filters was 14 to 23% of that of similar sized activated charcoal filters.

Cohen *et al.* (1991) reported that peat was capable of extracting substantial amounts of either free-phase or dissolved hydrocarbons from water. In solution, toluene was found to be more slowly adsorbed than either benzene or *m*-xylene. In general, the best hydrocarbon adsorption from solution could be achieved by using peats that were low in fibre and birefringent organics and high in ash and guaiacyl lignin pyrolysis products. Peat has also been used in several waste handing applications, including litter for cattle, horse, chicken, fox, or mink, as a treatment system for water purification plants or a fish farm, together with the waste from the composting process (Selin and Nyrönen, 1985).

Metal Removal

During last twenty years, most of the work on of peat has been focused on metal and organic removal from industrial waste streams. A number of potential processes to remove heavy metals have been proposed. Basically, the process can be divided into three steps (Ruel *et al.*, 1977):

(1) Contacting wastewater with peat

In this part of the process, the solution is treated with a precipitating agent such as sodium sulphide and then contacted with peat.

(2) Drying the peat by pressure

After use, the peat has the same amount of moisture as at the beginning. For easier handling (peat could be taken to a centralised incinerator) or for recovery purposes, it is necessary to remove part of the mechanically held water from the peat. This is done by applying mechanical pressure to it.

(3) Burning the peat and recovery of the metals

Since the ash content of peat is very small, the combustion will result in the formation and easy recovery of metals from the oxides.

The adsorption capacity of peat varies with the type of material being adsorbed but because of its relatively low cost compared to other adsorbents, it is believed that it will be able to compete successfully for particular applications.

1.6. ADSORPTION

Adsorption is the concentration of a molecule at the surface of an adsorbent. Some of the earliest work on adsorption of gases at different treated surfaces has been investigated by Faraday (1834), who first suggested that there must be specific adsorption of reactant molecules for surface catalysis. Adsorption results from unbalanced forces associated with surface molecules of adsorbates or adsorbents. The high potential energy of these molecules can be reduced by the attraction of other substances. Adsorption therefore presumably occurs exclusively on the surface of the adsorbent.

Adsorption is often categorised as two main types. In the first type, physical adsorption or physisorption involves intermolecular forces, where the bonding between adsorbent and adsorbate is caused by Van der Waals forces and hydrogen bonds. In the second type, chemical adsorption or chemisorption involves valency forces through sharing or exchange of electrons between adsorbent and adsorbate as covalent forces. This was first considered in 1916 by the American chemist Irving Langmuir. If the adsorbent is solid, the usual need is for large surface areas which offer many active sites for adsorbates. The capacity of the adsorbent depends on the surface area, the adsorbent itself, the adsorbate and temperature. A rather important but little understood process in adsorption on a liquid surface occurs when the adsorbate dissolves in the liquid. This process is often involved during removal of ions from watewaters.

1.6.1. Adsorption Isotherm

Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. Equilibrium studies in adsorption give the capacity of the adsorbent. It is described by an adsorption isotherm characterised by certain constants whose values express the surface properties and affinity of the sorbent. Adsorption equilibrium is established when the concentration of adsorbate in the bulk solution is in dynamic balance with that of the interface. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaing in the solution at a fixed temperature at equilibrium. Isotherms can be obtained by batch reaction at various pH values, temperature, and vary with the adsorbent, the adsorbate and other parameters of the adsorption processes.

Langmuir Adsorption Isotherm

Irving Langmuir, an American chemist, was born in Brooklyn, New York. In 1932, he was awarded the Nobel Prize in chemistry for "his discoveries and researches in the realm of surface chemistry". Beginning in 1916 Langmuir developed a relationship between the amount of gas adsorbed on a surface and the pressure of that gas; such equations are now referred to as Langmuir adsorption isotherms; a theoretical adsorption isotherm in the ideal case. The Langmuir adsorption isotherm is based on the assumptions that:

- adsorption proceeds only until a single adsorption layer is formed (a monolayer);
- adsorbed molecule are not free to move on the surface;
- the enthalpy of adsorption for each molecule is the same.

The Langmuir adsorption isotherm has a simple form, yields reasonable agreement with a large number of experimental isotherms that including those describing any different interface between two phases. Therefore, the Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption. The Langmuir adsorption isotherm is the most often used adsorption isotherm for adsorption of a solute from a liquid solution as:

$$q_e = \frac{X_m \cdot k \cdot C_e}{1 + k \cdot C_e},$$

where

q_e is adsorption density at the equilibrium solute concentration C_e, (mg of adsorbed per g of adsorbent);

C_e is the concentration of adsorbate in solution, (mg/l);

X_m is the maximum adsorption capacity corresponding to complete monolayer coverage, (mg of solute adsorbed)/(g of adsorbent);

k is a Langmuir constant related to energy of adsorption, (l of adsorbent/mg of adsorbate).

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{X_m \cdot k} + \frac{C_e}{X_m}.$$

The linear form can be used for linearization of experimental data by plotting C_e/q_e against C_e,

$$Slope = \frac{1}{X_m},$$

$$Intercept = \frac{1}{X_m \cdot k}.$$

Therefore the Langmuir constants X_m and k can be evaluated from the slope and intercept of the linear equation above.

Freundlich Isotherm

Herbert Max Finlay Freundlich, who was a German physical chemist, in 1906, presented an empirical adsorption isotherm that can be used for nonideal systems. The Freundlich isotherm is the earliest known relationship describing the adsorption equation. This fairly satisfactory empirical isotherm can be used for nonideal adsorption that is multilayer adsorption and is expressed by the following equation:

$$q_e = K_F \cdot C_e^{1/n},$$

where

q_e is the adsorption density, (mg of adsorbed per g of adsorbent);

C_e is the concentration of adsorbate in solution, (mg/l);

K_F and 1/n are empirical constants dependent on several environmental factors and n is greater than one.

The equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e.$$

Plot $\log(q_e)$ against $\log(C_e)$,

$$Slope = \frac{1}{n},$$

$$Intercept = \log K_F.$$

Experimental results conform to the Freundlich expression if a plot of $\log(q_e)$ against $\log(C_e)$ yields straight line. The constants can then be determined from slope and intercept. The Freundlich equation is most useful for dilute solutions over small concentration ranges.

1.6.2. Equilibrium Batch Adsorption

In a batch adsorption process, adsorbent is contacted with the solution in a tank for a period of time at fixed operation conditions. The adsorbent is separated from the mixed by settling, filtration or centrifugation and is then regenerated or discarded. The time required to approach equilibrium depends on the concentration of adsorbate, the dose of adsorbent, the particle size of adsorbent, the degree of agitation, temperature and pH value. For batch operations, the adsorbent is usually applied in powdered form to increase the surface area and reduce the diffusion resistance inside the pores. Agitation of the suspension improves contact of adsorbent with solution and decreases the mass transfer resistance at the surface. Higher pH values of the solution improve ion-exchange in the system provided that adsorption is largely by ion-exchange reactions rather than complexing. Endothermal adsorption reaction can be improved at higher temperature of reaction.

1.6.3. Rate of Adsorption

The steps in an adsorption process are mass transfer through the external boundary layer, internal diffusion through the porous structure, and adsorption on the interior surfaces. If one step is much slower than the others under a given conditions of reaction, it is called the rate-determining step or controlling resistance.

The transfer of adsorbate from bulk solution to outer surface of the adsorbent occurs by molecular and connective diffusion. Transport of material through a boundary-layer is often referred to as film diffusion. The transfer of adsorbate from the external surface to the interior of the adsorbent occurs by diffusion in the void space of the pores or by migration along the pore surface. Diffusion, in turn, is driven by concentration difference. Since solid and pore diffusion occur in parallel, the overall rate of internal transport is the sum of the two processes.

The rate equation for transfer of adsorbate from solution to adsorbent phase depends upon the nature of the interaction between adsorbate and adsorbent. In most adsorption reactions, the rate of adsorption at the fluid-solid interface is fast relative to the rates of external and internal mass transfer. Therefore, this step is usually not the rate-determining step.

The relative magnitudes of film and internal diffusion are determined by the particular system and conditions. The external mass transfer resistance decreases with increasing the degree of agitation in the batch system. The internal mass transfer resistance decreases with decreasing particle size since the adsorption area is increasing.

However, the situation can be confused when chemical adsorption steps occur, for one of these can often be the rate-determining step.

1.6.4. Adsorption From Multicomponent Solutions

Most of the research in the adsorption field deals with the effectiveness of adsorption for removing a single solute from water. However, wastewaters contain more than one component, so that as a next step multicomponent systems in solution have to be studied. Adsorption from multicomponent solutions is a very complex process and presents many difficulties. It can be assumed that each molecule of each component occupies one site on the surface and does not dissociate on adsorption. Suppose that the fraction of the surface occupied by molecules of solute A is θ_A and that the fraction occupied by solute B is θ_B. The bare fraction (that is the fraction occupied neither by A nor B) is $1-\theta_A-\theta_B$. If both substances are adsorbed without dissociation, the rate of adsorption of the components by means of the following expressions:

$$v_a^A = k_a^A[A](1-\theta_A-\theta_B),$$

and

$$v_a^B = k_a^B[B](1-\theta_A-\theta_B).$$

The rate of adsorption is proportional to the number of impacts of molecules on the unoccupied parts of the surface. It can be described as follows:

$$v_{-a}^A = k_{-a}^A\theta_A,$$

and

$$v_{-a}^{B} = k_{-a}^{B}\theta_{B}.$$

From the equilibrium conditions

$$v_{a}^{A} = v_{-a}^{A},$$

and

$$v_{a}^{B} = v_{-a}^{B},$$

it then is easy to obtain the relations

$$\theta_{A} = \frac{K_{A}[A]}{1+K_{A}[A]+K_{B}[B]},$$

$$\theta_{B} = \frac{K_{B}[B]}{1+K_{A}[A]+K_{B}[B]},$$

where

$$K_{A} = k_{a}^{A}/k_{-a}^{A},$$

and

$$K_{B} = k_{a}^{B}/k_{-a}^{B}.$$

It follows from these equations that the fraction of the surface covered by one substance is reduced if the amount of the other substance is increased. This is because the molecules of A and B are competing with one another for a limited number of surface sites, and this can be called competitive adsorption. There is evidence that sometimes two substances are adsorbed on two different sets of surface sites, in which case there is no competition between them (Laidler, 1987).

In studies of several binary mixture systems, success has been achieved in describing the competitive adsorption behaviour of two-component systems by the Langmuir isotherm and the Freundlich isotherm.

Langmuir Isotherm

One of the best-known relations for representation of single-solute adsorption equilibria is the Langmuir isotherm. A model for competitive adsorption based on the Langmuir equation was first developed by Butler and Ockrent (1930) to describe the adsorption equilibrium in multicomponent systems and is based on the same assumptions as the Langmuir equation for single adsorbates (Langmuir, 1918). This isotherm is applicable when each single component obeys a Langmuir behaviour in a monocomponent system. It is widely used to calculate the Langmuir constant X_m, the amount of solute adsorbed per unit weight of adsorbent, in the multi-adsorbate systems. The common form for depicting the distribution is to correlate the amount of solute adsorbed per unit weight of adsorbent with the residual solute concentration remaining in an equilibrium state. If there are two solutes present together in the adsorption system the competitive Langmuir isotherms of description are

$$q_{e,1} = \frac{X_{m,1} \cdot k_1 \cdot C_{e,1}}{1 + k_1 \cdot C_{e,1} + k_2 \cdot C_{e,2}}, \qquad (1.6.4\text{-}1)$$

$$q_{e,2} = \frac{X_{m,2} \cdot k_2 \cdot C_{e,2}}{1 + k_1 \cdot C_{e,1} + k_2 \cdot C_{e,2}}, \qquad (1.6.4\text{-}2)$$

where $q_{e,1}$ and $q_{e,2}$ are the amounts of solutes 1 and 2 adsorbed per unit weight of adsorbent at equilibrium concentrations $C_{e,1}$ and $C_{e,2}$, respectively. $X_{m,1}$ and $X_{m,2}$ are the maximum adsorption capacities of solutes 1 and 2, respectively. These are determined from single-solute systems and, therefore, correspond to a monolayer coverage of the adsorbent. k_1 and k_2 are the Langmuir constants and are a function of the energy of adsorption of solutes 1 and 2, respectively. These are also determined from single-solute systems. The Langmuir equation has been used in many cases for describing the adsorption isotherm of two organic solutes (Ockrent, 1932; Cooney and Strusi, 1972; Fritz and Schlünder, 1974; Murin and Snoeyink, 1979; and Srivastava and Tyagi, 1995).

Jain and Snoeyink (1973) have investigated competitive adsorption on activated carbon from aqueous bi-solute solutions of organic adsorbates and have developed a model that adequately predicts adsorption equilibria in such systems. According to Jain and Snoeyink, adsorption without competition has been incorporated into the Langmuir theory for binary adsorbate systems. Therefore, a Jain and Snoeyink model can be proposed to add a term into equation **(1.6.4-1)**.

$$q_{e,1} = \frac{\left(X_{m,1} - X_{m,2}\right) \cdot k_1 \cdot C_{e,1}}{1 + k_1 \cdot C_{e,1}} + \frac{X_{m,2} \cdot k_1 \cdot C_{e,1}}{1 + k_1 \cdot C_{e,1} + k_2 \cdot C_{e,2}}. \qquad (1.6.4\text{-}3)$$

The addition term of equation **(1.6.4-3)** is the Langmuir expression for the number of molecules of solute 1 that adsorb without competition on the surface area proportional to ($X_{m,1}$ - $X_{m,2}$). The second term on the right side of equation **(1.6.4-3)**, represents the number molecules of solute 1 adsorbed on the surface area proportional to $X_{m,2}$ under competition with solute 2, and is based on the Langmuir model for competitive adsorption. The number molecules of solute 2 adsorbed on the surface area proportional to $X_{m,2}$ under competition with solute 1 can be calculated from the identical equation **(1.6.4-2)**.

Srivastava and Tyagi (1995) investigated competitive adsorption of substituted phenols by activated carbon developed from the fertiliser waste slurry. They found that the results for the mutual suppression of equilibrium adsorption due to competition between substituted phenols are closer to the values predicted by the Jain and Snoeyink's modified model than to the Langmuir equations.

Freundlich Isotherm

Many adsorption equilibria follow the Freundlich adsorption isotherm which has found wide application in describing experimental data. In some cases, where it was not possible to describe the data by one set of adsorption coefficients over the range of concentrations studied, the isotherm was divided into several sections with different adsorption coefficients for each section.

In order to describe the Freundlich type multicomponent isotherm, Sheindorf *et al.* (1981) tested some well-known relationships from the studies of Jain and Snoeyink (1973), and Radke and Prausnitz (1972). They obtained satisfactory agreement with measured data and used their results to create a generalised multicomponent isotherm of the Freundlich type where the isotherm coefficients can be determined from the monocomponent isotherm for solid aqueous systems such as the adsorption of water pollutants on activated carbon.

For a bicomponent system the adsorption isotherm expressed in terms of weight of sorbate is written in the form:

$$q_1 = K_1 C_1 (C_1 + a_{12} C_2)^{n_1 - 1},$$

$$q_2 = K_2 C_2 (a_{21} C_1 + C_2)^{n_2 - 1}.$$

The above equations can be rearranged to the following linear form:

$$\frac{C_1}{C_2} = \frac{1}{C_2} \beta_1 - a_{12},$$

$$\frac{C_2}{C_1} = \frac{1}{C_1} \beta_2 - a_{21},$$

or in the equivalent form:

$$C_1 = \beta_1 - a_{12}C_2,$$

$$C_2 = \beta_2 - a_{21}C_1,$$

where

$$\beta_i = (K_i C_i / q_i)^{(1/1-n_i)}.$$

Jaroniec and Derylo (1982) studied theories of single-solute and bi-solute adsorption from dilute aqueous solutions on activated carbon. The results show that the full form of the Freundlich type equation, derived in terms of the general theory of adsorption on energetically heterogeneous solids, gives good representation of the bi-solute and single-solute data except at very low and high solute concentrations.

Fritz and Schlünder (1974) reported a general empirical equation for calculating the adsorption equilibria of organic solutes in aqueous solution by activated carbon as follows:

$$q_i = \frac{a_{i0} C_i^{b_{i0}}}{c_i + \sum_{j=1}^{n} a_{ij} C_j^{b_{ij}}},$$

in which q_i is the amount of i adsorbed per unit weight of adsorbent at equilibrium concentration C_i in a solution containing n solutes.

McKay and Al-Duri (1991) reported the extended empirical Freundlich isotherm of Fritz and Schlünder with a modification that greatly reduced the amount of experimentation and mathematics required for their system involving binary dyes and activated carbon. Al-Duri *et al.* (1992) used this modified extended Freundlich isotherm for binary dye mixtures and peat. They found that this modified isotherm was suitable for heterogeneous adsorption systems, especially systems where highly interactive, highly concentrated adsorbates were adsorbed on heterogeneous adsorbents. In a further study, comprising an adsorption system for dyes and activated carbon, Al-Duri and McKay (1992) showed that the effective diffusivity undergoes an exponential decay with increase in the initial sorbate concentration, for binary to ternary systems.

This is not, of course, the only work on competitive multicomponent adsorption. Other workers, such as Sheindorf *et al.* (1981) who presented a Freundlich type multicomponent isotherm and Martin and Al-Barhrani (1977) who examined the effect of an increase in the number of organic solutes in solution on the competitive adsorption of organic compounds and showed these were also important.

Other relevant studies include those of Jossens *et al.* (1978) who reported a three-parameter adsorption isotherm, Fritz *et al.* (1981) on competitive adsorption of two dissolved organics, and Myers and Zolandz (1980) on effects of pH changes on single component and multicomponent adsorption.

Most of the research in the multicomponent adsorption field deals with organic systems. However, in our case it is the heavy metals in wastewaters that are of interest, and this clearly also involves multicomponent solutions. Benjamin and Leckie (1981) studied adsorption of Cd, Zn, Cu, and Pb onto amorphous iron oxyhydroxide. The results suggest that the surface is composed of many groups of bonding sites. The strength of bonding between a given metal and the surface may vary by an order of magnitude or more from one site to another. At small adsorption densities all types of sites are available in excess, and adsorption can be described by the Langmuir isotherm. However, at higher adsorption densities, availability of the strongest binding sites decreases, leading to a decrease in the apparent adsorption equilibrium constant. This phenomenon occurs under conditions where only a few percent of all surface sites are occupied, and is inconsistent with available single-site models.

Gould and Genetelli (1984) reported effects of competition on heavy metal binding by anaerobically digested sludges. They tested zinc, nickel, copper, and cadmium as metal pairs: thus there were twelve metal pairs in all. In general terms, they found that for any bi-solute system, there was an increase in the number of active ligands, overall, when both metals were present, as compared with single-solute system.

1.6.5. Some Natural Adsorbents

Fungal

A number of schemes have been developed to remove heavy metals from wastewaters by biomass. Selected samples of waste microbial biomass used in industrial fermentation processes and wastewater biological treatment plants have been studied for their radium, uranium, and thorium biosorption ability from aqueous solution (Tsezos and Volesky, 1982; and Tsezos and Keller, 1983). They found solution pH affected the exhibited uptake. In general, lower biosorptive uptake was exhibited at pH value was lower than 4. That the most effective biomass type studied exhibited radium removals in excess of 99% of the radium in solution.

A common fungus *Rhizopus arrhizus* has been reported to take up uranium from aqueous solution. The mechanism of uranium uptake was a biosorption mechanism consisting of at least three processes. Uranium co-ordination and adsorption in the cell-wall chitin structure occur simultaneously and rapidly whereas precipitation of uranylhydroxide within the chitin microcystalline cell-wall structure takes place at a lower rate (Tsezos and Volesky, 1982). A model of adsorption of uranium with inactive cells of *Rhizopus arrhizus* successfully predicts the batch reactor uranium concentration profiles and has provided significant insights on the biosorbent's function (Tsezos *et al.*, 1988).

Mustafa and Haq (1988) reported the adsorption of Cu(II), Co(II), and Ni(II) ions on iron hydroxide from aqueous electrolyte solution as a function of temperature. Adsorption was found to increase with increasing temperature. The adsorption maximum of Cu(II), Co(II), and Ni(II) ions on the iron hydroxide surface was found to decrease in the series: Cu(II), Co(II), and Ni(II).

Biomass was also been used to remove copper, cadmium, and uranyl ions from waste solution (Norberg and Persson, 1984). The metal-biopolymer interaction in 0.1 M $NaClO_4$ was practically the same as when no neutral salt is added. The metal uptake was dependent on pH and a reversible process suitable for metal complexation.

The adsorption process and the organic matter interaction between the marine phytoplankton species *Dunaliella tertiolecta* and copper ions have also been investigated by differential pulse anodic stripping voltammetry (Gonzalez-Davila *et al.*, 1995). They indicated that the rate of uptake occurred in two steps. The adsorption equilibrium results show a two-site model which considers the algal surface as having two major functional groups: high-affinity binding and low-affinity binding. The high-affinity constant was of the exudates excreted by the algae, showing that extracellular ligands play an important role in decreasing the concentration of the free copper concentration.

Bruemmer *et al.* (1988) reported adsorption of nickel, zinc, and cadmium with a synthetic geothite. This involved (i) adsorption of metals on external surfaces, (ii) solid-state diffusion of metals from external to internal binding sites, and (iii) metal binding and fixation at positions inside the geothite particles. The general parameters of these processes were related to the hydrolytic properties and the ionic radii of the metals.

In a novel approach to the problem, Brady *et al.* (1994) used granular biosorbent biomass, prepared by treating yeast with hot alkali, to remove heavy metal from solution. The biomass accumulated a wide range of heavy metal cations (Fe^{3+}, Cu^{2+}, Cr^{3+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Ag^{+}, Ni^{2+}, and Fe^{2+}) but not anions ($Cr_2O_7^{2-}$) or an alkaline-earth metals (Ca^{2+}). Biosorption to the granular biomass was rapid. Although the biomass was capable of removing > 99% of zinc, chromium and copper from electroplating wastewater, it was capable of removing only 50-60% of chromium from tannery wastewater.

Srivastava *et al.* (1994) reported on uptake of lead and zinc by lignin from black liquor - a paper industry waste material. The uptake of lead was greater than the uptake of zinc, and the sorption capacity increased with increasing pH. Adsorption on lignin follows the Freundlich and Langumir models.

Agricultural

The use of agricultural and biological materials for the removal and recovery of heavy metals from solutions has been considerably investigated. Dye-treated and natural oil-palm fibres for a palm-oil mill were both used to remove copper and related heavy metal cations from solution (Low *et al.*, 1993). They found dye coating had a pronounced effect on metal sorption. The results on the uptake by fibres of metal cations from electroplating wastes show that the dye-treatment oil-palm fibre is a potentially useful material for the treatment of wastewaters containing heavy metals.

A series of natural materials, such as *Aspergillus terreus*, *Mucor ramannianus*, compost, peat, peanut shell, walnut shell, human hair, apricot seed shell, walnut shell, orangeskin, *Zygorhynchus het*, *Rhizopus sexu*, penicillium caps, and bone have been tested to remove cadmium from water (Azab and Peterson, 1989). They found ten of the tested materials showed higher than sorption capacity that of activated charcoal and ion-exchange resin. The potential of various biological materials can be increased by alkali treatment.

Wood, peat, lignite, subbituminous coal, bituminous coal, anthracite, graphite, charcoal, canneloid coal, phosphate rock, bentonite, oil shale, calcite, gilsonite, and silica flour have all been tried to see if they will remove uranium from aqueous solutions (Moore, 1954). The results showed peat, lignite, and subbituminous coal are the most effective agents for the removal of uranium from solution. Phosphate rock may be considered as a fair extracting agent under the conditions of these experiments. It is suggested that the common association between uranium and carbonaceous material in nature may result from the ability of these substances to remove uranium from natural solution by the formation of metalo-organic compounds.

Kashirtseva (1960) investigated copper sorption by organic and mineral sorbing agents. He found the degree of sorption depended on the total amount of dissolved copper in solution, the velocity of the circulating solution, on the duration of contact between the sorbent and fresh solutions, and on the degree of diffusion of the solution within the sorbent. Organic matter, namely pine loam, peat, lignite, and humic acid, absorbs copper from very dilute solutions; other sorbents, namely; sand, kaolin, feldspar, and quartz, absorb one-tenth as much as the organic sorbents.

1.7. CONCLUDING COMMENTS

The term heavy metals, as we usually understand it, means metals which are potentially harmful to most organisms at some level of exposure and absorption. We chose three heavy metals for this research, copper, nickel, and lead, for a numbers of reasons. For instance, reports of metal toxicity mention these three metals very frequently. This is hardly surprising, for they occur very widely and are toxic to most organism at low concentrations. Due to human activity, their presence in the environment has increased in some areas to levels which threaten the health of aquatic and terrestrial organisms, man included. Indeed, copper, nickel, and lead pollution arise from the following manufacturing and chemical industries: chlorine-diaphragm cell, chlorine-mercury cell, hydrofluoric acid, titanium dioxide-sulphate process and chloride ilmenite process, aluminium fluoride, chrome pigments, sodium dichromate, copper sulphate, nickel sulphate, sodium bisulphite, batteries, electroplating, and sodium hydrosulphite formate process.

It should also be noted that these metals are all divalent. This is important, and was deliberate for if enabled comparisons of adsorptive behaviour to be easily made.

Various processes can be employed to remove heavy metals from waste streams. There are two points which always concern water pollution control experts. The first one is the cost of any treatment system. The second one considers environmental problems including operation and disposal. However, in the most often used process, coagulation and precipitation result in large sludge quantities, while the chemicals used in the process, such as calcium, aluminium, and iron hydroxides represent a potential environmental difficulty, since high concentrations have to be dumped, merely moving the problem elsewhere. Due to the formation of metal complexes, remediation of metal-bearing wastes by conventional chemical treatment can be expensive and produce chemical sludges that require disposal.

There is a need to develop low-cost treatment technologies for the removal of heavy metals in developing countries. Adsorption by activated carbon is one of the methods that can be used for the removal of heavy metals from wastewater, especially when the metals are in low concentration. Since activated carbon is expensive, an alternative inexpensive adsorbent would drastically reduce the cost of an adsorption system. Many waste or naturally occurring materials have been investigated for the fields of water pollution control. The application of low-cost natural materials for removal of copper, nickel, and lead such as peat (Ong and Swanson, 1966; Bunzl *et al.*, 1976; Coupal and Lalancette, 1976; Smith *et al.*, 1977; Tummavuori and Aho, 1980; Dissanayake and Weerasooriya, 1981; Gosset *et al.*, 1986; and Chen *et al.*, 1990), hydrous oxide gels (Kinniburgh *et al.*, 1976), δ-manganese dioxide (Gray and Malati, 1979), synthetic pumice (Hara *et al.*, 1979), kaolin, illite and montmorillonite clay (Farrah *et al.*, 1980), goethite (Ralistrieri and Murray, 1982), bagasse, acacia, laurel and techtona bark (Kumar and Dara, 1982), Pinus pinaster bark (Vázquez *et al.*, 1994), waste rubber (Rowley *et al.*, 1984), sphagnum peat (Aho and Tummavuori, 1984), fly-ash (Panday *et al.*, 1985; and Yadava *et al.*, 1989), rice hulls (Suemitsu *et al.*, 1986), bagasse pith (McKay *et al.*, 1987), banana pith (Low *et al.*, 1995), moss (Low and Lee, 1987; and Lee and Low, 1989), sphagnum moss peat (McLellan and Rock, 1988), activated carbons (Ferro-García *et al.*, 1988), iron hydroxide (Mustafa and Haq, 1988), tea leaves (Tan and Abd. Rahman, 1988), chitin (Gonzalez-Davila and Millero, 1990), china clay and wollastonite (Yadava *et al.*, 1991), sphagnum peat (Viraraghavan and Dronamraju, 1993), penicillium biomass (Niu *et al.*, 1993), oil-palm fibres (Low *et al.*, 1993), yeast cell walls (Brady *et al.*, 1994), yeast biomass (Brady and Tobin, 1994), and algae (Özer *et al.*, 1994) have been reported.

Peat covers huge areas of the USSR, Canada, Finland, USA, Sweden, Norway and other countries. Peat has inherent characteristics such as a low density, a high porosity, an ion exchange property, and thermal and acoustic insulation properties, which are worthy of a systematic evaluation with a view to solving actual problems of modem society, such as has been initiated recently in the USSR, Finland, and Canada (Ruel *et al.*, 1977). Indeed peat is a relatively inexpensive and widely available as well as greatly polar and porous material. Therefore, adsorption capacity can be greater than most other low-cost materials by polar functional groups of lignin and capacious specific surface area. The polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids phenolic hydroxides and ethers in the peat surface can influence the adsorption of organic compounds. These groups may interact with the chelated heavy metals by involving the formation of an electron donor-acceptor complexes of the chelate and the active sites (such as polar functional groups). Possible hydrogen bonding between the surface groups and the chelated metals or free ligands could also enhance adsorption. The removal of metals using peat has been quantified through studies of laboratory, pilot (Coupal and Lalancette, 1976; and Trujillo *et al.*, 1991), and full scale plants (Green *et al.*, 1994). However, our understanding of mechanisms is incomplete. As peat is a polar material, metal removal could be due to a variety of mechanisms, including, for instance, physical and chemical adsorption.

In the work represented in this thesis, an attempt has therefore been made to investigate the adsorption of heavy metals such as copper, nickel, and lead in general, the most usual global contaminants, using sphagnum moss peat that is commercially available in Britain and Ireland and has an average cost for a standard pack (50 l) of £ 5.00. The study then forms a benchmark, as it were, for comparisons with other biological waste materials which do not demand destruction of our peat reserves. Basically, this study has followed:

1. single-solute and multi-solute systems tests for adsorption capacity by isotherms to evaluate the ability of the components of a simple sphagnum moss peat system to remove copper, nickel, and lead from aqueous solutions;
2. impact of adsorbate, peat dose, pH, temperature, and type of adsorbate;

3. investigation into adsorption kinetics and mechanisms.

Taken overall, the results of this study can be developed to a column design to remove heavy metals from waste streams.

CHAPTER TWO

MATERIALS AND METHODS

2.1. MATERIALS

The major interest of this study was to investigate adsorption of heavy metals such as copper, nickel and lead using sphagnum moss peat that is naturally, commercially available and was supplied by Bord Na Mona, Dublin. This is low-cost material: the average price of a 50 litre pack was approximately five pounds. This variety of moss peat is generally marketed as a soil conditioner for horticultural purposes because of its character of adsorbability to keep water and manure for plants.

2.1.1. Preparation of Sphagnum Moss Peat

The raw sphagnum moss peat was dried in an oven at 105°C for a period of 24 hours, and then screened through a 14 mesh sieve (B.S. 410/43) to remove any large solids. This was done to produce a uniform material for the complete set of absorption tests which was stored in an air-tight plastic container for all investigations.

2.1.2. Preparation of Metal Solutions

Analytical grade reagents were used in all cases. The stock solutions of copper(II), nickel(II) and lead(II) (1000 mg/l) were prepared in distilled water using copper sulphate, nickel sulphate and lead nitrate, respectively. All working solutions were prepared by diluting the stock solution with distilled water. The pH adjustments were made with sulphuric acid or sodium hydroxide solutions.

2.2. EXPERIMENTS PROCEDURE

2.2.1. pH Measurements

All the pH measurements were carried out using a pH meter (Corning pH meter 240). The pH meter was standardised by means of buffer solutions of pH 4.0 and 7.0 before each set of measurements.

2.2.2. Metal Ions Measurements

Atomic adsorption spectrometry (AAS) is extremely popular, because of its low cost and ease and rapidity of use. The simplest form of AAS is the flame technique which is of rather limited sensitivity. A standard method for the examination of metal ion concentration (Greenberg *et al.*, 1992) was used. This was measured by atomic absorption spectrometry (AAS) flame spectrophotometry with single element hollow cathode lamps (Instrumentation Laboratory *aa/ae* spectrophotometer 751), and in some cases, by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Although single-flask tests were done, the filtrate analyses were replicated ($n = 5$). The data were, therefore, reported as averages with, typically, a standard deviation of 5%.

All working standard solutions, were prepared by diluting a standard solution containing 1000 mg/l (Fison Plc.) with distilled water. An operating condition was chosen either by selecting a wavelength or by rotating the burner.

2.2.3. Characterisation of Sphagnum Moss Peat

It was also important to establish concentrations of metal ions originally in the peat as a base-line: **Table 2.2.3-1** shows the results of these analyses. A visual qualitative evaluation of the surface area of sphagnum moss peat was made with the help of a microscope, and confirmed by scanning electron photomicrographs. The material for the photomicrographs was prepared and the photomicrographs taken by Mr. Meng-Chieh Yu in Taiwan. **Figures 2.2.3-1a** to **2.2.3-1d** illustrate the great porosity of sphagnum moss peat in its natural state. It was, therefore, anticipated that its adsorption capacity should be great for the reason of surface area.

The metal content of the peat was determined by resuspending the peat (0.5 g) in approximately 25 ml of 1 + 1 HNO_3 and digested by heating. After filtration, the sample was diluted to 100 ml with Milli-Q (Millipore) ultra-pure water. Metal concentration was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

TABLE 2.2.3-1: Some Inorganic Constituents Present in the Sphagnum Moss Peat.

Constituent	Concentration (μg/g of Peat)	Constituent	Concentration (μg/g of Peat)
Iron	890	Cadmium	1.1
Aluminium	660	Potassium	< 1
Sodium	285	Chromium	< 1
Manganese	24	Copper	< 1
Zinc	19	Mercury	< 1
Lead	13.5	Silver	< 1
Nickel	5.5	Zirconium	< 1

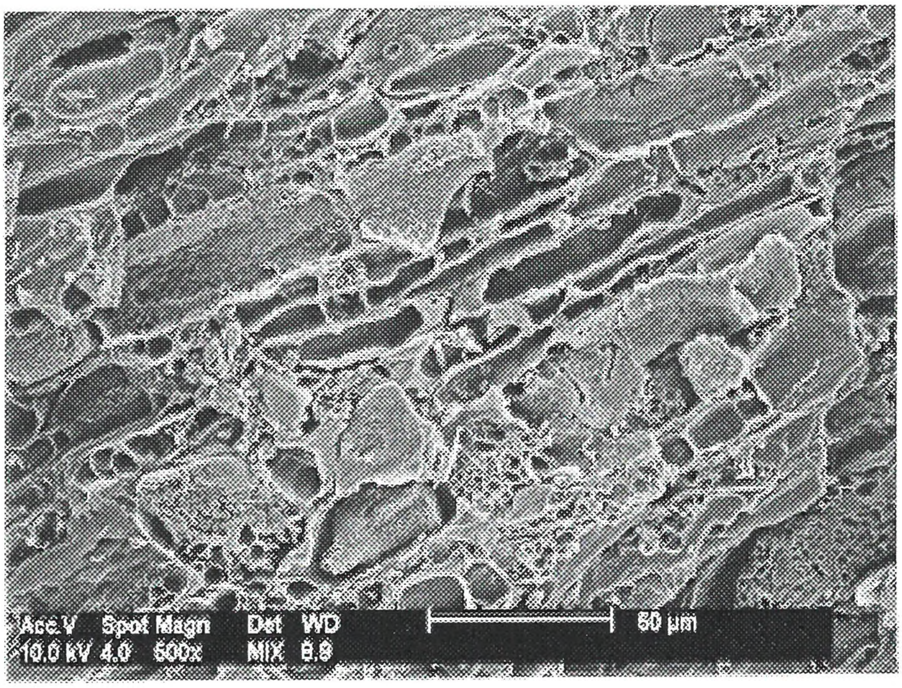


Figure 2.2.3-1a: The structure of sphagnum moss peat.

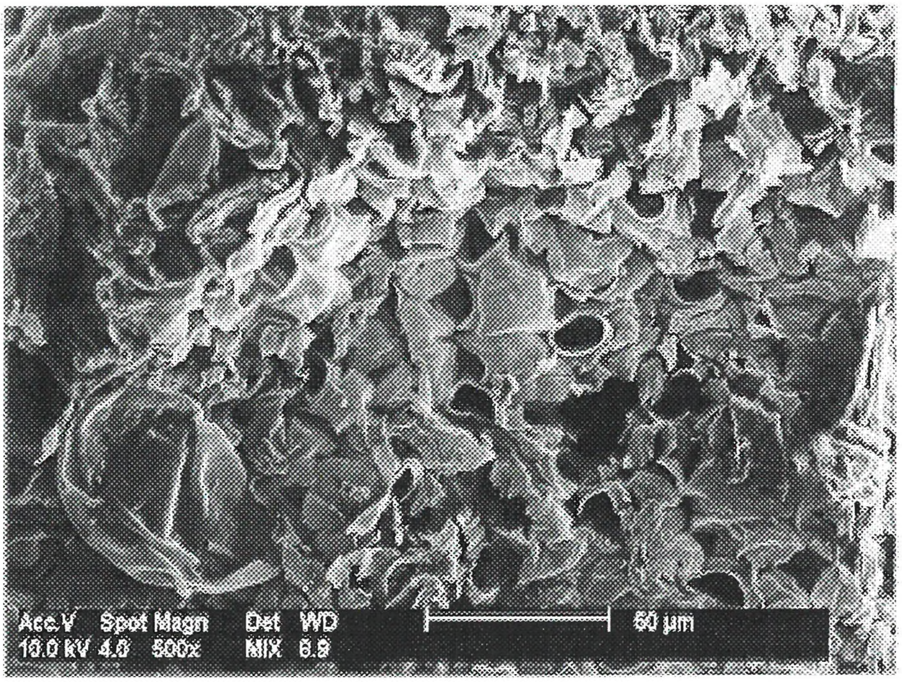


Figure 2.2.3-1b: The structure of sphagnum moss peat.

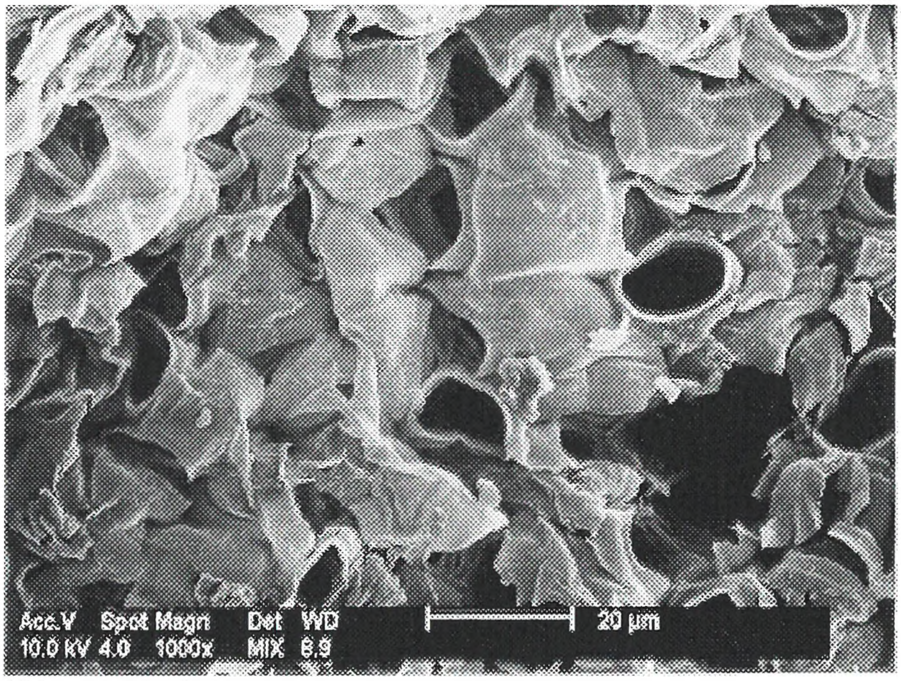


Figure 2.2.3-1c: The structure of sphagnum moss peat.

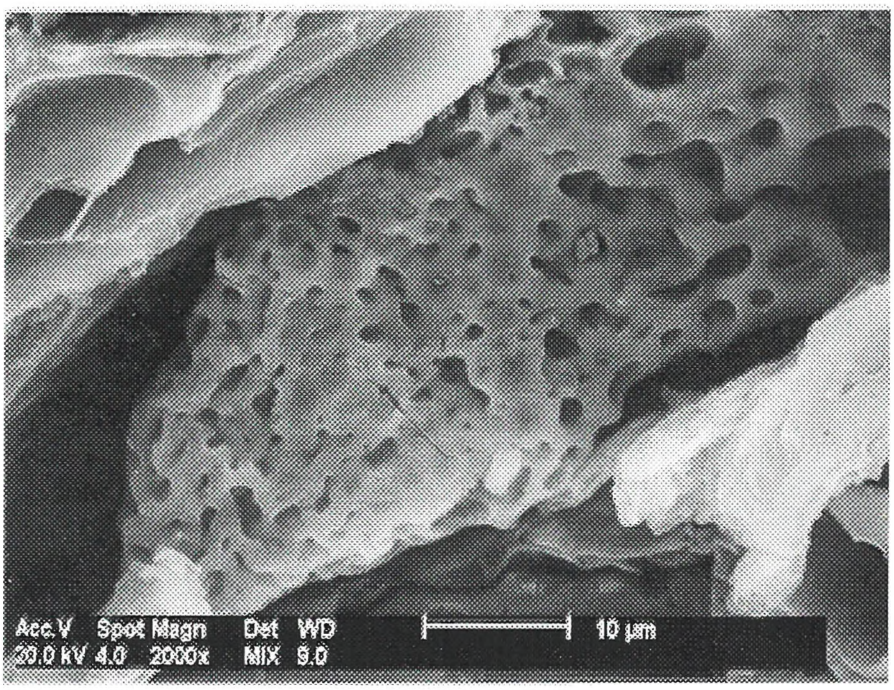


Figure 2.2.3-1d: The structure of sphagnum moss peat.

2.2.4. Adsorption in Single-Solute System

There are three series in all, each including one of the three heavy metals (Cu, Ni, and Pb). The procedure for the adsorption test was carried out as follows:

Batch sorption experiments were conducted at a constant temperature on a rotary shaker at 100 rpm using capped conical flasks. In all sets of experiments, one gram of moss peat was thoroughly mixed into 250 ml cation solution. After shaking the flasks for predetermined time intervals, the reaction mixtures were filtered through Whatman filter paper (No. 1), the final pH was recorded, and the filtrate was analysed for the concentration of cation.

pH Effect

In order to evaluate the effect of pH on the adsorption phenomenon, cation solutions at various initial pH values were investigated as described below. The initial pH adjustments were carried out either by sulphuric acid or sodium hydroxide solution. For copper(II), five different runs at pH 2.0, 3.0, 4.0, 4.5 and 5.0 were performed, varying initial copper(II) concentration from 20 mg/l to 300 mg/l at a temperature of 25°C. For nickel(II), six different tests at pH 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 each used a range of initial nickel(II) concentrations from 10 to 200 mg/l at a temperature of 25°C. For lead three different runs at pH 4.0, 5.0 and 6.0 were performed, varying the initial lead(II) concentration from 10 mg/l to 120 mg/l at a temperature of 20°C.

Adsorbent Dose Effect

The effect of moss peat doses was carried out with an initial copper(II) concentration of 200 mg/l at pH 5.0 and temperature of 25°C. The peat doses were varied from 4.0 g/l to 40 g/l; the shake-flask was than filtered and analysed for pH and the concentration of copper(II).

For tests involving variations in the amounts of moss peat, the initial nickel(II) concentration was 200 mg/l, and the pH was 5.0. The dose of peat sorbent was varied over the range 4.0 to 40 g/l. The conical flasks were shaken at 25°C as before for four hours, after which pH was measured and nickel(II) content was determined as described above.

Temperature Effect

Batch sorption experiments were carried out at the desired temperature (12, 20, 29 and 37°C) on a rotary shaker at 100 rpm using capped 250 ml conical flasks.

In the adsorption isotherm tests, 0.40 g of peat was thoroughly mixed with aqueous solutions of lead (100 ml). The initial pH adjustments were carried out either by sulphuric acid or sodium hydroxide solution. Three different runs at pH 4.0, 5.0 and 6.0 were performed, varying the initial lead(II) concentration from 10 mg/l to 120 mg/l. After shaking the flasks for four hours, the reaction mixtures were filtered through filter paper (Whatman No. 1) and the filtrate was analysed for pH and the concentration of lead(II).

2.2.5. Adsorption in Multi-Solute System

The procedure for this experiment is similar to the previous section (adsorption in single-solute system) except for the solutions of metals which were used.

The concentrations of metals used were similar to those for the single-solute system; namely 20 to 100 mg/l for the copper system, 5 to 80 mg/l for the nickel system and 5 to 90 mg/l for the lead system.

Adsorption of Copper and Nickel System:

Batch sorption experiments were conducted in a constant temperature room at 25°C on a rotary shaker at 100 rpm using capped 250 ml conical flasks. In the adsorption isotherm tests, 0.60 g of peat was thoroughly mixed into 150 ml of solution. The initial pH was adjusted to 5.0 either by sulphuric acid or sodium hydroxide solution. Three series of copper and nickel mixed solution in the mole ratio of 1:1.3, 1.7:1 and

1:2.6 (Cu:Ni) were investigated in the concentration range 5 to 100 mg/l. After shaking the flasks for 3 hours, the reaction mixtures were filtered (Whatman No. 1) and the filtrate was analysed for the concentration of copper(II) and nickel(II), respectively.

Adsorption of Lead/Copper and Lead/Nickel Systems:

Batch sorption experiments were conducted in a constant temperature room at 25°C on a rotary shaker at 100 rpm using capped 250 ml conical flasks. In the adsorption isotherm tests, 0.60 g of peat was thoroughly mixed into 150 ml of solution. The initial pH adjustment to 5.0 was either by sulphuric acid or sodium hydroxide solution. Lead and nickel mixed solution in the mole ratio of 1:3.8 (Pb:Ni) and lead and copper mixed solution in the mole ratio of 1:3.2 (Pb:Cu) were tested in the concentration range 5 to 100 mg/l for lead/nickel system and 5 to 80 mg/l for lead/copper system. After shaking the flasks for 3 hours, the reaction mixtures were filtered (Whatman No. 1) and the filtrate was analysed for the concentration of lead(II) and nickel(II), respectively.

Adsorption of Copper, Lead and Nickel System:

Batch sorption experiments were conducted in a constant temperature room at 25°C on a rotary shaker at 100 rpm using capped 250 ml conical flasks. In the adsorption isotherm tests, 0.60 g of peat was thoroughly mixed into 150 ml of solution. Initial pH was adjusted to 5.0 either by sulphuric acid or sodium hydroxide solution, and lead, copper and nickel mixed solution in the mole ratio of 1:3.9:5.7 (Pb:Cu:Ni) was tested. A series of copper, nickel and lead mixed solutions over the concentration range 5 to 80 mg/l for copper, 5 to 100 mg/l for nickel and 5 to 50 mg/l for lead were then investigated. After shaking the flasks for 3 hours, the reaction mixtures were filtered (Whatman No. 1) and the filtrate was analysed for the concentration of copper(II) nickel(II) and lead(II), respectively.

Dose Effect in Bi-Solute of Copper and Nickel System:

The effect of sorbent doses was tested with initial copper and nickel ion concentrations of 200 mg/l at pH 5.0, while varying the peat doses from 4.0 g/l to 40 g/l. The conical flasks were shaken at 25°C as before for 5 hours, after which copper(II) and nickel(II) concentrations were determined as described above.

2.2.6. Adsorption Kinetics in Single-Solute System

Copper

In the sorption kinetic experiments, 5 g of peat was thoroughly mixed with 1.25 l copper(II) solution (1000 mg/l). The peat suspensions were shaken for two hours at a constant temperature of 25°C and 2 ml samples were collected and filtered through a 0.45 μm membrane filter every 3 minutes for first 15 minutes, every 5 minutes for the next 15 minutes, every 10 minutes for the next half hour and every 15 minutes for the last hour. The filtrates were analysed using atomic absorption spectrophotometry.

Nickel

For each of the sorption kinetic tests, 5 g peat was thoroughly mixed with 1.25 l nickel(II) solution in the range 50 to 400 mg/l. Peat suspensions were shaken as before for 2 hours at a constant temperature of 25°C, and 2 ml samples were collected and filtered through a 0.45 μm membrane filter every 3 minutes for the first 15 minutes, every 5 minutes for the next 15 minutes, every 10 minutes for the next half hour and, finally, every 30 minutes for the last hour. The filtrates were analysed by atomic absorption spectrophotometry.

Lead

In the sorption kinetic experiments, 1.2 g of peat was thoroughly mixed with 300 ml of 100 mg/l lead(II) solution. The peat suspensions were shaken for three hours at the desired temperature (12, 20, 29 and 37°C) using capped 500 ml conical flasks and 2 ml samples were collected and filtered through a 0.45 μm membrane filter every 3 minutes for the first 15 minutes, every 5 minutes, for the next 15 minutes, every 10 minutes for next half hour, every 15 minutes for the next hour and then at 30 minutes intervals for the last hour. The filtrates were analysed using atomic absorption spectrophotometry.

2.2.7. Adsorption Kinetics in Multi-Solute System

Adsorption of Copper and Nickel:

The sorption experiments were conducted in a constant temperature room (25°C) on a rotary shaker (100 rpm) using capped 500 ml conical flasks. For single-solute systems, the peat (1.2 g) was mixed with the aqueous solution (300 ml) containing the metal ions (10, 25, 50 and 100 mg/l). The pH was adjusted to a value of 5.0. The peat suspensions were then shaken for 3 hours. Samples (2 ml) were taken periodically, filtered through a membrane filter (0.45 μm) and their metal concentration measured. Although replicate samples were not taken, replicate measurements ($n = 5$) of the metal concentrations were made and an average value reported. Typically, the standard deviation of these replicates was 5%. For bi-solute systems, 3.2 g of peat were used together with a larger volume (800 ml) of the solution of metal ions containing equal concentrations (w/v) of the two metals. In these cases, when, for example, copper concentrations were measured, copper was considered as the primary metal and nickel as the secondary metal.

Adsorption of Copper and Lead:

A series of batch sorption kinetic experiment tested the kinetic characteristics of the adsorption of metal ions onto moss peat. The experiments were conducted on a bi-solute basis using copper(II) and lead(II). 1.2 g of peat were transferred to 300 ml of bi-solute solution in the concentration of 50 mg/l for copper and nickel respectively at pH 5.0. Peat suspensions were shaken as previous conditions for three hours at constant temperature of 25°C and 2 ml samples were filtered through a 0.45 μm membrane filter at suitable time intervals and analysed for metal ions by atomic adsorption spectrometry.

Adsorption of Copper, Lead and Nickel:

A batch sorption kinetic experiment tested the kinetic characteristics of the adsorption of metal ions onto moss peat in the triple-solute system copper, nickel and lead. The experiments were conducted on a single-solute basis using copper(II) and nickel(II) as well as triple-solute with three ions. For the single-solute system, 1.2 g of peat were transferred to 300 ml of single-solute solution in the concentration of 50 mg/l at pH 5.0. For triple-solute systems, 3.2 g of peat were used together with a larger volume (800 ml) of the solution of metal ions containing equal concentrations (50 mg/l) of the three metals. Peat suspensions were shaken as previously described for 3 hours at constant temperature of 25°C and 3 ml samples were filtered through a 0.45 μm membrane filter at suitable time intervals and analysed for metal ions by atomic adsorption.

CHAPTER THREE

RESULTS AND DISCUSSION
SORPTION EQUILIBRIA

It has been shown in a number of reports that peat has an ability to adsorb metals from aqueous systems. Indeed, a system involving binding of heavy metal ions to peat is an important model for many biosorption processes. Besides pH and temperature, the type of anionic system and the concentrations of the metallic ions are some of the governing factors determining the maximum uptake capacity of the peat system. A biosorption system was therefore tested, using metallic ion solutions in different reactions.

Two important physicochemical aspects for the evaluation of the sorption process as a unit operation are the equilibria of the sorption and the kinetics. Sorption equilibrium is established when the concentration of metal in the bulk solution is in dynamic balance with that of the interfaces.

3.1. COPPER

3.1.1. Adsorption Equilibria

Figure 3.1.1-1 shows a series of typical isotherms for the copper-peat system at various pH values and using a range of ion concentrations. It is generally seen that the adsorption capacity, q_e, increases gradually with increasing solution pH. The result shows that for increasing equilibrium copper concentration, the adsorption capacity increased very little at pH 2.0. At pH 3.0 the increase was slightly greater, but the most significant increase was found in the range pH 4.0 to 5.0. For all cases, the greatest increase occurred at the lower copper concentrations.

3.1.2. Adsorption Isotherms

In order to determine the effectiveness of peat for a particular metal-bearing waste, adsorption isotherms should be developed that indicate the amount of material adsorbed at a particular concentration. These tests are usually performed on several different peats at various concentrations in order to determine which provides the most effective treatment. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, the most common of which are the Langmuir and Freundlich isotherms. However they are usually unsatisfactory when applied to systems where true ion exchange is involved (Helfferich, 1962), although the Langmuir isotherm has been used to simulate some ion exchange reactions and the Freundlich isotherm for complexation reactions in a saturation-type reaction (Chen *et al.*, 1990).

Langmuir Isotherms

The adsorption data were analysed according to the linear form of the Langmuir isotherm. The plots of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) are shown in **Figure 3.1.2-1**. These isotherms were found to be linear over the

Figure 3.1.1-1: Typical isotherms for the copper-peat system at various initial pH values.

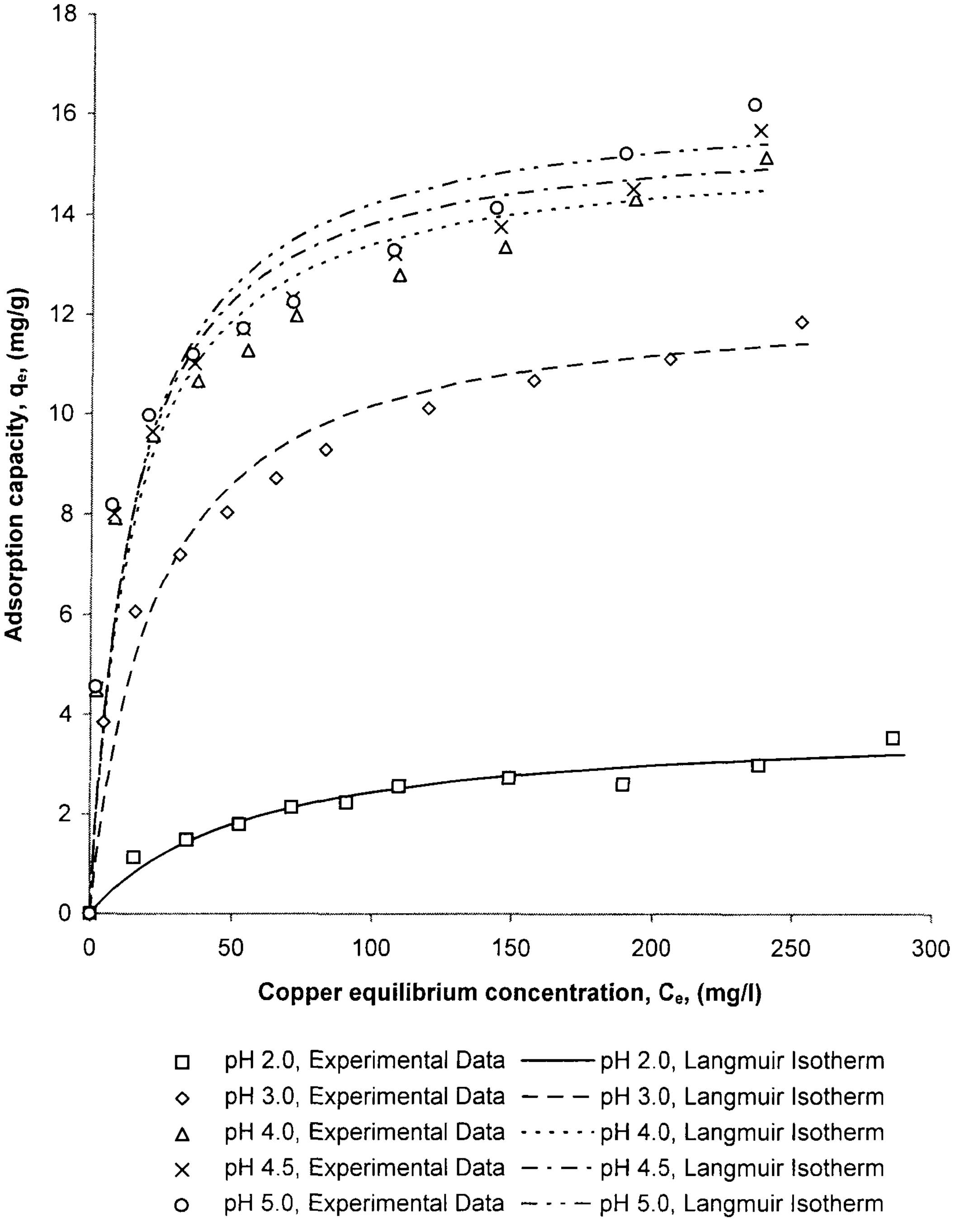
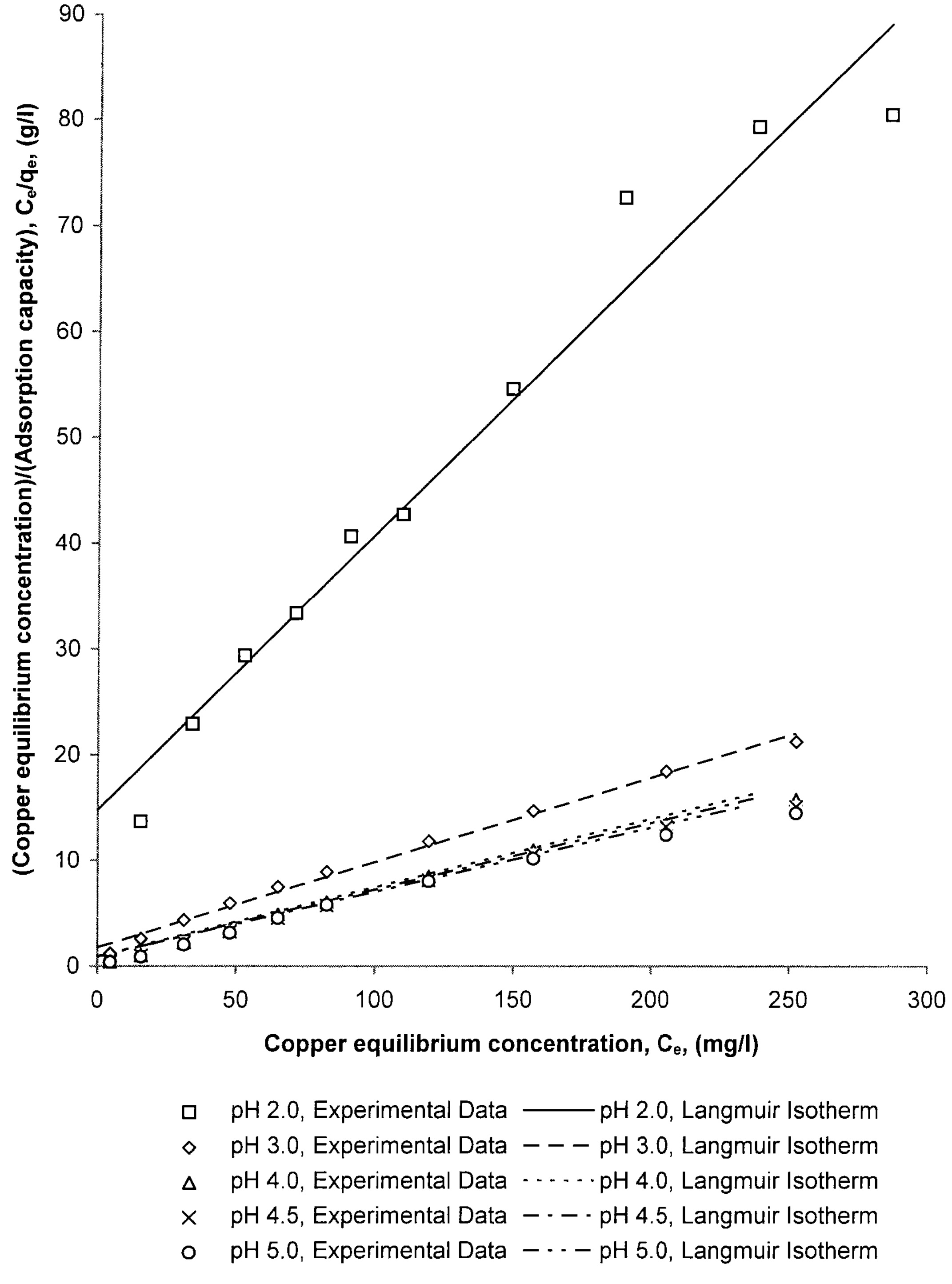


Figure 3.1.2-1: Linearised Langmuir isotherms at various initial pH values for copper-peat system.



whole concentration range and the correlation coefficients were found to be between 0.963 and 0.994 (**Table 3.1.2-1**). These values for the correlation coefficients indicate that there is a strong positive relationship for the data and that the copper-peat adsorption data follows the Langmuir model of adsorption.

The Langmuir constants are shown in **Table 3.1.2-1** and it can be seen that the maximum adsorption capacity, X_m, increases with increasing solution pH values. The higher values of adsorption capacity were found to be 15.4, 15.8, and 16.4 mg/g of peat. These occurred at initial pH values of 4.0, 4.5, and 5.0. When the pH was adjusted to 2.0, the adsorption capacity was reduced to a value as low as 3.85 mg/g. A separation of the ions (i.e. H^+ and M^{2+}) can never occur, and observed adsorption is always a compromise between the tendency of the more strongly adsorbable ion to go to the interface, and of the more weakly adsorbable one to remain in the solution. This could well imply that ion exchange is playing a significant role since the carboxylic acid group in weakly acidic exchanges would effectively cease to be dissociated at this low pH. However, the high value of the correlation coefficients suggest to that this is not true ion exchange (Helfferich, 1962).

TABLE 3.1.2-1: Adsorption Isotherm Constants of Copper-Peat Binding.

	Langmuir Constants			Freundlich Constants		
pH_{in}	Corr. Coeff. r^2	X_m (mg/g)	100×k (l/mg)	Corr. Coeff. r^2	K_F (mg/g)	10×(1/n)
2.00	0.963	3.85	1.75	0.973	0.415	3.71
3.00	0.994	12.4	4.55	0.987	2.74	2.71
4.00	0.993	15.4	6.91	0.964	4.34	2.34
4.50	0.993	15.8	7.08	0.965	4.41	2.37
5.00	0.990	16.4	6.62	0.965	4.58	2.35

The variations of the Langmuir constant, X_m, in relation to the initial pH are shown in **Figure 3.1.2-2**. Over the pH range that was examined, the relationship had a correlation coefficient of 0.999 and can be expressed as:

$$X_m = \frac{pH_{in} - 1.84}{3.39 \times 10^{-2} + 5.02 \times 10^{-2}(pH_{in} - 1.84)}, \qquad (3.1.2\text{-}1)$$

where

pH_{in} is initial solution pH value which was between 2.0 and 5.0.

The Langmuir constant, k, which is a measure of adsorption energy, also increases with increasing solution pH values. Again, the higher values of the Langmuir constant, k, were found to be at initial adjusted pH 4.0, 4.5, and 5.0. The variation of the Langmuir constant, k, against adjusted pH is shown in **Figure 3.1.2-3**. Thus, within the range of 2.0 to 5.0, the relationship had a correlation coefficient of 0.966 can be expressed as:

$$k = \frac{pH_{in} - 1.88}{6.92 + 1.23 \times 10(pH_{in} - 1.88)}. \qquad (3.1.2\text{-}2)$$

These two relationships, therefore, provide a technique for predicting the Langmuir-type adsorption for any initial pH (within the range which was examined). Whilst this is useful tool, it is also pertinent to compare the current data with the results obtained by other workers. An examination of **Table 3.1.2-2** shows that the value for the maximum adsorption (the Langmuir constant X_m) is comparable with values reported previously. This table also shows the adsorption capacities reported in earlier studies where X_m had not been derived specifically.

The maximum adsorption capacity, X_m, found for peat used in this study was 16.4 mg/g (**Table 3.1.2-1**). This value is very comparable with the results from earlier studies using unmodified peat in batch tests. **Table 3.1.2-2** shows that these values

Figure 3.1.2-2: Variation of adsorption capacity (X_m) of peat for copper against initial pH (pH_{in}).

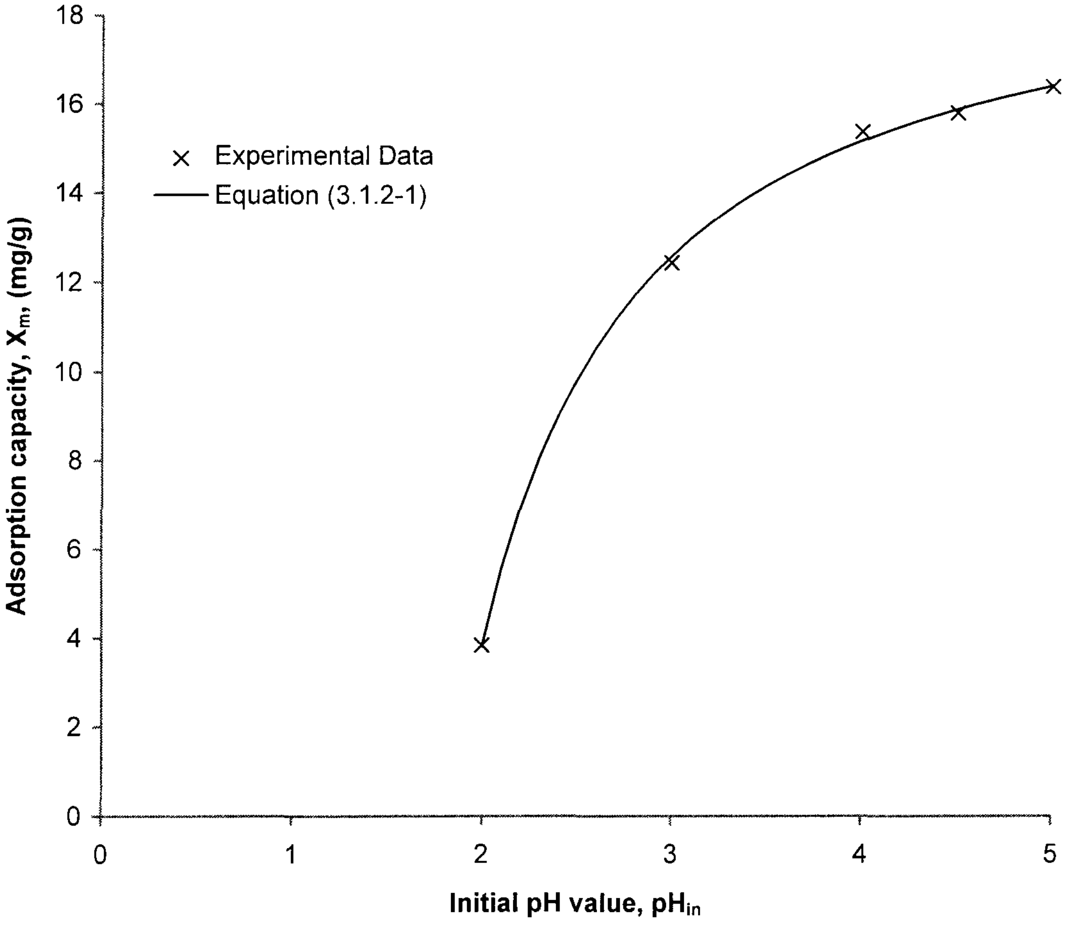
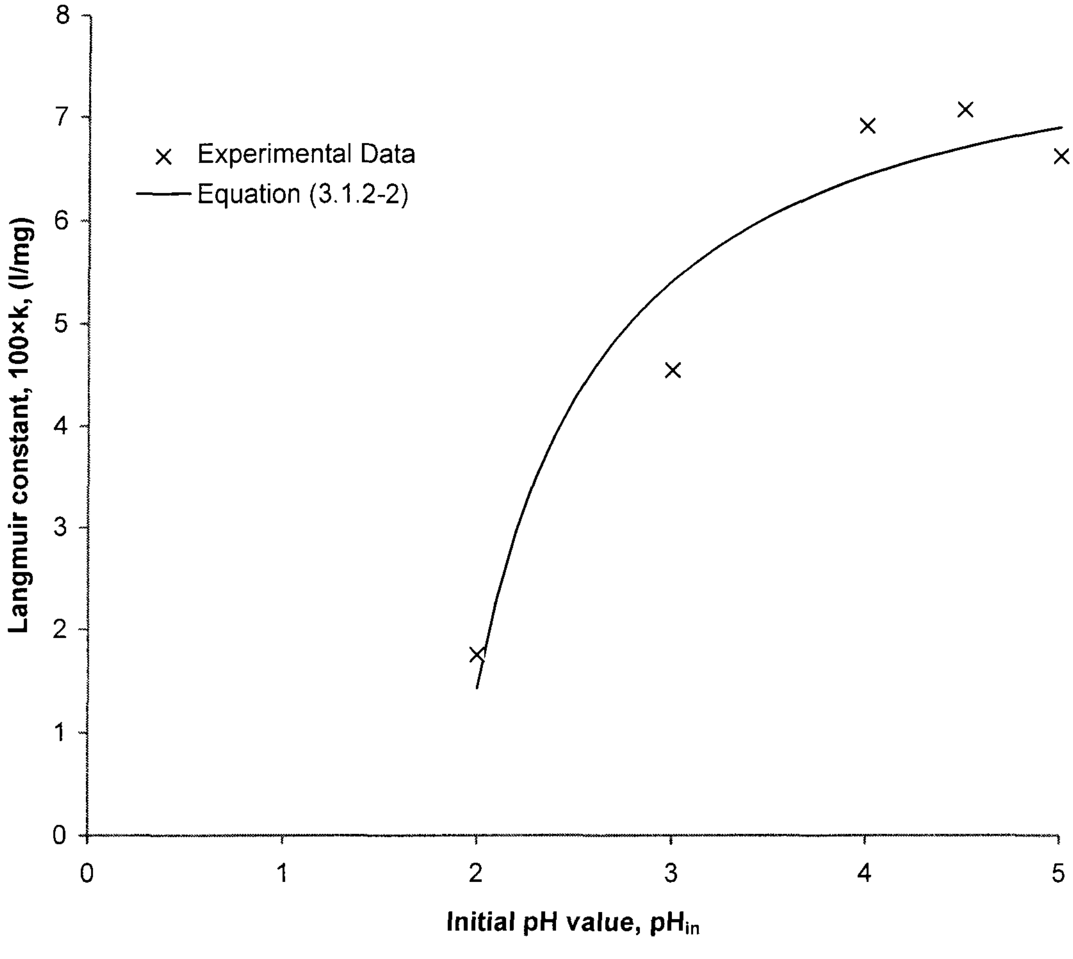


Figure 3.1.2-3: Variation of Langmuir constant (k) for copper-system against initial pH (pH_{in}).



ranged from 1.76 to 75.6 mg/g with the average being 20.1 mg/g. **Table 3.1.2-2** also shows that peats which had been acid-treated had significantly higher capacities.

TABLE 3.1.2-2: Maximum Capacities for Adsorption of Copper by Peat.

Capacity (mg/g)	X_m (mg/g)	Material	Reference
22	-	Peat (Hungary)	Szabo (1958)
10	-	Peat* (England)	Ong and Swansor (1966)
16.5	-	Peat*	Bunzl *et. al.* (1976)
>52.4	-	Peat* (Ireland)	Smith *et. al.* (1977)
>7.5	-	Peat (Ireland)	
75.6	-	Peat* (Ireland)	Smith *et. al.* (1978)
17.8	-	Peat (Ireland)	
5.10	-	Peat (Rastunsuo)	Tummavuori and Aho (1980)
2.6	-	Peat	Eger *et. al.* (1980)
38.7	-	Peat* (Muthurajawela)	Dissanayake and Weerasooriya (1981)
12.7	-	(i) Moss Peat	Aho and Tummavuori (1984)
20.0	-	(ii) Moss Peat	
12.1	-	Eutropnic Peat	Gosset *et. al.* (1986)
12.1	-	Oligotrophic Peat	
-	27.1	Moss (Calymperes Delessertii Besch)	Low and Lee (1987) Lee and Low (1989)
23.0	-	Sphagnum Moss Peat	Mclellan and Rock (1988)
-	19.6	Eutrophic Peat*	Chen *et. al.* (1990)
-	6.41	Oligotrophic Peat*	
-	1.76	Sphagnum Peat Moss	Allen *et al.* (1992)
18.5	-	Sphagnum Peat	Viraraghavan and Dronamraju (1993)
-	16.4	Sphagnum Moss Peat	This Work

* Acid treated.

(i) Peat for energy production.

(ii) Peat for agricultural use.

In terms of Langmuir parameters the isotherms are given by the following equations:

$$q_e = \frac{C_e}{\frac{1}{X_m \cdot k} + \frac{1}{X_m} C_e},$$

at pH 2.0,

$$q_e = \frac{C_e}{1.48 \times 10 + 2.60 \times 10^{-1} C_e};$$

at pH 3.0,

$$q_e = \frac{C_e}{1.77 + 8.05 \times 10^{-2} C_e};$$

at pH 4.0,

$$q_e = \frac{C_e}{9.41 \times 10^{-1} + 6.50 \times 10^{-2} C_e};$$

at pH 4.5,

$$q_e = \frac{C_e}{8.94 \times 10^{-1} + 6.33 \times 10^{-2} C_e};$$

at pH 5.0,

$$q_e = \frac{C_e}{9.21 \times 10^{-1} + 6.10 \times 10^{-2} C_e};$$

Freundlich Isotherms

An alternative isotherm used for the adsorption data has also been used to calculate the ultimate sorption capacity of peat by substituting the required equilibrium concentrations in the Freundlich equation. When the data were linearised (**Figure 3.1.2-4**), the correlation coefficients were found to vary between 0.964 and 0.987. The constants in the Freundlich isotherms were determined for the various pH values of the solutions, and are listed in **Table 3.1.2-1**.

The Freundlich constants are also shown in **Table 3.1.2-1**. 1/n, which is a measure of the adsorption intensity, decreased from 0.371 to a value of 0.235 with increasing solution pH values. Similar values of the Freundlich constant, 1/n, were found at initial pH values of 4.0, 4.5, and 5.0. The variation of the Freundlich constant, 1/n, against initial pH is shown in **Figure 3.1.2-5**. The linear relationship over the measured pH range had a correlation coefficient of 0.999 can be expressed as:

$$\frac{1}{n} = \frac{pH_{in} - 1.45}{-1.15 + 4.60(pH_{in} - 1.45)}, \qquad (4.1.2\text{-}3)$$

where

pH_{in} was between 2.0 and 5.0.

The Freundlich constant, K_F, which is a measure of adsorption capacity, and is characteristic for the adsorbent and the adsorbed, increased with increasing solution pH values. The highest adsorption capacity of copper was 4.58 mg/g of peat at pH 5.0. Both Langmuir and Freundlich constants showed the same increasing trend with increasing solution pH values. The variation of the Freundlich constant against initial pH is shown in **Figure 3.1.2-6**, and shows a linear relationship with a correlation coefficient of 0.983 can be expressed as:

$$K_F = \frac{pH_{in} - 1.91}{2.11 \times 10^{-1} + 1.46 \times 10^{-1}(pH_{in} - 1.91)}, \qquad (3.1.2\text{-}4)$$

Figure 3.1.2-4: Linearised Freundlich isotherms at various initial pH values for the copper-peat system.

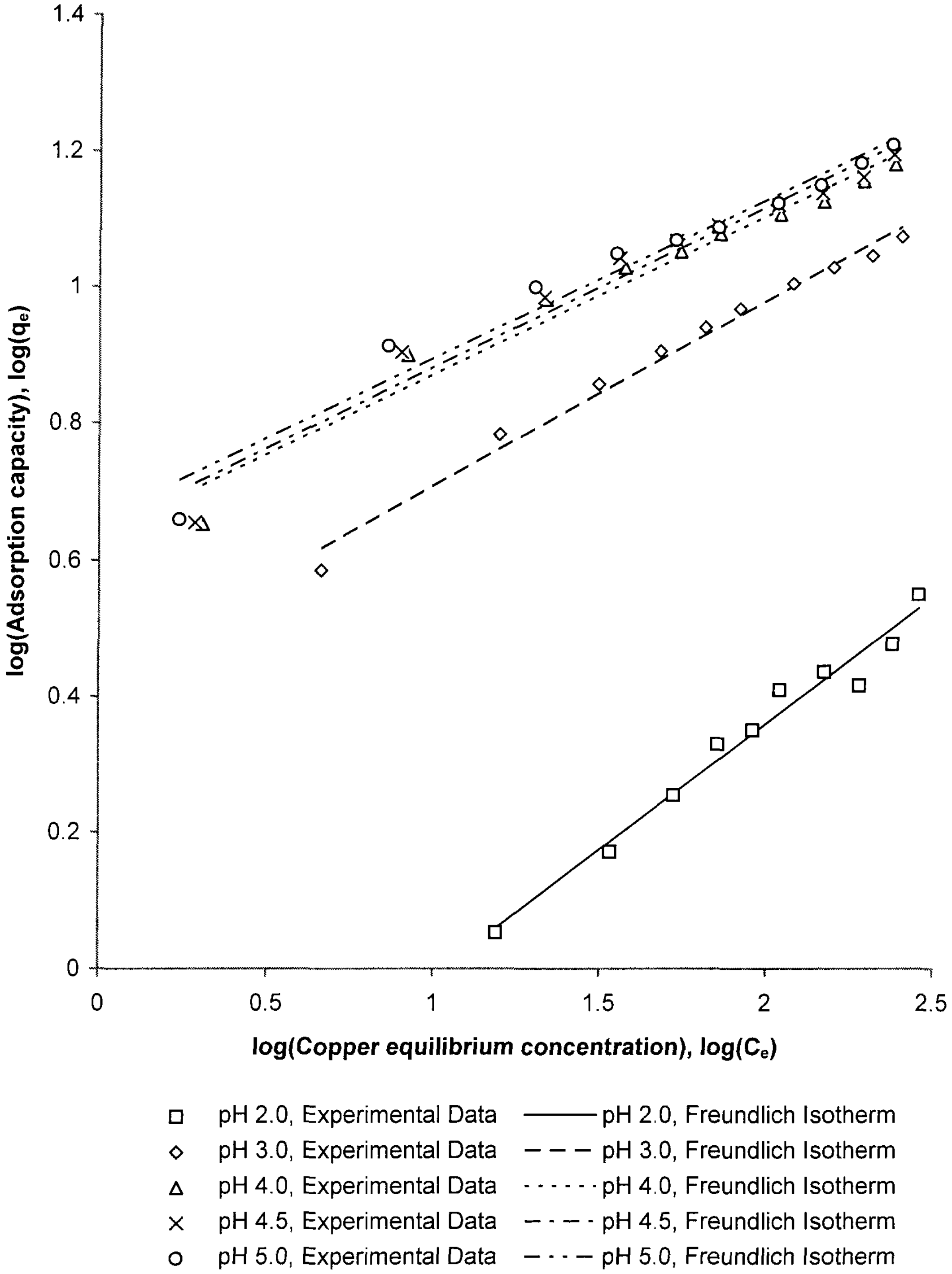


Figure 3.1.2-5: Variation of Freundlich constant (1/n) with initial pH (pH_{in}) for the copper-peat system.

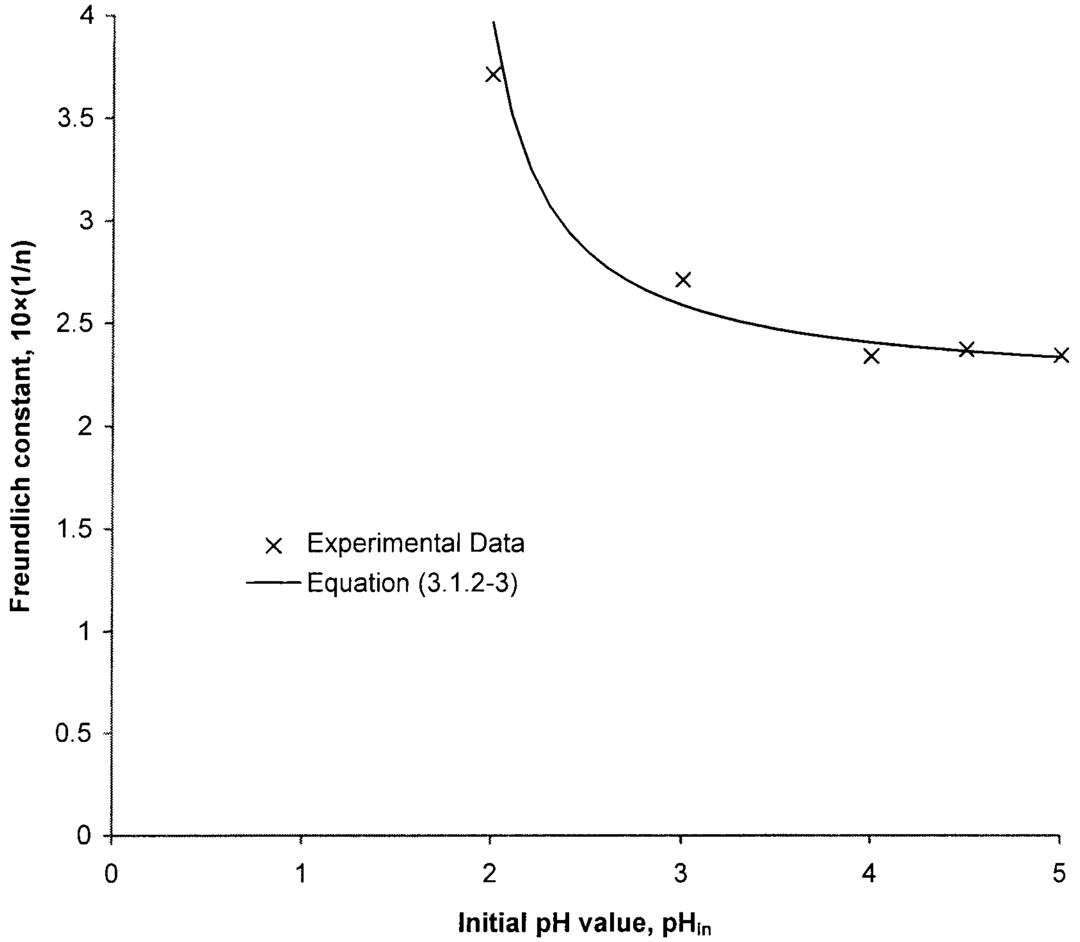
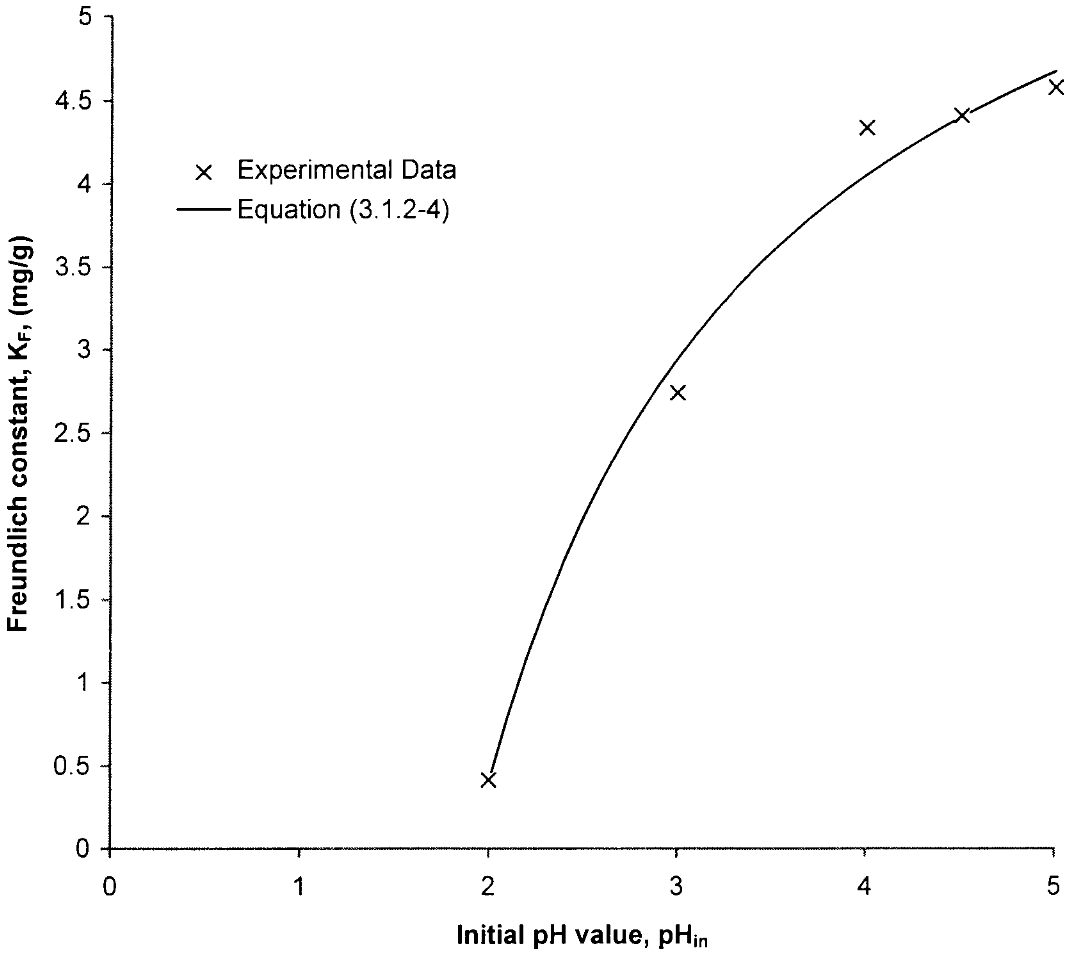


Figure 3.1.2-6: Variation of Freundlich constant (K_F) with initial pH (pH_{in}) for the copper-peat system.



where

pH_{in} was between 2.0 and 5.0.

3.1.3. Effect of Copper on Equilibrium pH

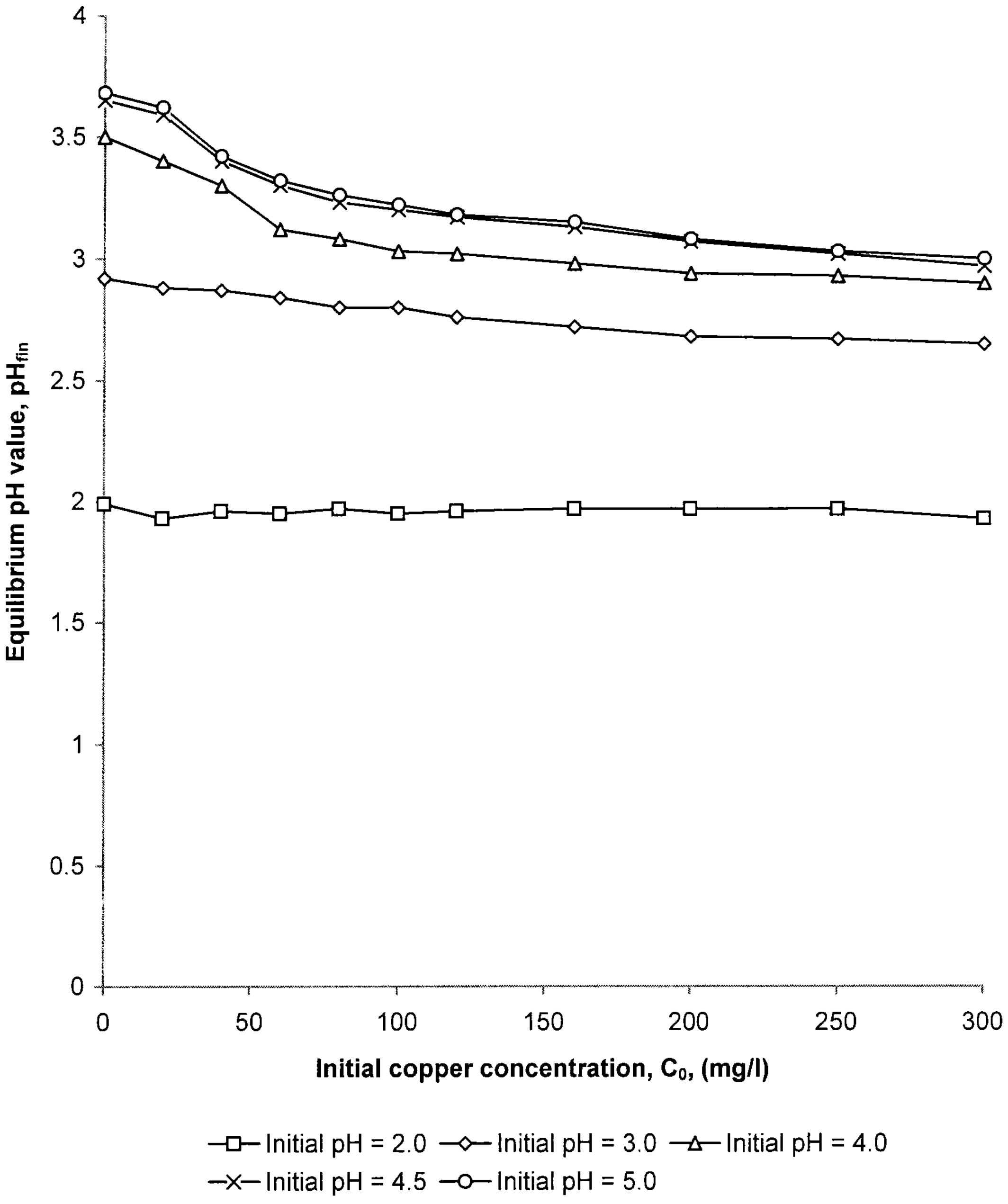
There are several possible explanations for the pH variations which occur when peat is mixed with metal cation solutions. That could be from the acidic group's properties: there are carboxylic and phenolic functional groups present in humic substances (Bloom and McBride, 1979; Boyd *et al.*, 1981) or ion exchange reactions, such as proton release when metal cations bind to peat (Bunzl *et al.*, 1976; Bloom and McBride, 1979; and Aho and Tummavuori, 1984).

Figure 3.1.3-1 shows that when the initial pH was between 4.0 and 5.0, as the initial copper concentration, C_0, increased, the equilibrium pH, pH_{fin}, decreased. However at lower pH values there was little or no effect. This suggests that as more copper ions are adsorbed onto the peat, more hydrogen ions are released from the peat into the solution, consequently decreasing the pH of the reaction mixture. According to Dissanayake and Weerasooria (1981), pH was found to have a marked effect on copper ion adsorption. Below pH 2-2.5, the adsorption of copper ions by peat was low. When the adsorption of copper ions was carried out at an initial pH of 2.0, the pH_{fin} were between 1.9 and 2.0 and adsorption density was much lower for all the concentrations tested in this work.

The values of pH_{fin} in the solution without copper are higher than those for the solution with copper and pH_{fin} decreased with increasing initial copper concentration. The effect at higher pH_{in} is greater than that at a lower pH_{in}, therefore, it can be concluded that the adsorption process includes ion exchange reactions.

Clearly the resulting equilibrium pH is governed by two major factors: the initial pH and the copper present in the solution initially when temperature and peat dose were fixed. This phenomenon can also be represented as a functional relationship of these two parameters, given by:

Figure 3.1.3-1: Equilibrium pH (pH_{fin}) at various initial copper concentrations (C_0) and pH.



$$pH_{fin} = f\left(pH_{in}, C_0^{-1}\right),$$

where

C_0 is initial copper concentration, (mg/l).

3.1.4. Copper Removal

The copper sorption capacity of various materials is shown in **Table 3.1.4-1**. A number of tests on adsorption of copper using peat have taken place. Thus the removal of Cu(II) by fly ash has been reported (Panday *et al.*, 1985). The removal decreases from 100 to 89.7% by increasing the Cu(II) concentration from 6.35 mg/l to 12.7 mg/l at pH 6.5, 30°C and fly ash dose of 20 g/l. In this work, the removal of Cu(II) by peat decreases from 91.3 to 21.6% by increasing the Cu(II) concentration from 20 mg/l to 300 mg/l at pH 5.0, 25°C and peat dose of 4.0 g/l. This current work also indicated that removal of Cu(II) by peat increased from 31.7 to 90.4% by increasing the peat dose from 4.0 g/l to 40 g/l. Thus the capacity of adsorption of Cu(II) by peat was higher than that of fly ash in these circumstances. A comparison of the Langmuir constants showed that the maximum adsorption capacity, X_m, for the copper-peat system is 16.4 mg/g at pH 5.0 and 25°C, 1.38 mg/g at pH 6.5 and 30°C for the copper-fly ash system. Copper interactions with anaerobically digested sludge have been reported by equilibrating sludge solids with solutions containing acetate salts of copper over a range of pH from 5.0 to 8.0 (Gould *et al.*, 1978). The Langmuir isotherm constant, X_m, was 49.0 mg/g for a competitive model, 28.2 mg/g for an uncompetitive model and 36.2 mg/g for a noncompetitive model. Various agricultural by-products such as treated bagasse, modified bark (acacia, laurel and techtona), rice hulls, and biomasses have also been investigated. Kumar and Dara (1982) found bagasse and modified barks are particularly effective in removing copper ions from solution. Suemitsu *et al.* (1986) pointed out that rice hulls, when coated with the reactive dyes Procion Red or Procion Yellow, were highly effective for removal of many metal ions from aqueous solution. Nagendra *et al.*

(1993) showed that three biomasses could remove copper from solution and alkali treatment could increase capacity of copper.

TABLE 3.1.4-1: Maximum Capacities for Adsorption of Copper by Different Adsorbents.

Capacity (mg/g)	X_m (mg/g)	Material	Reference
-	49.0	Anaerobically Digested Sludge	Gould and Genetelli (1978)
-	1.40	Kaolin Clay	Farrah *et al.* (1980)
-	2.54	Illite Clay	
-	23.3	Montmorillonite Clay	
4.44	-	Treated Bagasse	Kumar and Dara (1982)
3.46	-	Treated Acacia Bark	
3.08	-	Treated Laurel Bark	
3.69	-	Treated Techtona Bark	
1.53	-	Fly-Ash	Panday *et al.* (1985)
3.58	-	Rice Hulls	Suemitsu *et al.* (1986)
7.88	-	Dyestuff-Treated (Red) Rice Hulls	
7.00	-	Dyestuff-Treated (Yellow) Rice Hulls	
27.3	-	Tea Leaves	Tan and Abd. Rahman (1988)
-	14.0	Amorphous Iron Hydroxide	Mustafa and Haq (1988)
-	9.22	Activated Carbon	Ferro-García *et al.* (1988)
0.438	-	Chitin	Gonzalez-Davila and Millero (1990)
-	6.89	*Aspergillus oryzae*	Huang *et al.* (1991)
-	6.06	*Rhizopus oryzae*	
13.8	-	*Aspergillus oryzae*	Huang *et al.* (1991)
31.8	-	Treated *Aspergillus oryzae*	
35.7	-	Sludge Solid	Tien and Huang (1991)
42.9	-	*Chlorella vulgarise*	Aksu *et al.* (1992)
29.0	-	*Zoogloea ramigera*	
1.89	-	Oil-Palm Fibres	Low *et al.* (1993)
-	15.9	Dye-Treated Oil-Palm Fibre	
-	1.98	Natural Oil-Palm Fibre	
-	28.5	*G. lucidum*	Nagendra *et al.* (1993)
-	64.5	Treated *G. lucidum*	
-	10.1	Treated *A. niger*	
-	16.3	Treated Sludge	
22.2	-	Yeast Biomass	Brady *et al.* (1994)
25.4	-	Yeast Cell Walls	Brady and Duncan (1994)
-	13.5	Banana Pith	Low *et al.* (1995)
-	16.4	Sphagnum Moss Peat	This Work

Figure 3.1.4-1 demonstrates that copper ion adsorption by peat is pH dependent. The optimum pH range for copper adsorption was pH 4.0 to 5.0. Since the surface of peat contains acidic functional groups, the optimum pH range is likely to be under weakly acidic conditions. At pH 2.0, there is minimal copper removal, which may be due to the proton exclusion effect, and there is competition of H^+ for surface active sites which lead to minimum or negligible copper ion uptake at low pH, as the pH is increased from 2.0 to 5.0, the removal increases. However, increases above pH 4.0 produce less of an effect than was achieved among 2.0 and 4.0. This effect was most pronounced at low concentrations. The linear relationship with a correlation coefficients of 0.996 can be expressed as:

$$R = \frac{pH_{in} - \gamma}{\alpha + \beta \cdot (pH_{in} - \gamma)},$$

where

R is copper removal, (%);

α, β, and γ are characteristics of the copper removal/pH curve;

γ is the pH value when $R = 0$;

$1/\beta$ is defined as the plateau value of R, (%);

$1/\alpha$ is the tangent to the curve when $R = 0$.

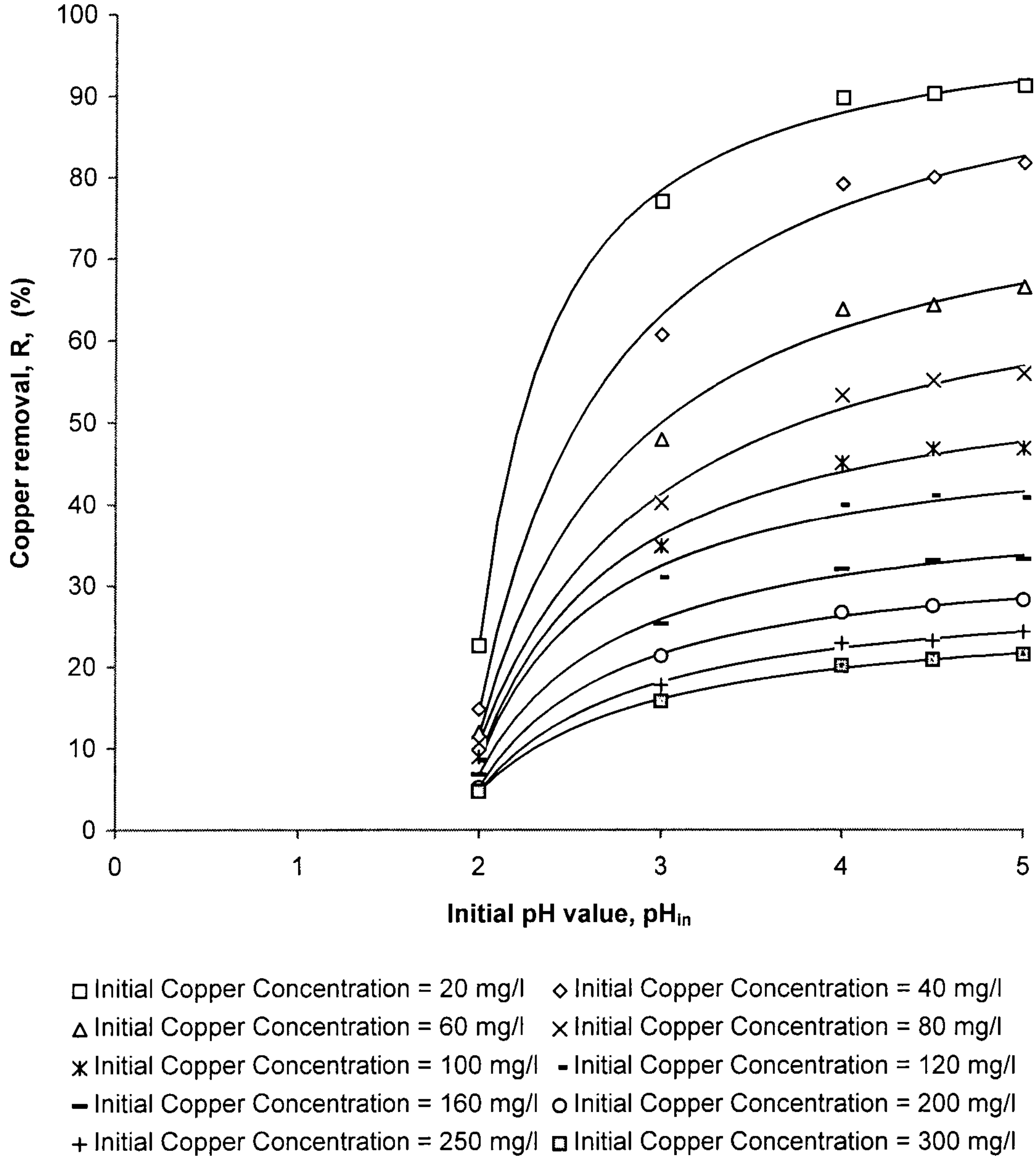
at $C_0 = 40$ mg/l,

$$R = \frac{pH_{in} - 1.89}{6.47 \times 10^{-3} + 1.00 \times 10^{-2}(pH_{in} - 1.89)};$$

at $C_0 = 60$ mg/l,

$$R = \frac{pH_{in} - 1.88}{8.83 \times 10^{-3} + 1.21 \times 10^{-2}(pH_{in} - 1.88)};$$

Figure 3.1.4-1: Effect of initial pH (pH_{in}) on copper removal (R) by peat at various initial copper concentrations.



at $C_0 = 80$ mg/l,

$$R = \frac{pH_{in} - 1.85}{1.20 \times 10^{-2} + 1.38 \times 10^{-2}\left(pH_{in} - 1.85\right)};$$

at $C_0 = 100$ mg/l,

$$R = \frac{pH_{in} - 1.88}{1.16 \times 10^{-2} + 1.73 \times 10^{-2}\left(pH_{in} - 1.88\right)};$$

at $C_0 = 120$ mg/l,

$$R = \frac{pH_{in} - 1.88}{1.19 \times 10^{-2} + 2.02 \times 10^{-2}\left(pH_{in} - 1.88\right)};$$

at $C_0 = 160$ mg/l,

$$R = \frac{pH_{in} - 1.87}{1.59 \times 10^{-2} + 2.45 \times 10^{-2}\left(pH_{in} - 1.87\right)};$$

at $C_0 = 200$ mg/l,

$$R = \frac{pH_{in} - 1.88}{1.95 \times 10^{-2} + 2.89 \times 10^{-2}\left(pH_{in} - 1.88\right)};$$

at $C_0 = 250$ mg/l,

$$R = \frac{pH_{in} - 1.86}{2.49 \times 10^{-2} + 3.31 \times 10^{-2}\left(pH_{in} - 1.86\right)};$$

at $C_0 = 300$ mg/l,

$$R = \frac{pH_{in} - 1.83}{2.99 \times 10^{-2} + 3.66 \times 10^{-2}(pH_{in} - 1.83)}.$$

The relationship between copper removal and the initial copper concentrations at different initial pH value is shown in **Figure 3.1.4-2**. A double logarithmic plot of the data showed that there were linear relationships with correlation coefficients of 0.980. These relationships can be expressed as:

at pH 2.0,

$$R = 1.50 \times 10^2 C_0^{-0.615}; \tag{3.1.4-1}$$

at pH 3.0,

$$R = 7.63 \times 10^2 C_0^{-0.675}; \tag{3.1.4-2}$$

at pH 4.0,

$$R = 1.10 \times 10^3 C_0^{-0.698}; \tag{3.1.4-3}$$

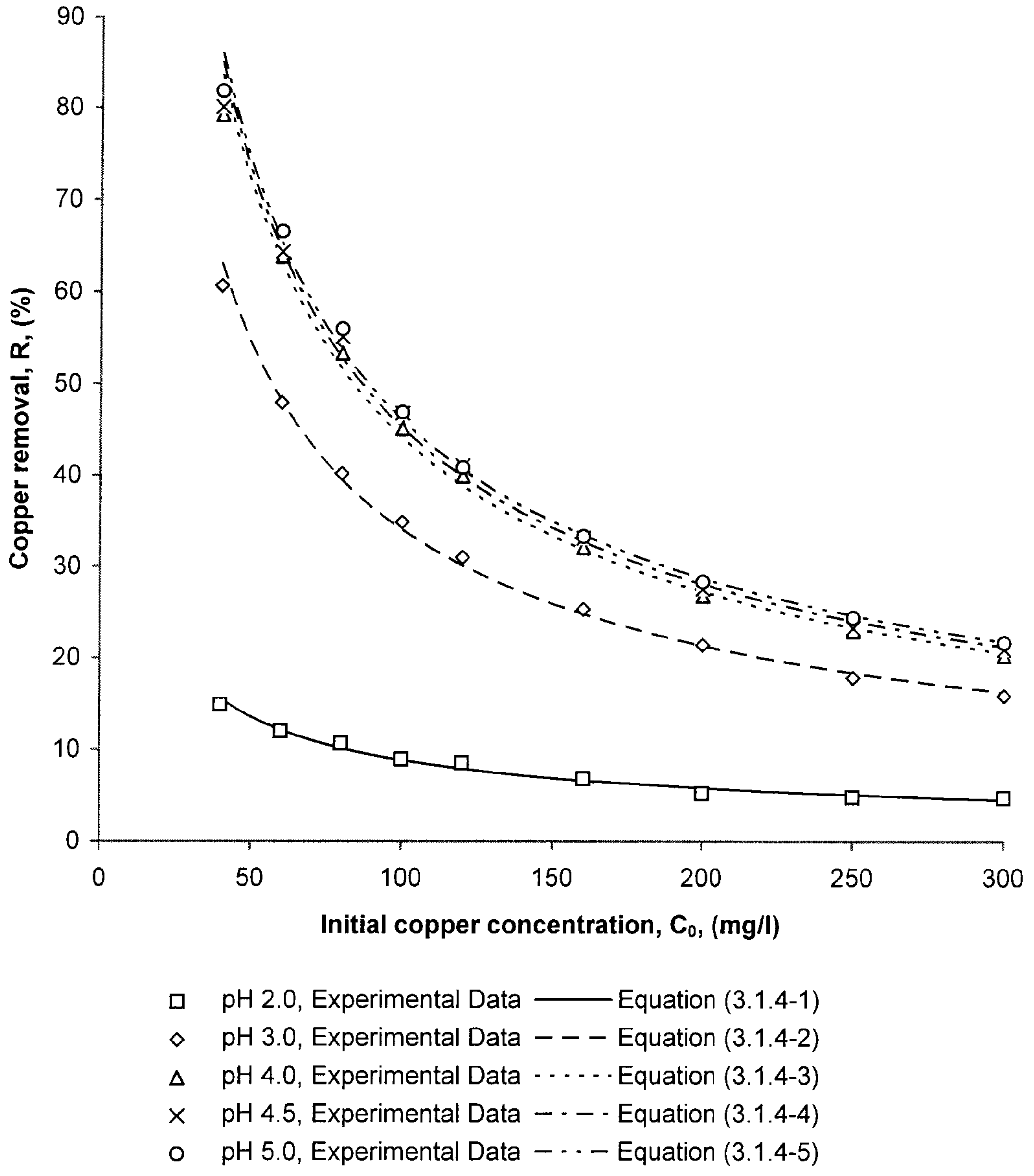
at pH 4.5,

$$R = 1.08 \times 10^3 C_0^{-0.690}; \tag{3.1.4-4}$$

at pH 5.0,

$$R = 1.07 \times 10^3 C_0^{-0.683}. \tag{3.1.4-5}$$

Figure 3.1.4-2: Effect of initial copper concentration (C_0) on copper removal (R) by peat at various initial pH (pH_{in}) values.



This means, therefore, that there is an inverse functional relationship which can be expressed, at any particular pH as:

$$R = b_1 \cdot C_0^{-b_2}.$$

The efficiency of copper removal by peat is controlled by the initial pH of the reaction mixture and the initial copper concentrations when temperature and peat dose were fixed. **Figure 3.1.4-2** demonstrates this effect and shows that the efficiency of copper removal increased with increasing pH_{in} and decreasing initial copper concentrations. The relationship between α, β, and γ, the initial copper concentrations, were linear with correlation coefficients of 0.981, 0.988, and 0.999. The relationship can be expressed as:

$$\alpha = 8.85 \times 10^{-5} C_0 + 3.15 \times 10^{-3},$$

$$\beta = 1.06 \times 10^{-4} C_0 + 6.36 \times 10^{-3},$$

$$\gamma = \frac{C_0}{5.44 \times 10^{-1} C_0 - 1.07}.$$

Substituting for α, β, and γ, R can be represented as:

$$R = \frac{5.44 \times 10^{-1} C_0 (pH_{in}) - 1.07 pH_{in} - C_0}{5.79 \times 10^{-5} C_0^2 (pH_{in}) + 3.35 \times 10^{-3} C_0 (pH_{in}) - 6.79 \times 10^{-3} pH_{in} - 6.00 \times 10^{-5} C_0^2 - 4.73 \times 10^{-3} C_0 - 3.37 \times 10^{-3}}.$$

where

R is the efficiency of copper removal, (%);

C_0 is the initial copper concentrations, (mg/l);

pH_{in} is the initial pH of the reaction mixture.

This equation can then be used to derive the percent copper removal at any given initial copper concentrations and the adjusted pH value. The three dimension plot of the equation is shown in **Figure 3.1.4-3**.

3.1.5. Effect of Peat Dose on Adsorption

The percentage of copper ion removal at equilibrium with various peat doses at 25°C, is presented in **Table 3.1.5-1**.

TABLE 3.1.5-1: Effect of Peat Dose on Adsorption Data: Initial Copper Ion Concentration, C_e; Percent Copper Ion Removal at Equilibrium, R_e; and Copper Ion Removal Capacity at Equilibrium, q_e; With Various Peat Doses at a Temperature of 25°C.

m_s (g/l)	C_e (mg/l)	R_e (%)	q_e (mg/g)	pH_{fin}
4	137	31.7	15.9	2.65
8	99.1	50.4	12.6	2.61
16	58.4	70.8	8.85	2.68
24	36.0	82.0	6.83	2.75
32	24.1	87.9	5.50	2.82
40	19.2	90.4	4.52	2.87

The effect of varying the peat dose, m_s, using an initial copper concentration of 200 mg/l is summarised in **Figure 3.1.5-1**. It can be seen that removal increases with increasing adsorbent doses for a given initial copper concentration (**Table 3.1.5-1**). This is to be expected because, for a fixed initial solute concentration, increasing adsorbent doses provide greater surface area (or adsorption sites). The data in **Table 3.1.5-1** can be used to derive a mathematical relationship (using the boundary conditions

Figure 3.1.4-3: Effect of initial copper concentration (C_0) on copper removal (R) by peat at various initial pH (pH_{in}) values.

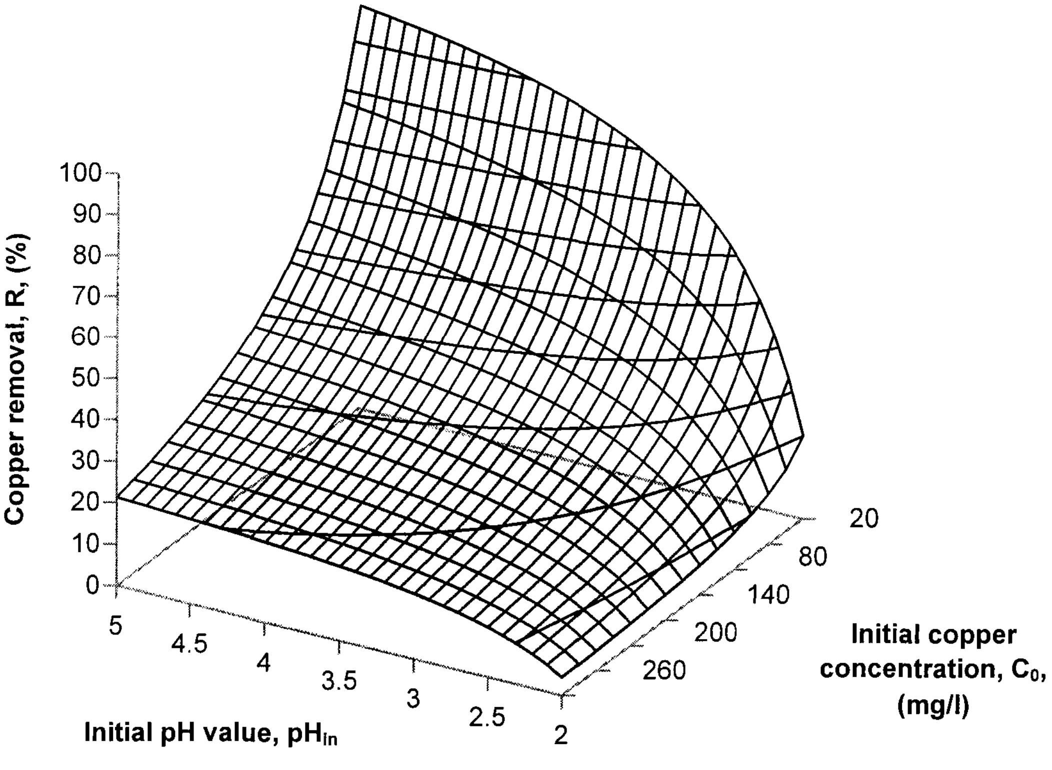
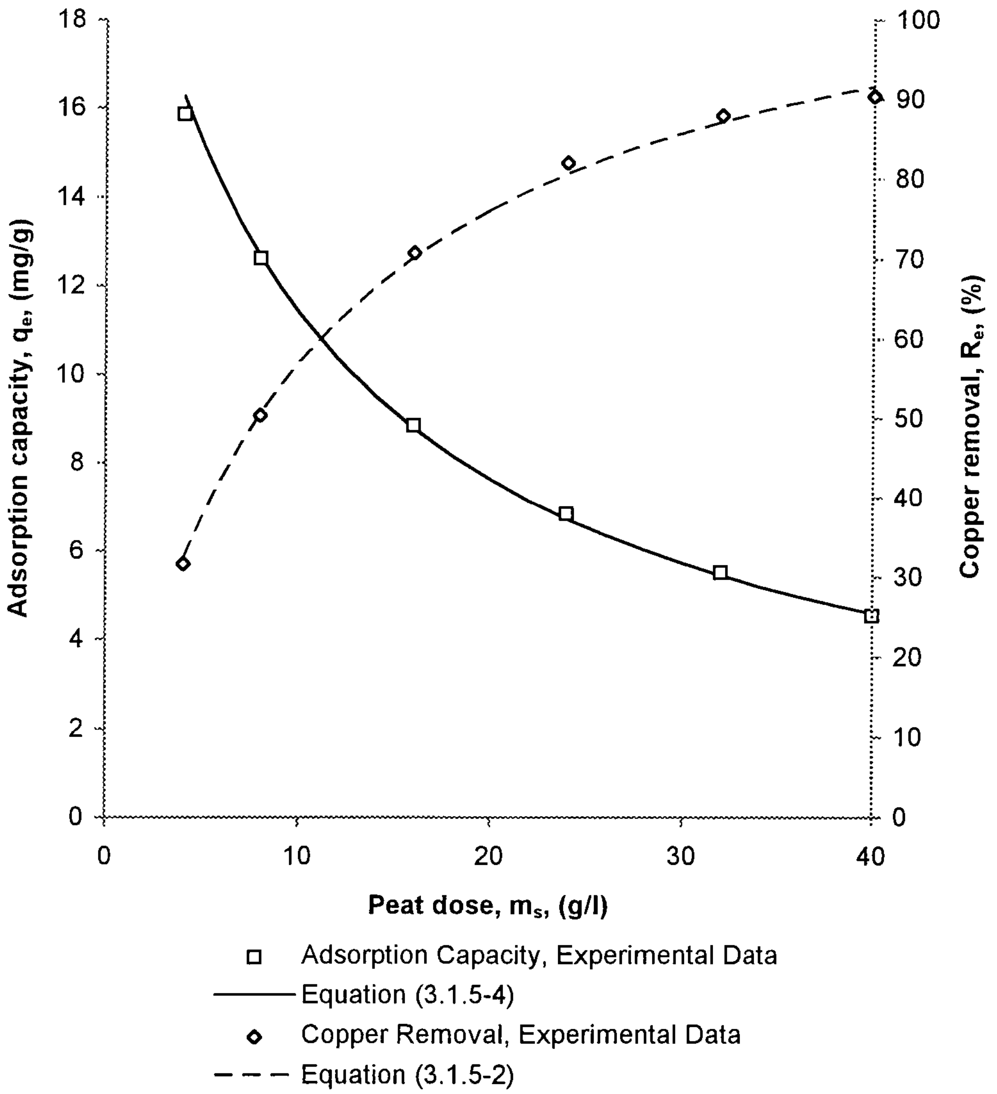


Figure 3.1.5-1: Copper removal (R_e) and adsorption capacity (q_e) of peat as a function of peat dose (m_s).



m_s = 4.0 to 40 g/l). The relationship, which has a correlation coefficient as high as 0.999 is:

$$R_e = \frac{m_s}{S_1 + \frac{m_s}{R_0}}, \tag{3.1.5-1}$$

and linear form

$$\frac{m_s}{R_e} = S_1 + \frac{1}{R_0} m_s .$$

where

R_e is the percentage of metal ion removal at equilibrium, (%);

m_s is the peat dose, (g/l);

R_0 is the maximum percentage of metal ion removal at equilibrium, (%), when peat dose is infinity;

$1/S_1$ is the tangent to the curve when $m_s = 0$, (%l/g).

A predictive model for the percent copper ion removal for any peat dose within the test limits at pH = 5.0 and initial copper concentration of 200 mg/l can be presented as:

$$R_e = \frac{m_s}{8.81 \times 10^{-2} + 8.72 \times 10^{-3} m_s} . \tag{3.1.5-2}$$

The adsorption capacity curve in **Figure 3.1.5-1** indicates that adsorption capacity decreased from 15.9 mg/g to 4.52 mg/g of peat when the doses were increased from 4.0 to 40 g/l. This leads to the conclusion that, in order to obtain the optimum peat dose, higher copper concentrations should be tested in conjunction with high doses. The relationship between adsorption capacity and peat dose had a high correlation coefficient of 0.999 and was of the form:

$$q_e = \frac{1}{\frac{1}{q_m} + S_2 \cdot m_s}, \qquad (3.1.5\text{-}3)$$

where

q_e is adsorption capacity, (mg/g);

m_s is peat dose, (g/l);

q_m is infinity adsorption capacity, (mg/g); when peat dose approach zero;

$-S_2/q_m^2$ is the tangent to the curve when $m_s = 0$, (g^2l/mg^3).

The resulting model is:

$$q_e = \frac{1}{4.40 \times 10^{-2} + 4.36 \times 10^{-3} m_s}, \qquad (3.1.5\text{-}4)$$

Also, **Figure 3.1.5-2** shows variation of C_e against m_s for C_0 = 200 mg/l, which indicates a relationship shown in equation **(3.1.5-5)**. The linearised (m_s/C_e) and (m_s) plot showed a correlation coefficient as high as 0.985 and the relationship between C_e and m_s is of the type:

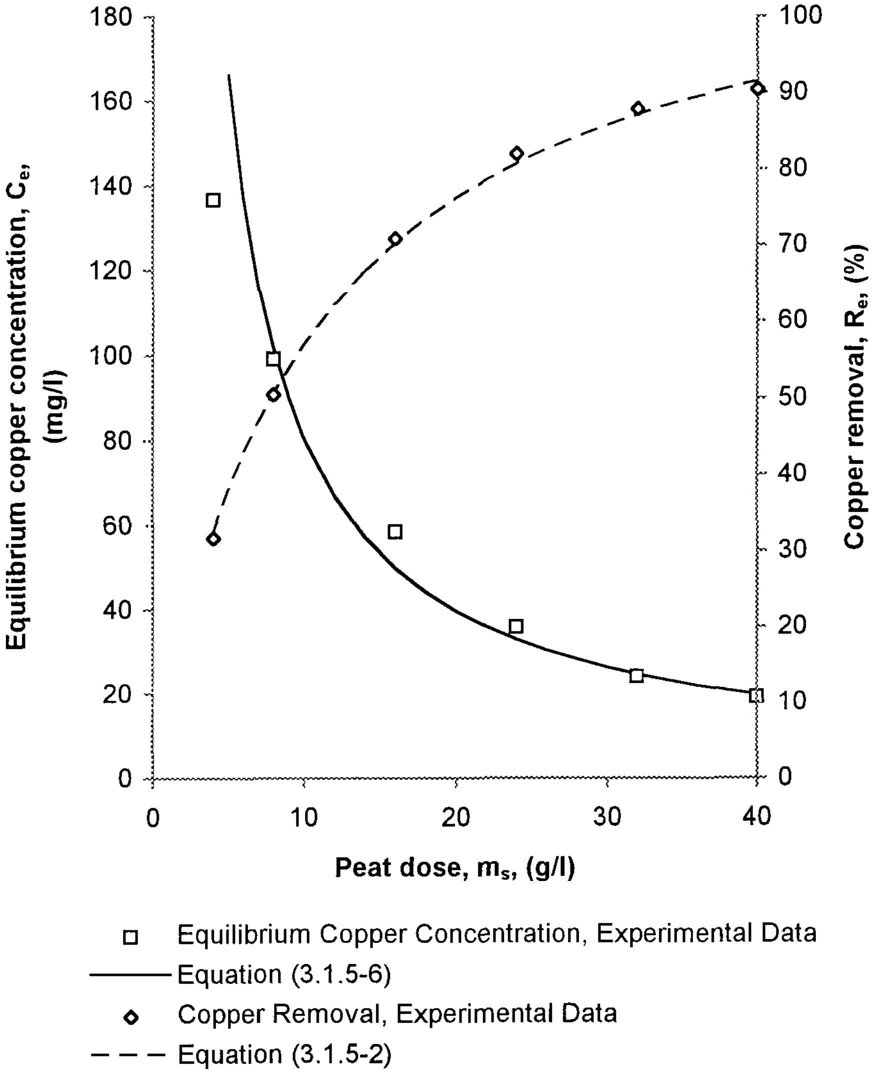
$$C_e = \frac{1}{A_1 + A_2 \cdot m_s}, \qquad (4.1.5\text{-}5)$$

where

A_1 and A_2 represent coefficients, (l/mg) and (l^2/mgg).

The values of A_1 and A_2 were found to be -3.60×10^{-4} l/mg and 1.28×10^{-3} l^2/mgg respectively; thus equation **(3.1.5-5)** can be written and rearranged as:

Figure 3.1.5-2: Equilibrium copper concentration (C_e) and copper removal (R_e) by peat as a function of peat dose (m_s).



$$C_e = \frac{1}{-3.60 \times 10^{-4} + 1.28 \times 10^{-3} m_s}. \qquad (3.1.5\text{-}6)$$

This equation can be used to predict the equilibrium copper concentration for any given value of C_0 (here 200 mg/l) and m_s (in the range 4.0 to 40 g/l) for observed test conditions at pH 5.0. High values for the correlation coefficient show the strength of this relationship. A similar empirical relationship can be obtained for various initial copper concentrations to demonstrate the dependence of constants A_1 and A_2 on C_0.

3.2. NICKEL

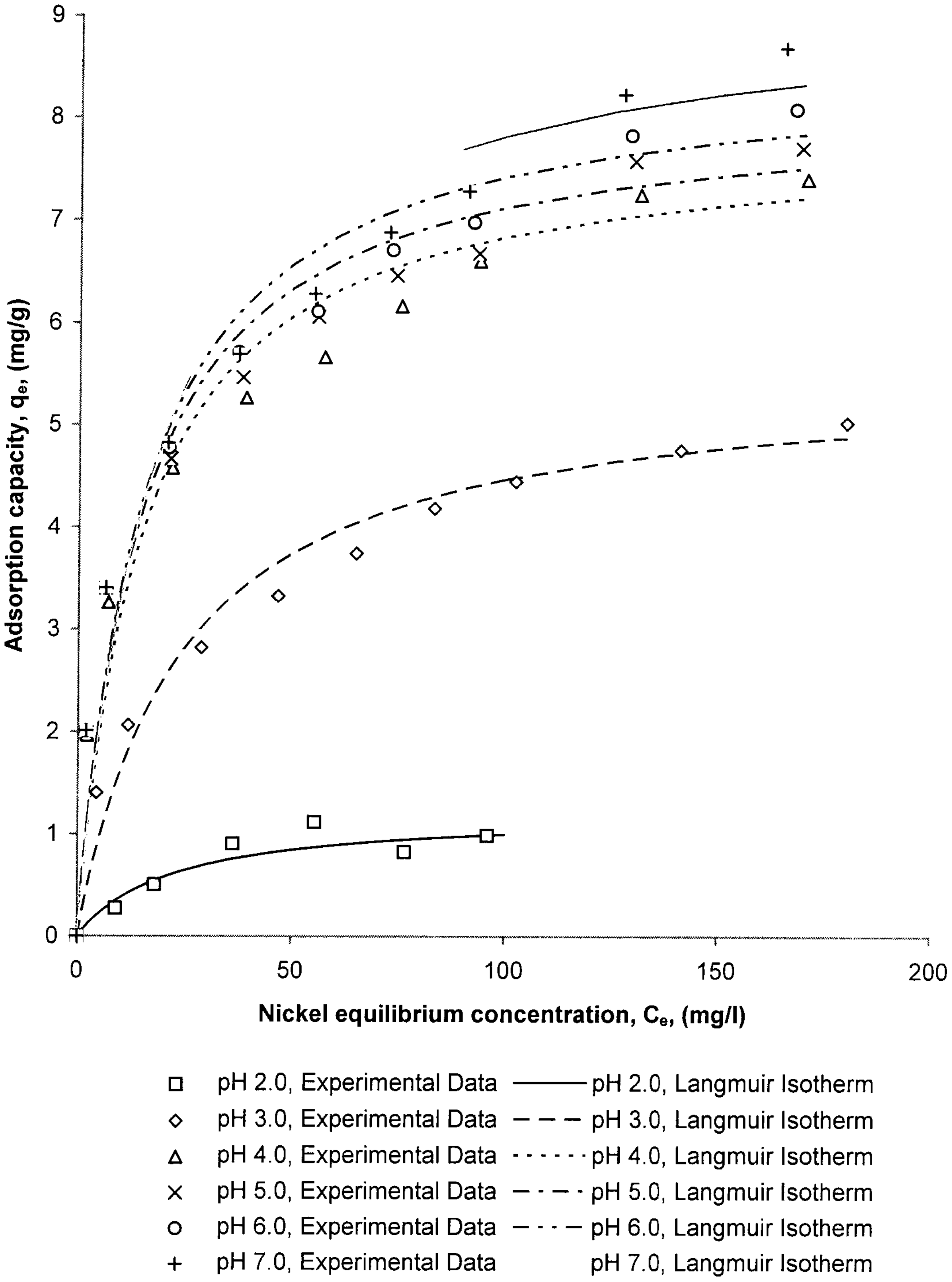
3.2.1. Adsorption Equilibria

Figure 3.2.1-1 shows typical isotherms for the nickel-peat system. It is generally seen that the adsorption capacity, q_e, increases gradually with increasing solution pH. The result shows that the adsorption capacity was very little increased at pH 2.0, whereas it was slightly more increased at pH 3.0. But the most increase was noticed over the range pH 4.0 to 7.0. At the lower concentration levels, the adsorption capacity was influenced to a far greater extent by variations in the nickel concentration than at the higher values for equilibrium concentration, where the curves were relatively flat.

3.2.2. Adsorption Isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. The adsorption data were analysed in terms of both the Langmuir and the Freundlich equations.

Figure 3.2.1-1: Typical isotherms for the nickel-peat system at various initial pH values.



Langmuir Isotherms

The adsorption of nickel ions was found to follow the Langmuir adsorption isotherm. Plots of the specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) are shown in **Figure 3.2.2-1**. These plotes of the linearised isotherms are seen to be indeed linear over the whole concentration range and the correlation coefficients were found to be between 0.895 and 0.991 **(Table 3.2.2-1)**. These fairly high values of correlation coefficients indicate that there is a strong positive relationship for the data for nickel-peat adsorption which clearly follows the Langmuir model.

The Langmuir constants are shown in **Table 3.2.2-1** and it can be seen that the maximum adsorption capacity, X_m, increases with increasing solution pH values. The higher values of adsorption capacity were found to be 7.84, 8.13, 8.52, and 9.18 mg/g of peat. These occurred at initial pH values of 4.0, 5.0, 6.0, and 7.0. When the pH was adjusted to 2.0, the adsorption capacity was reduced to a value as low as 1.23 mg/g.

TABLE 3.2.2-1: Adsorption Isotherm Constants of Nickel-Peat Binding.

	Langmuir Constants			Freundlich Constants		
pH_{in}	Corr. Coeff. r^2	X_m (mg/g)	100×k (l/mg)	Corr. Coeff. r^2	K_F (mg/g)	10×(1/n)
2.00	0.895	1.23	4.47	0.827	0.104	0.530
3.00	0.989	5.53	4.19	0.996	0.869	0.347
4.00	0.991	7.84	6.85	0.985	1.72	0.296
5.00	0.991	8.13	7.08	0.982	1.79	0.297
6.00	0.990	8.52	6.75	0.986	1.80	0.305
7.00	0.984	9.18	5.76	0.992	1.76	0.319

The variation of the Langmuir constant, X_m, with the initial pH is shown in **Figure 3.2.2-2** and the linear relationship with a correlation coefficient of 0.996 can be expressed as:

Figure 3.2.2-1: Linearised Langmuir isotherms at various initial pH values for the nickel-peat system.

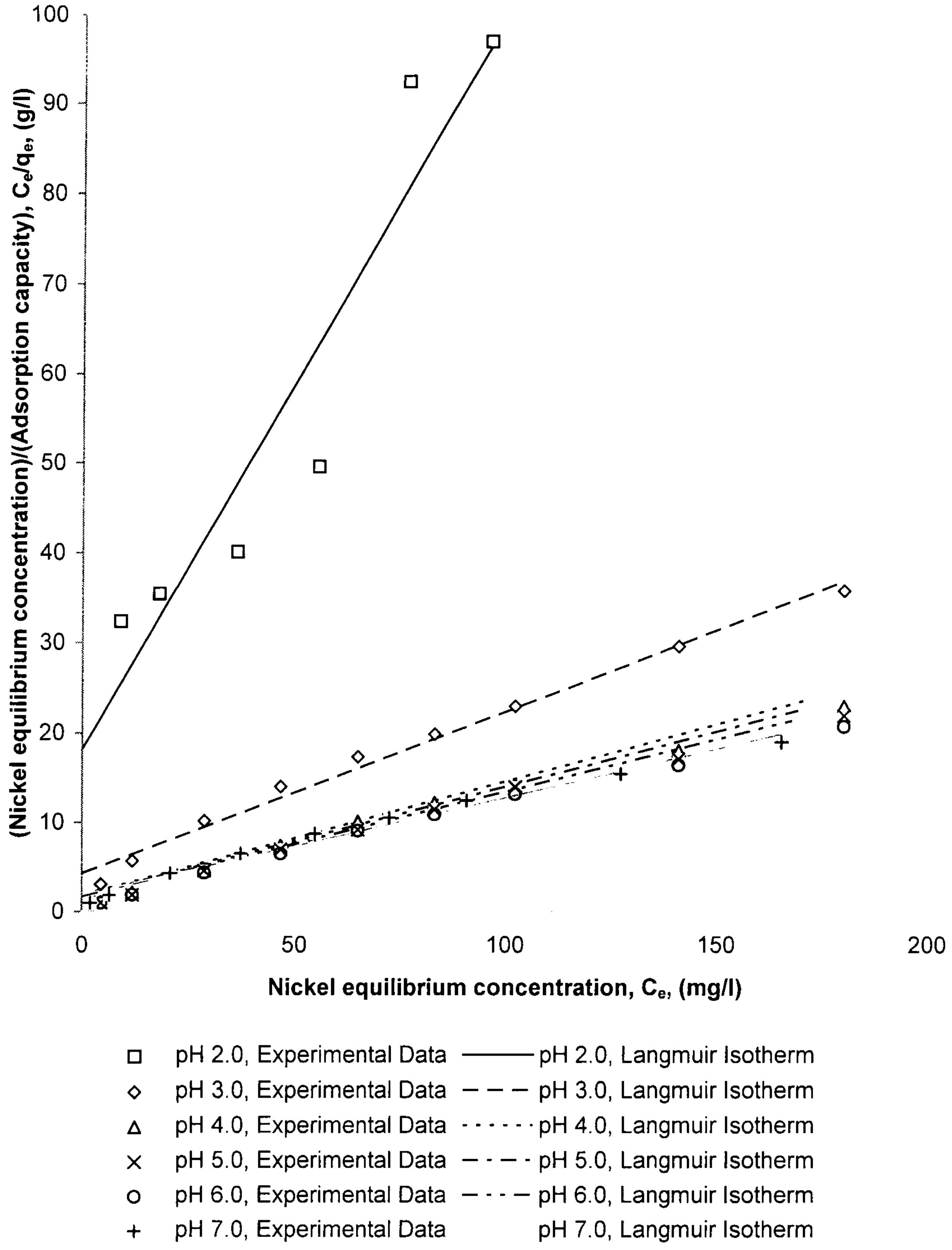
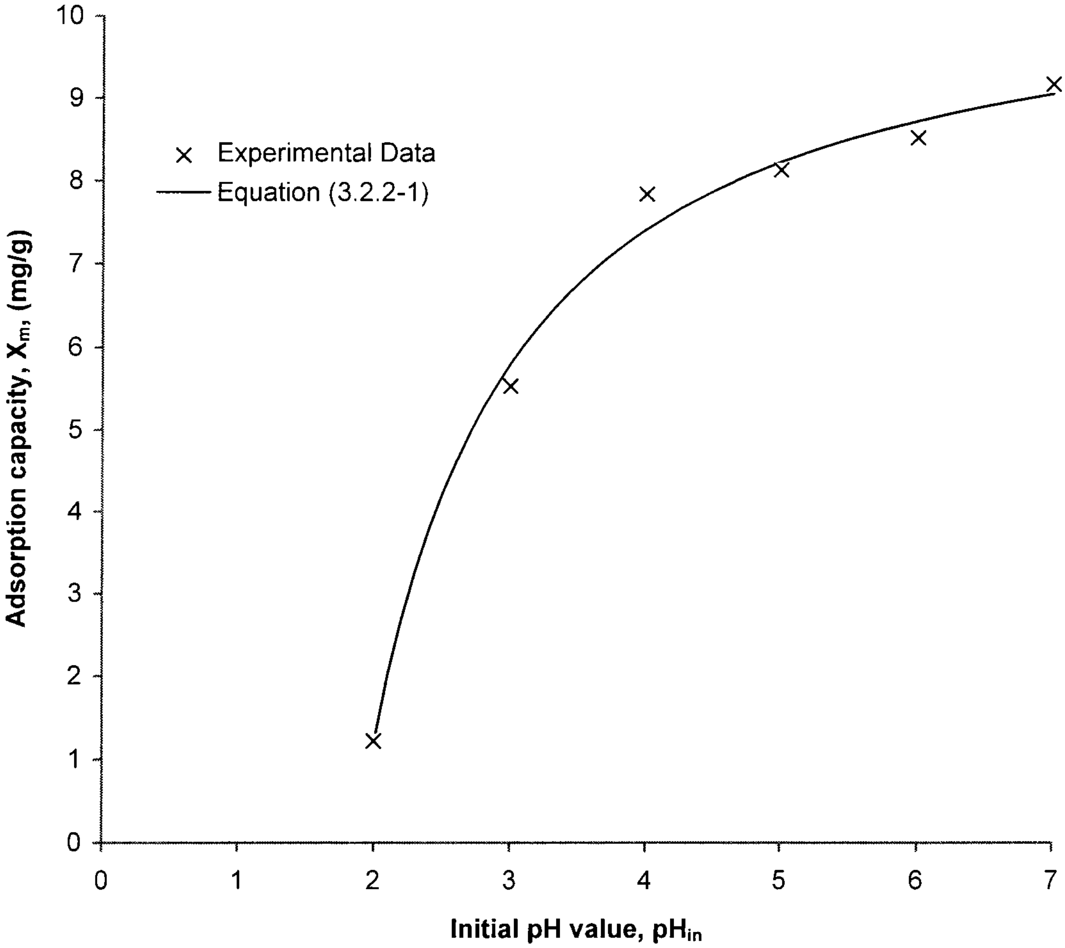


Figure 3.2.2-2: Variation of adsorption capacity (X_m) against initial pH (pH_{in}).



$$X_m = \frac{pH_{in} - 1.88}{8.89 \times 10^{-2} + 9.30 \times 10^{-2}(pH_{in} - 1.88)}. \qquad (3.2.2\text{-}1)$$

where

pH_{in}.is initial solution pH value which was between 2.0 to 7.0.

The Langmuir constant, k, which is a measure of adsorption energy, also increases with increasing solution pH values. Again, the higher values of the Langmuir constant k were found to be at initial pH 4.0, 5.0, 6.0 and 7.0. The variation of the Langmuir constant, k, against initial pH is shown in **Figure 3.2.2-3**.

In terms of Langmuir parameters the isotherms are given by the following equations:

$$q_e = \frac{C_e}{\frac{1}{X_m \cdot k} + \frac{1}{X_m} C_e},$$

at pH 2.0,

$$q_e = \frac{C_e}{1.82 \times 10 + 8.15 \times 10^{-1} C_e};$$

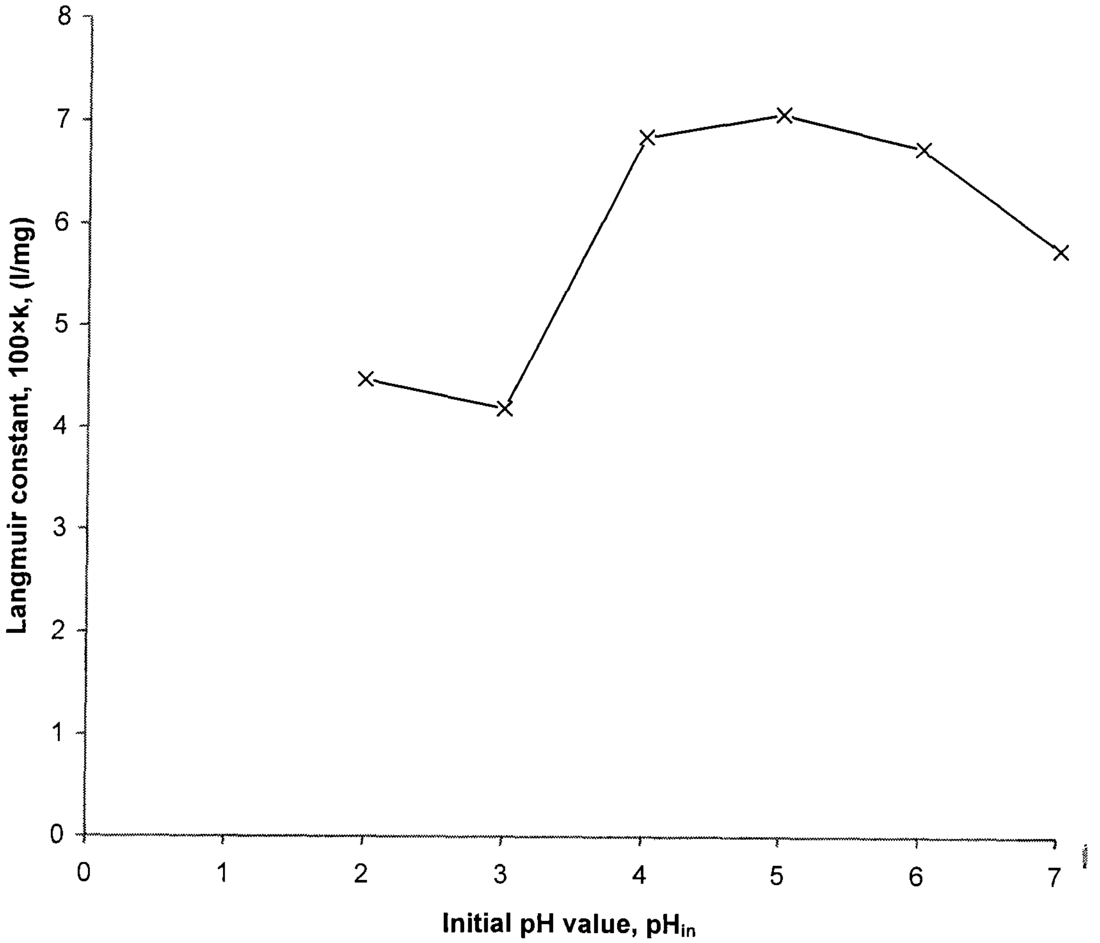
at pH 3.0,

$$q_e = \frac{C_e}{4.31 + 1.81 \times 10^{-1} C_e};$$

at pH 4.0,

$$q_e = \frac{C_e}{1.86 + 1.28 \times 10^{-1} C_e};$$

Figure 3.2.2-3: Variation of Langmuir constant (k) for nickel-system against initial pH (pH_{in}).



at pH 5.0,

$$q_e = \frac{C_e}{1.74 + 1.23 \times 10^{-1} C_e};$$

at pH 6.0,

$$q_e = \frac{C_e}{1.74 + 1.17 \times 10^{-1} C_e};$$

at pH 7.0,

$$q_e = \frac{C_e}{1.89 + 1.09 \times 10^{-1} C_e}.$$

Freundlich Isotherms

The adsorption data have also been used to calculate the ultimate sorption capacity of peat by substituting the required equilibrium concentrations in the Freundlich equation. When the data were linearised **(Figure 3.2.2-4)** the correlation coefficients were found to vary between 0.827 and 0.996 **(Table 3.2.2-1)**.

The Freundlich constant, 1/n, **(Table 3.2.2-1)**, which is a measure of the adsorption intensity, decreased from 0.530 to a value of 0.296 with increasing solution pH_{in} values, when the pH_{in} was 2.0 to 4.0. Similar values of the Freundlich constant, 1/n, were found at initial adjusted pH values of 4.0, 5.0, 6.0, and 7.0; 0.296, 0.297, 0.305, and 0.319. The Freundlich constant, K_F, **(Table 3.2.2-1)**, which is a measure of adsorption capacity, showed similar values, namely 1.72, 1.79, 1.80, and 1.76 at pH_{in} 4.0, 5.0, 6.0, and 7.0, but at pH_{in} 2.0 and 3.0, values were lower at 0.104 and 0.869. From the Freundlich constant 1/n, the adsorption intensity of nickel seems stronger than copper. Gosset *et al.* (1986) have reported that the nickel cation is able to bind to peat strongly in solution. There is much complexing at pH 1.2-2. The variation of the Freundlich constant, 1/n, against initial pH in our work is shown in **Figure 3.2.2-5**.

Figure 3.2.2-4: Linearised Freundlich isotherms at various initial pH values for the nickel-peat system.

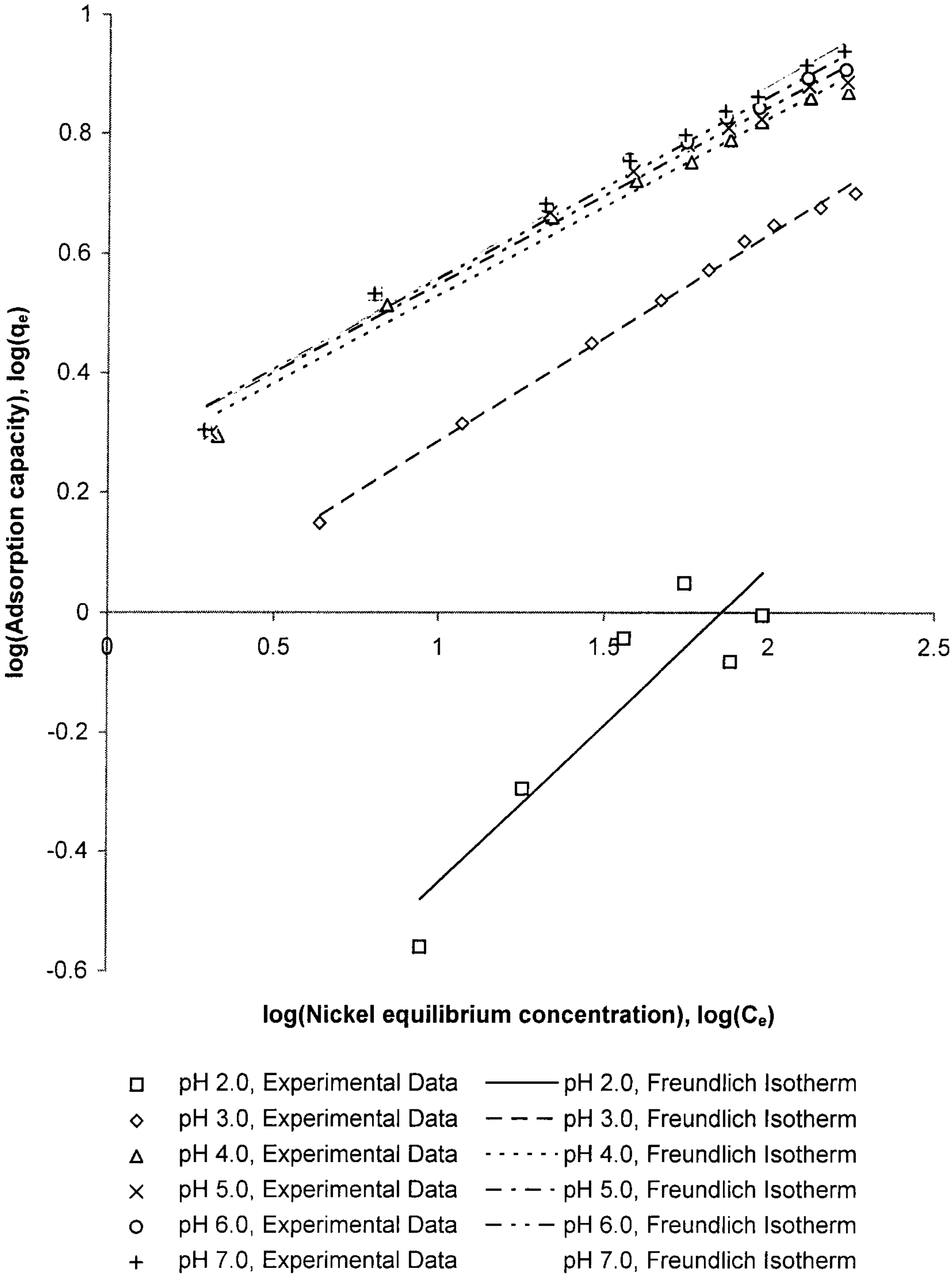
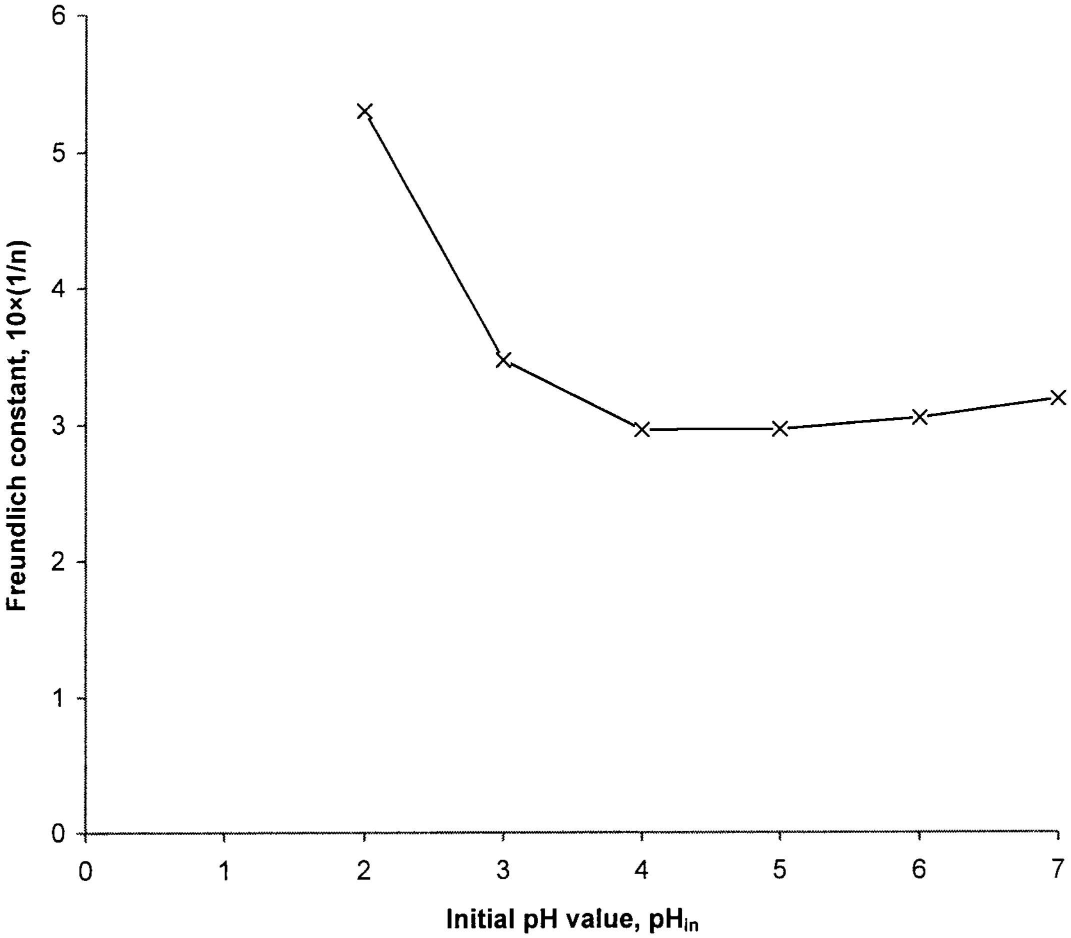


Figure 3.2.2-5: Variation of Freundlich constant (1/n) with initial pH (pH_{in}) for the nickel-peat system.



The Freundlich constant, K_F, a measure of adsorption capacity, increased with increasing solution pH values. The highest adsorption capacity of copper was 1.80 mg/g of peat at pH 6.0. Both Langmuir and Freundlich constants showed the same increasing trend with increasing solution pH values. The variation of the Freundlich constant against initial pH is shown in **Figure 3.2.2-6**, and shows a linear relationship with a correlation coefficient of 0.960 which can be expressed as:

$$K_F = \frac{pH_{in} - 1.96}{4.31 \times 10^{-1} + 4.59 \times 10^{-1}(pH_{in} - 1.96)}, \qquad (3.2.2\text{-}2)$$

where

pH_{in}.was between 2.0 to 7.0.

3.2.3. Effect of Nickel on Equilibrium pH

Figure 3.2.3-1 shows that as the initial nickel concentration increases, the resultant equilibrium pH is decreased. An initial nickel concentration of 200 mg/l is able to cause a decrease of pH levels to 1.89, 2.84, 3.24, 3.29, 3.29, and 3.30 units from pH_{in} values of 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 respectively. Equilibrium pH values initially fell with increasing nickel content, but only at relatively low nickel concentrations. Thereafter, they remained roughly constant. It is, therefore, concluded that as more nickel ions are adsorbed onto the peat, more hydrogen ions are released from the peat into the solution, consequently decreasing the pH of the reaction mixture. When pH_{in} was 2.0 the nickel adsorption capacity, q_e, was found to be lower than 1 mg/g for most initial concentrations. In this region, for nickel, the linearised Freundlich isotherm was negative, because of the low adsorption capacity.

There are two sources to increase hydrogen ion concentration in the process of adsorption. Peat specimens possess acidic groups such as carboxylic, phenolic, and enolic. Such groups are believed to be responsible for the cation exchange capacity,

Figure 3.2.2-6: Variation of Freundlich constant (K_F) with initial pH (pH_{in}) for the nickel-peat system.

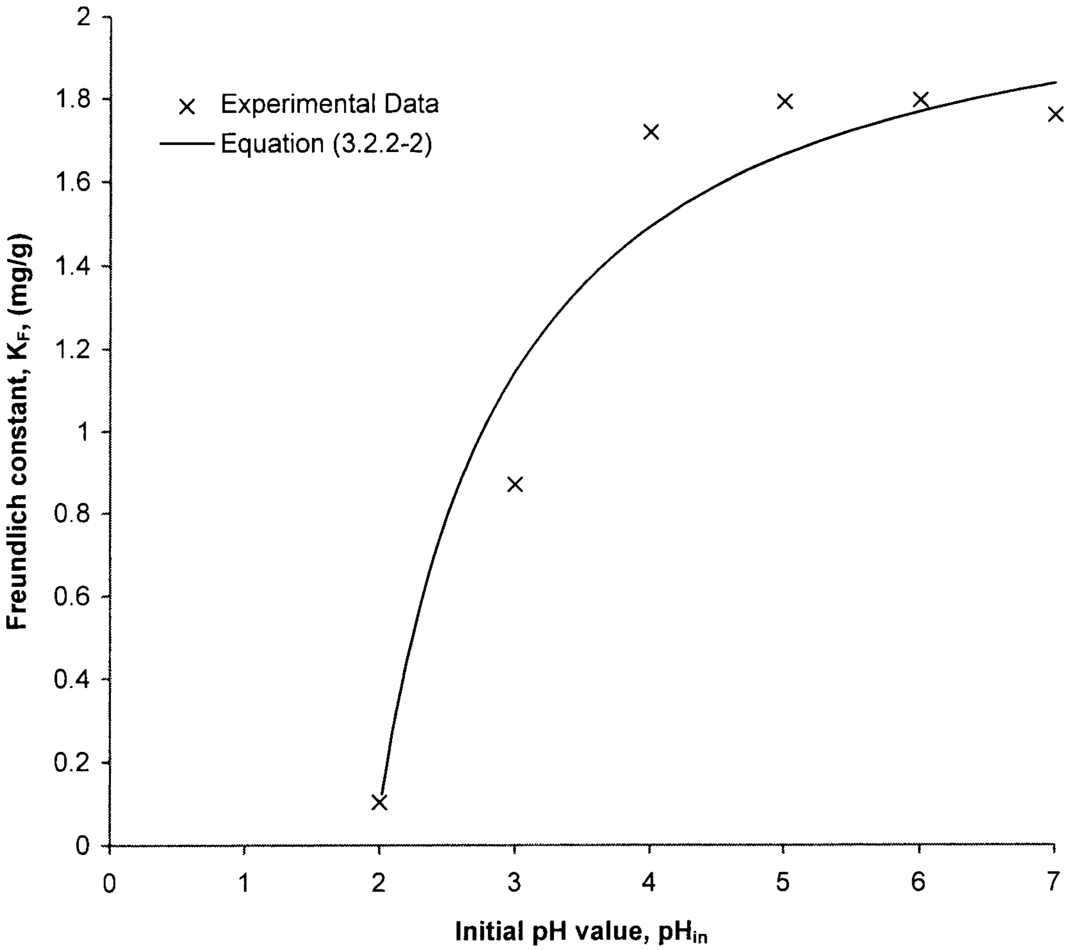
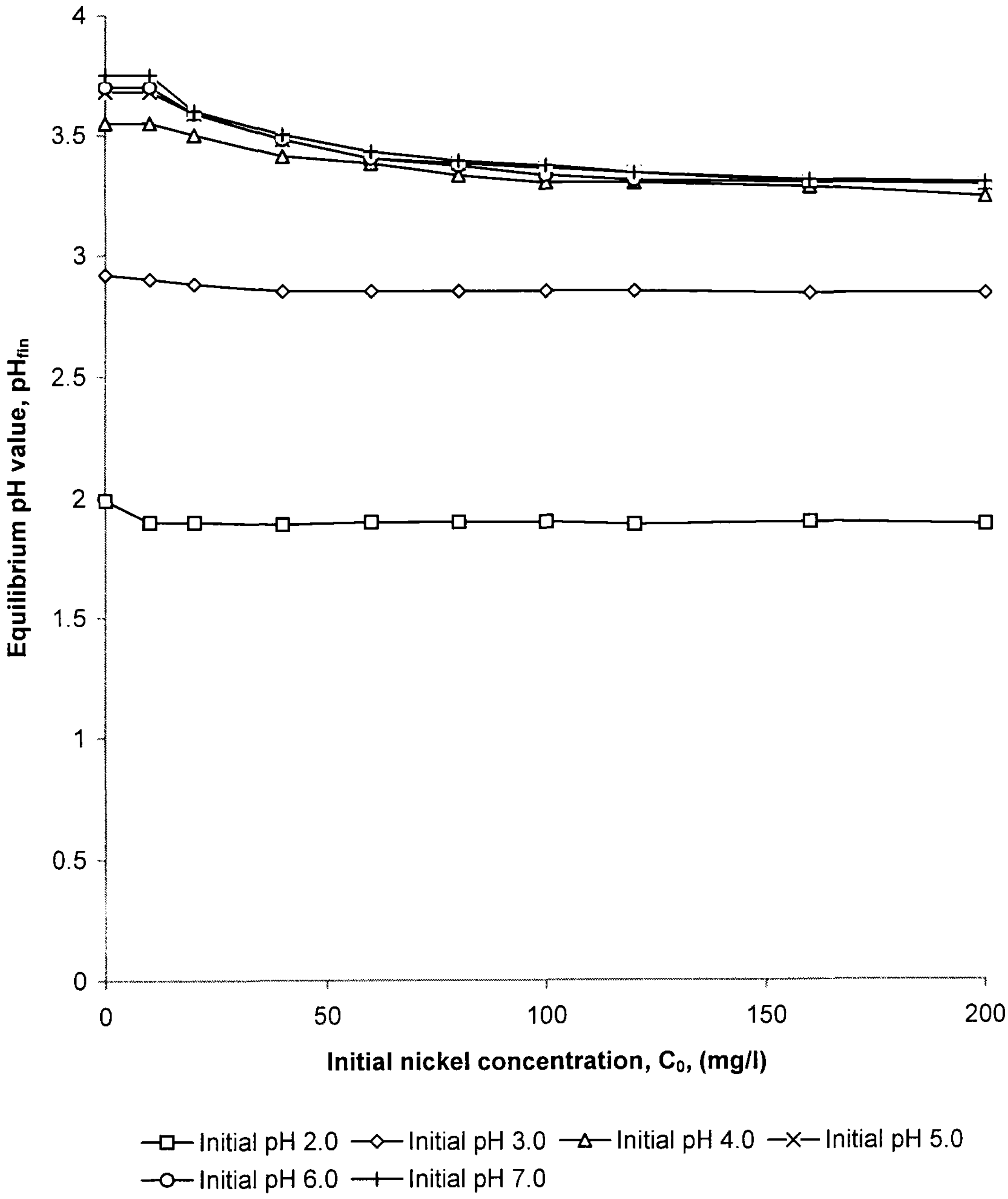


Figure 3.2.3-1: Equilibrium pH (pH_{fin}) at various initial nickel concentrations (C_0) and pH.



which generally lies between 2 and 3 milliequivalents per gram (Broadbent and Bradford, 1952). The intrinsic ionisation constant for the carboxylic groups appears to be about 10^{-5} (Dawson and Danielson, 1950), and these are the only acidic groups thought to be ionised to an appreciable extent at a pH of 7.0 and below. pH of the solution decreased in a solution where C_0 = 0 mg/l and pH of the solution decreased with increasing initial metal ion concentration **(Table 3.2.3-1)**.

Hydrogen ion concentration was increased by ion exchange during the adsorption process. It can be calculated from pH_0 and pH_{200} as follows:

$$\left[H^+\right] = 10^{-pH_{200}} - 10^{-pH_0},$$

where

pH_0 is pH of solution at equilibrium for C_0 = 0 mg/l;

pH_{200} is pH of solution at equilibrium for C_0 = 200 mg/l.

Hydrogen ion concentration increased from the intrinsic ionisation constant for the carboxylic groups of peat. It can be evaluated from pH_{in} and pH_0 as follows:

$$\left[H^+\right] = 10^{-pH_0} - 10^{-pH_{in}},$$

where

pH_{in} is initial pH of solution;

pH_0 is pH of solution at equilibrium for C_0 = 0, (mg/l).

Table 3.2.3-1 shows that the pH of the solution decreased when C_0 = 0 mg/l and that as the initial metal ion concentration is increased, the decrease in pH becomes correspondingly greater and greater. The ion exchange capacity was calculated to be about 0.3 milliequivalents per gram peat, and the intrinsic ionisation was evaluated to be about 0.2 milliequivalents per gram peat.

TABLE 3.2.3-1: Hydrogen Ion Milliequivalent per Gram Peat for Different Initial pH.

pH_{in}	pH_0 (C_0 = 0 mg/l)	Ionisation H^+, (meq/g)	pH_{200} (C_0 = 200 mg/l)	Ion Exchange H^+, (meq/g)
2.00	1.99	0.23	1.89	2.6
3.00	2.92	0.20	2.84	0.24
4.00	3.55	0.18	3.24	0.29
5.00	3.68	0.20	3.29	0.30
6.00	3.70	0.20	3.29	0.31
7.00	3.75	0.18	3.30	0.32

3.2.4. Nickel Removal

The process of removal of nickel by adsorption has been studied on various adsorbents (**Table 3.2.4-1**).

The efficiency of nickel removal by peat is controlled by the initial pH of the reaction mixture. **Figure 3.2.4-1** demonstrates this effect and shows that the removal is favoured both by higher pH values and lower nickel concentrations present initially. The percent increase in the removal efficiency with pH_{in} was noticed in the range pH 2.0 to 4.0. However, when the pH of the reaction mixture was set between 4.0 and 7.0, the efficiency of removal showed rather a slow increase. It is revealing that 80.6% Ni(II) removal was achieved when nickel concentrations down to 10 mg/l were treated at pH 7.0. Above this concentration at pH 7.0, the percent removal decreased with increasing initial nickel ion concentration. The maximum removal for 200 mg/l at pH 7.0, was found to be only 17.4%. On the other hand, approximately 11% removal was achieved when 10 mg/l of nickel was treated at pH 2.0. The linear relationship with a correlation coefficient of 0.987 can be expressed as:

Figure 3.2.4-1: Effect of initial pH (pH_{in}) on nickel removal (R) by peat at various initial nickel concentrations.

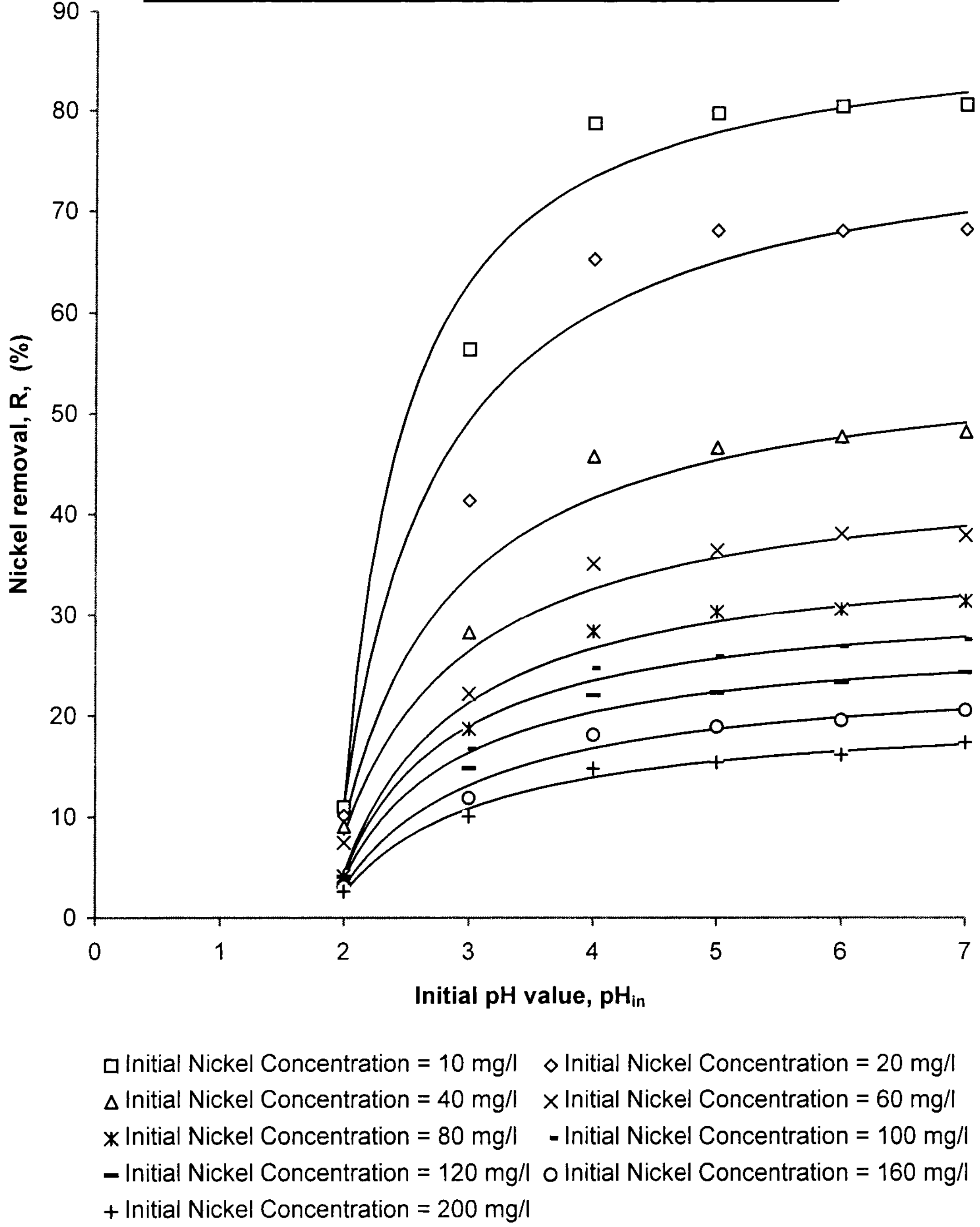


TABLE 3.2.4-1: Maximum Capacities for Adsorption of Nickel.

Capacity (mg/g)	X_m (mg/g)	Material	Reference
-	7.66	Anaerobically Digested Sludge	Gould and Genetelli (1978)
-	3.40	δ-Manganese Dioxide	Gray and Malati (1979)
2.40	-	Peat (Rastunsuo)	Tummavuori and Aho (1980)
7.45	-	Treated Bagasse	Kumar and Dara (1982)
3.4	-	Treated Acacia Bark	
4.2	-	Treated Laurel Bark	
3.5	-	Treated Techtona Bark	
11.2	-	Eutrophnic Peat	Gosset *et. al.* (1986)
11.7	-	Oligotrophic Peat	
5.58	-	Rice Hulls	Suemitsu *et al.* (1986)
6.16	-	Dyestuff-Treated (Red) Rice Hulls	
6.08	-	Dyestuff-Treated (Yellow) Rice Hulls	
23.0	-	Sphagnum Moss Peat	McLellan and Rock (1988)
-	6.75	Amorphous Iron Hydroxide	Mustafa and Haq (1988)
5.22	-	*Aspergillus oryzae*	Huang *et al.* (1991)
12.4	-	Treated *Aspergillus oryzae*	
40.8	-	Sludge Solid	Tien and Huang (1991)
-	3.46	China Clay	Sharma *et al.* (1991)
0.672	-	Sphagnum Peat	Viraraghavan and Dronamraju (1993)
0.5	-	Oil-Palm Fibres	Low *et al.* (1993)
6.46	-	Yeast Biomass	Brady *et al.* (1994)
-	9.18	Sphagnum Moss Peat	This Work

$$R = \frac{pH_{in} - \gamma}{\alpha + \beta \cdot (pH_{in} - \gamma)},$$

at $C_0 = 10$ mg/l,

$$R = \frac{pH_{in} - 1.94}{4.87 \times 10^{-3} + 1.13 \times 10^{-2}(pH_{in} - 1.94)};$$

at $C_0 = 20$ mg/l,

$$R=\frac{pH_{in}-1.91}{8.43\times10^{-3}+1.27\times10^{-2}\left(pH_{in}-1.91\right)};$$

at C_0 = 40 mg/l,

$$R=\frac{pH_{in}-1.87}{1.36\times10^{-2}+1.77\times10^{-2}\left(pH_{in}-1.87\right)};$$

at C_0 = 60 mg/l,

$$R=\frac{pH_{in}-1.85}{1.87\times10^{-2}+2.21\times10^{-2}\left(pH_{in}-1.85\right)};$$

at C_0 = 80 mg/l,

$$R=\frac{pH_{in}-1.90}{2.21\times10^{-2}+2.70\times10^{-2}\left(pH_{in}-1.90\right)};$$

at C_0 = 100 mg/l,

$$R=\frac{pH_{in}-1.89}{2.40\times10^{-2}+3.13\times10^{-2}\left(pH_{in}-1.89\right)};$$

at C_0 = 120 mg/l,

$$R=\frac{pH_{in}-1.87}{2.88\times10^{-2}+3.56\times10^{-2}\left(pH_{in}-1.87\right)};$$

at C_0 = 160 mg/l,

$$R=\frac{pH_{in}-1.86}{4.04\times10^{-2}+4.06\times10^{-2}\left(pH_{in}-1.86\right)};$$

at $C_0 = 200$ mg/l,

$$R = \frac{pH_{in} - 1.86}{499 \times 10^{-2} + 485 \times 10^{-2}(pH_{in} - 1.86)}.$$

Nickel removal against the variation of the initial nickel concentrations at various initial pH values is shown in **Figure 3.2.4-2**. A double logarithmic plot of the data showed a linear relationship with correlation coefficients of 0.881, 0.994, 0.979, 0.976, 0.976, and 0.981 when the pH_{in} values were 2.0 to 7.0. These relationships can be expressed as:

at pH 2.0,

$$R = 4.57 \times 10 C_0^{-0.515}; \qquad (3.2.4\text{-}1)$$

at pH 3.0,

$$R = 2.25 \times 10^2 C_0^{-0.573}; \qquad (3.2.4\text{-}2)$$

at pH 4.0,

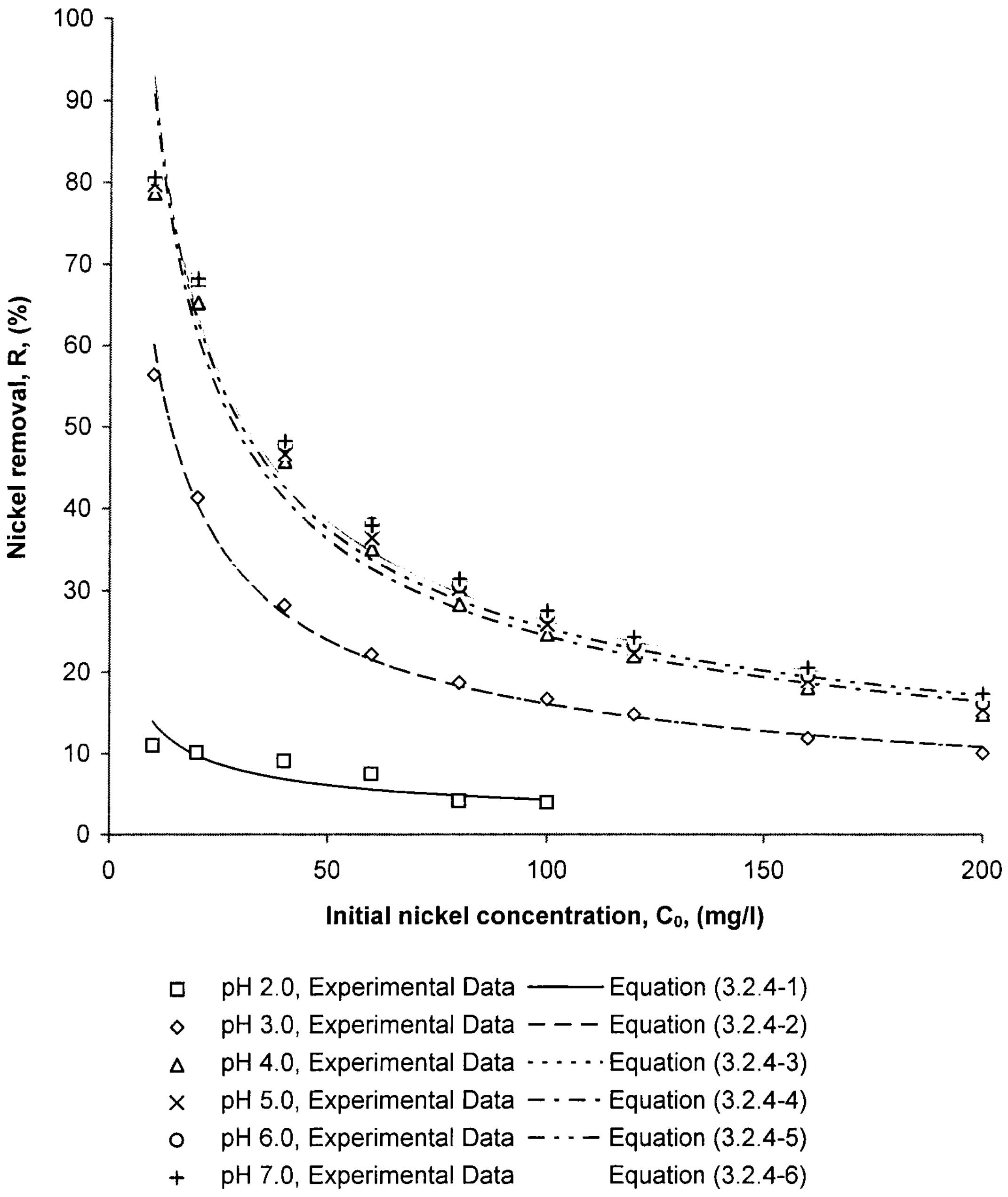
$$R = 3.38 \times 10^2 C_0^{-0.571}; \qquad (3.2.4\text{-}3)$$

at pH 5.0,

$$R = 3.41 \times 10^2 C_0^{-0.564}; \qquad (3.2.4\text{-}4)$$

at pH 6.0,

Figure 3.2.4-2: Effect of initial nickel concentration (C_0) on nickel removal (R) by peat at various initial pH values.



$$R = 3.31 \times 10^{2} C_{0}^{-0.550}; \qquad (3.2.4\text{-}5)$$

at pH 7.0,

$$R = 3.11 \times 10^{2} C_{0}^{-0.529}; \qquad (3.2.4\text{-}6)$$

This means, therefore, that there is an inverse functional relationship which can be expressed at any particular pH as:

$$R = b_{1} \cdot C_{0}^{-b_{2}}.$$

The efficiency of nickel removal by peat is controlled by the initial pH of the reaction mixture and the initial nickel concentrations. **Figure 3.2.4-3** demonstrates this effect and shows that the efficiency of nickel removal is increased with increasing $\mathrm{pH_{in}}$ and decreasing initial nickel concentrations. The relationship between α, β, and γ and the initial nickel concentrations had correlation coefficients of 0.992, 0.991 and 0.999. The relationship can be expressed as:

$$\alpha = 8.67 \times 10^{-4} C_{0}^{0.746},$$

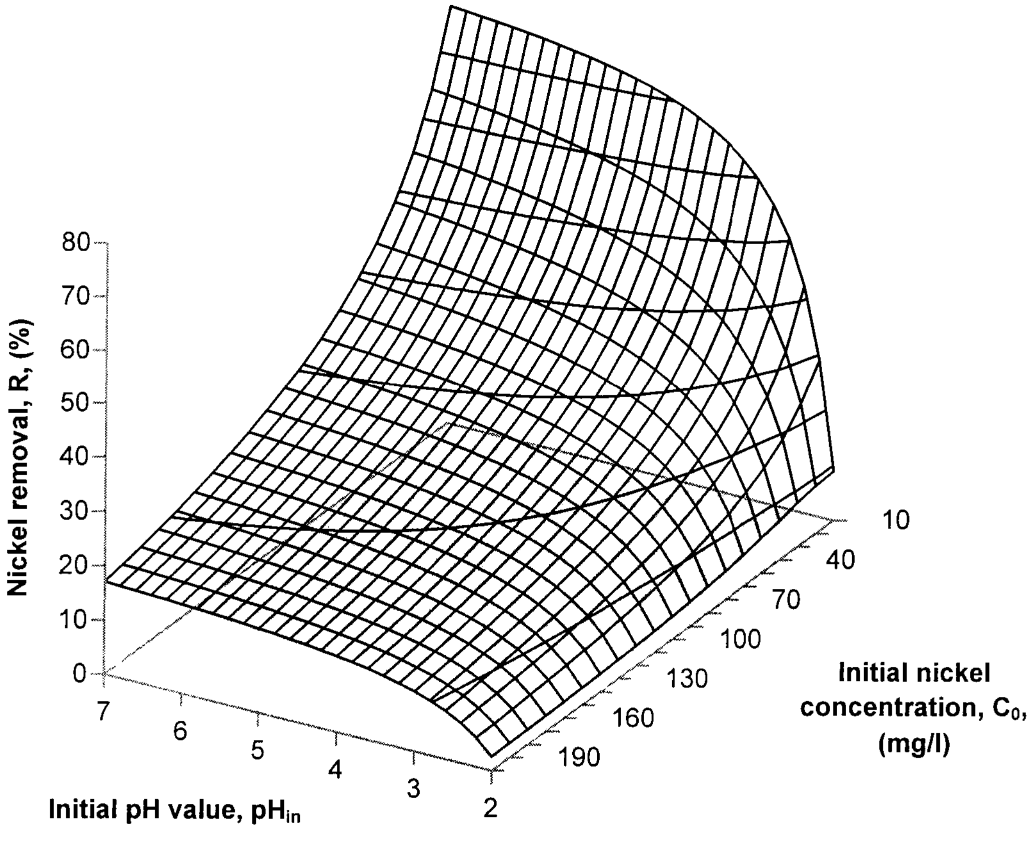
$$\beta = 1.99 \times 10^{-4} C_{0} + 1.00 \times 10^{-2},$$

$$\gamma = \frac{C_{0}}{5.38 \times 10^{-1} C_{0} - 3.43 \times 10^{-1}}.$$

Substituting for α, β, and γ, *R* can be represented as:

$$R = \frac{5.38 \times 10^{-1} C_{0}(pH_{in}) - 3.43 \times 10^{-1}(pH_{in}) - C_{0}}{1.07 \times 10^{-4} C_{0}^{2}(pH_{in}) + 5.32 \times 10^{-3} C_{0}(pH_{in}) - 3.43 \times 10^{-3}(pH_{in}) - 1.00 \times 10^{-6} C_{0}^{2} + 4.67 \times 10^{-4} C_{0}^{1.75} - 3.00 \times 10^{-4} C_{0}^{0.746}}.$$

Figure 3.2.4-3: Effect of initial nickel concentration (C_0) on nickel removal (R) by peat at various initial pH (pH_{in}) values.



where

R is the efficiency of nickel removal, (%);

C_0 is the initial nickel concentration, (mg/l);

pH_{in} is the initial pH of the reaction mixture.

This equation can then be used to derive the percent nickel removal at any given initial nickel concentration and initial pH value. The three dimensional plot of the equation is shown in **Figure 3.2.4-3**.

3.2.5. Effect of Peat Dose on Adsorption

The percentage of nickel ion removal at equilibrium with various peat doses at 25°C, is presented in **Table 3.2.5-1**.

TABLE 3.2.5-1: Effect of Peat Dose on Adsorption Data: Initial Nickel Ion Concentration, C_e; Percent Nickel Ion Removal at Equilibrium, R_e; and Nickel Ion Removal Capacity at Equilibrium, q_e; With Various Peat Doses at a Temperature of 25°C.

m_s (g/l)	C_e (mg/l)	R_e (%)	q_e (mg/g)	pH_{fin}
4	166	16.9	8.44	3.41
8	146	26.9	6.72	3.31
16	115	42.6	5.33	3.21
24	93.5	53.2	4.44	3.20
32	76.9	61.5	3.85	3.19
40	67.1	66.4	3.32	3.19

The effect of peat on initial nickel concentration at 200 mg/l is shown in **Figure 3.2.5-1**. It is apparent that the equilibrium concentration decreases with increasing adsorbent doses for a given initial nickel concentration (**Table 3.2.5-1**). This is obvious because for a fixed initial nickel concentration, increasing adsorbent doses provide greater surface area (or adsorption sites), resulting in higher nickel removals and hence decreasing equilibrium concentration. The data in **Table 3.2.5-1** can be used to derive a mathematical relationship (using the boundary conditions m_S = 4.0 to 40 g/l). The relationship equation (**3.1.5-1**), which has a correlation coefficient as high as 0.996 is:

$$R_e = \frac{m_s}{2.11 \times 10^{-1} + 9.83 \times 10^{-3} m_s}. \qquad (3.2.5\text{-}1)$$

The above equation can be used to predict the percent nickel removal for m_s (in the range 4.0 to 40 g/l) for observed test conditions at pH 5.0, and initial nickel concentration C_0 = 200 mg/l.

The adsorption capacity curve on the **Figure 3.2.5-1** indicates that adsorption capacity decreased from 8.44 to 3.32 mg/g of peat as the doses were increased from 4.0 to 40 g/l. This leads to the conclusion that, in order to obtain the optimum peat dose, higher nickel concentrations should be tested on high doses. The relationship between adsorption capacity and peat dose can be found (equation **3.1.5-3**) the correlation coefficient as high as shows 0.996 (using the boundary m_s = 4.0 and 40 g/l).

$$q_e = \frac{1}{1.05 \times 10^{-1} + 4.91 \times 10^{-3} m_s}, \qquad (3.2.5\text{-}2)$$

Also, **Figure 3.2.5-2** shows variation of C_e against m_s for C_0 = 200 mg/l, which indicates a relationship shown in equation (**3.1.5-5**). The linearised m_s/C_e and m_s plot showed a correlation coefficient as high as 0.998.

Figure 3.2.5-1: Nickel removal (R_e) and adsorption capacity (q_e) of peat as a function of peat dose (m_s).

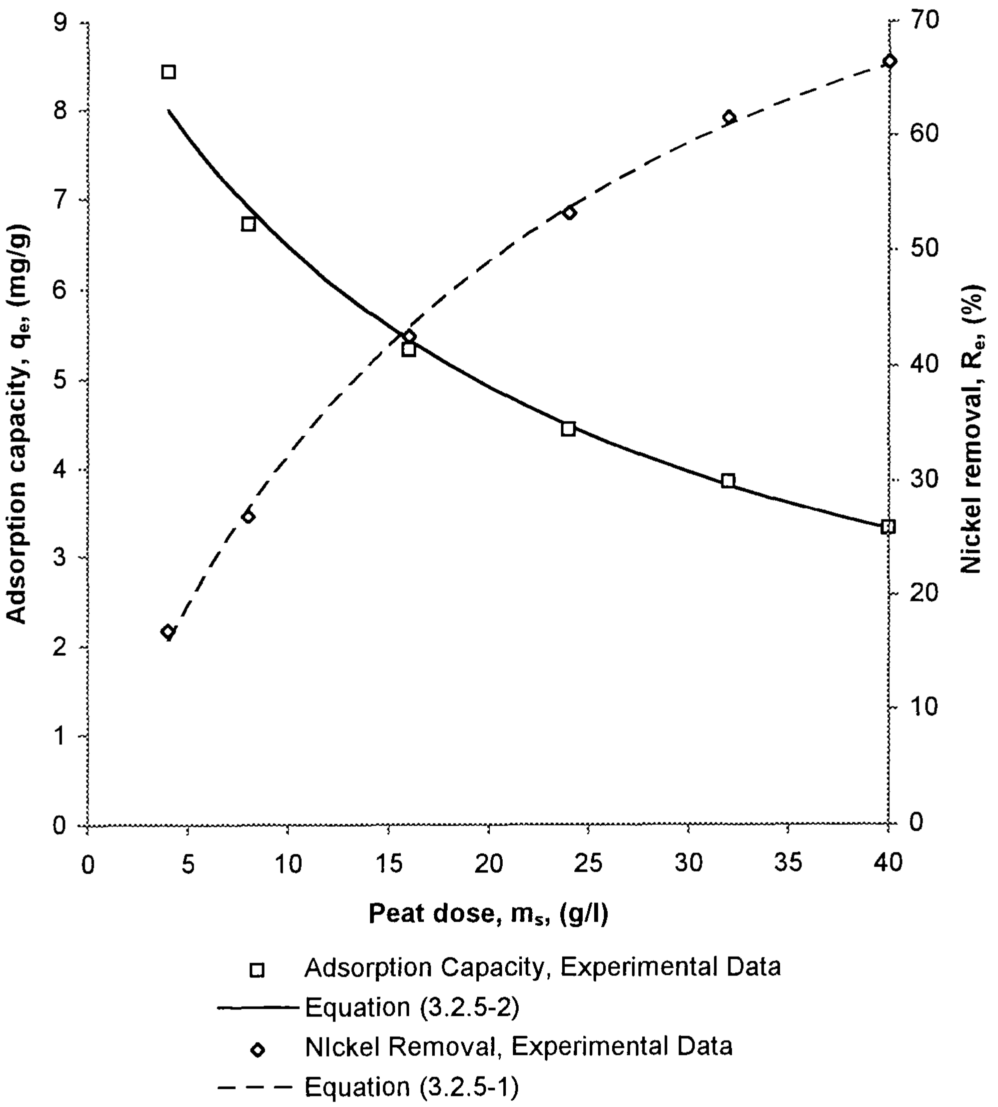
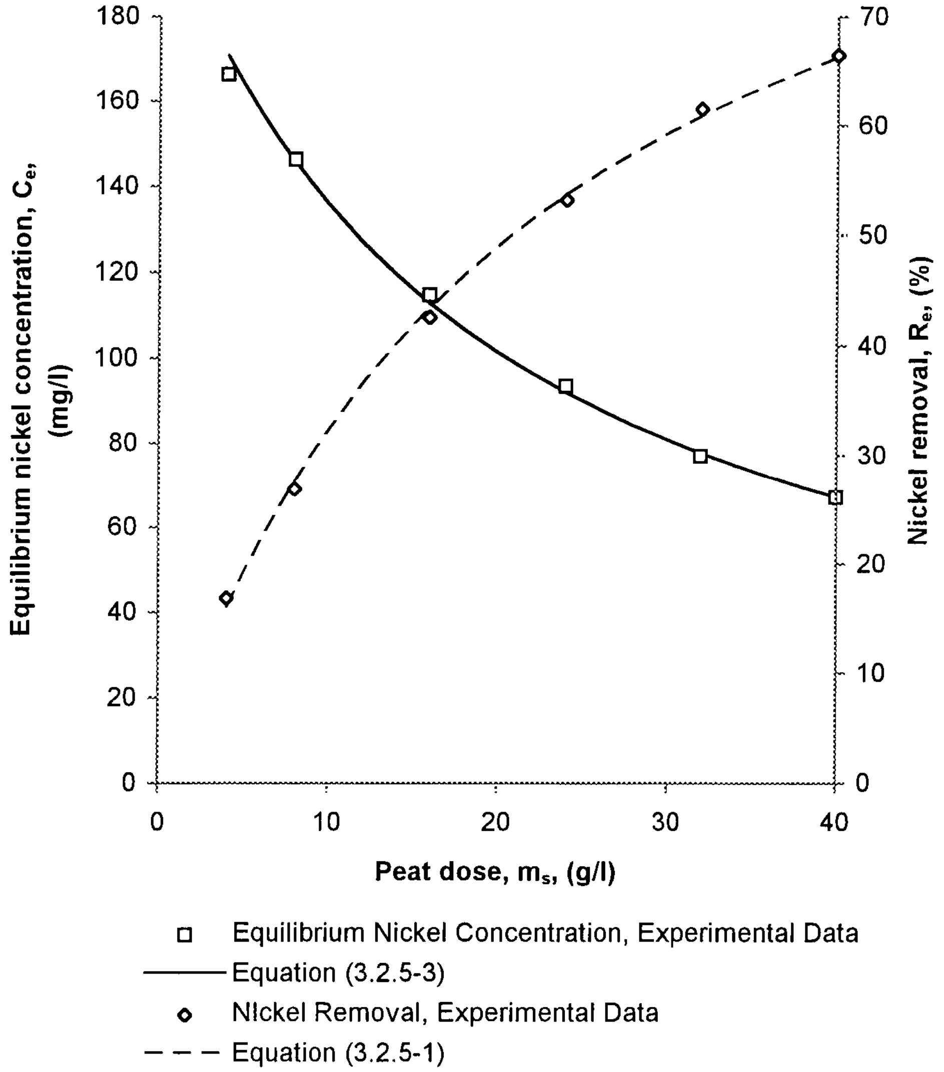


Figure 3.2.5-2: Equilibrium nickel concentration (C_e) and nickel removal (R_e) by peat as a function of peat dose (m_s).



$$C_e = \frac{1}{2.50 \times 10^{-4} m_s + 4.86 \times 10^{-3}} . \qquad (3.2.5\text{-}3)$$

The above equation can be used to predict the equilibrium nickel concentration for any given value of C_0 (here 200 mg/l) and m_s (in the range 4.0 to 40 g/l) for observed test conditions at pH 5.0. Fairly high values for the coefficient of correlation show the strength of the presented relationship. A similar empirical relationship can be obtained for other, differing initial nickel concentrations thus demonstrating the dependence of constants A_1 and A_2 on C_0.

3.3. LEAD

3.3.1. Adsorption Equilibria

The lead ion adsorption capacity of peat was also determined by equilibrium studies. Lead ion uptake was plotted against the equilibrium concentration, showing that the lead-peat adsorption system is indeed a positive adsorption. **Figures 3.3.1-1** and **3.3.1-2** indicate that typical isotherms for the lead-peat system at various pH values and 20°C as well as various temperatures and pH 5.0 adsorption increases initially with concentration, but then the peat reaches saturation.

3.3.2. Adsorption Isotherms

The adsorption of lead onto peat was examined by application of three commonly used adsorption isotherm models: the linear, Langmuir, and Freundlich models.

Figure 3.3.1-1: Typical adsorption curves for the lead-peat system at 20°C and various initial pH values.

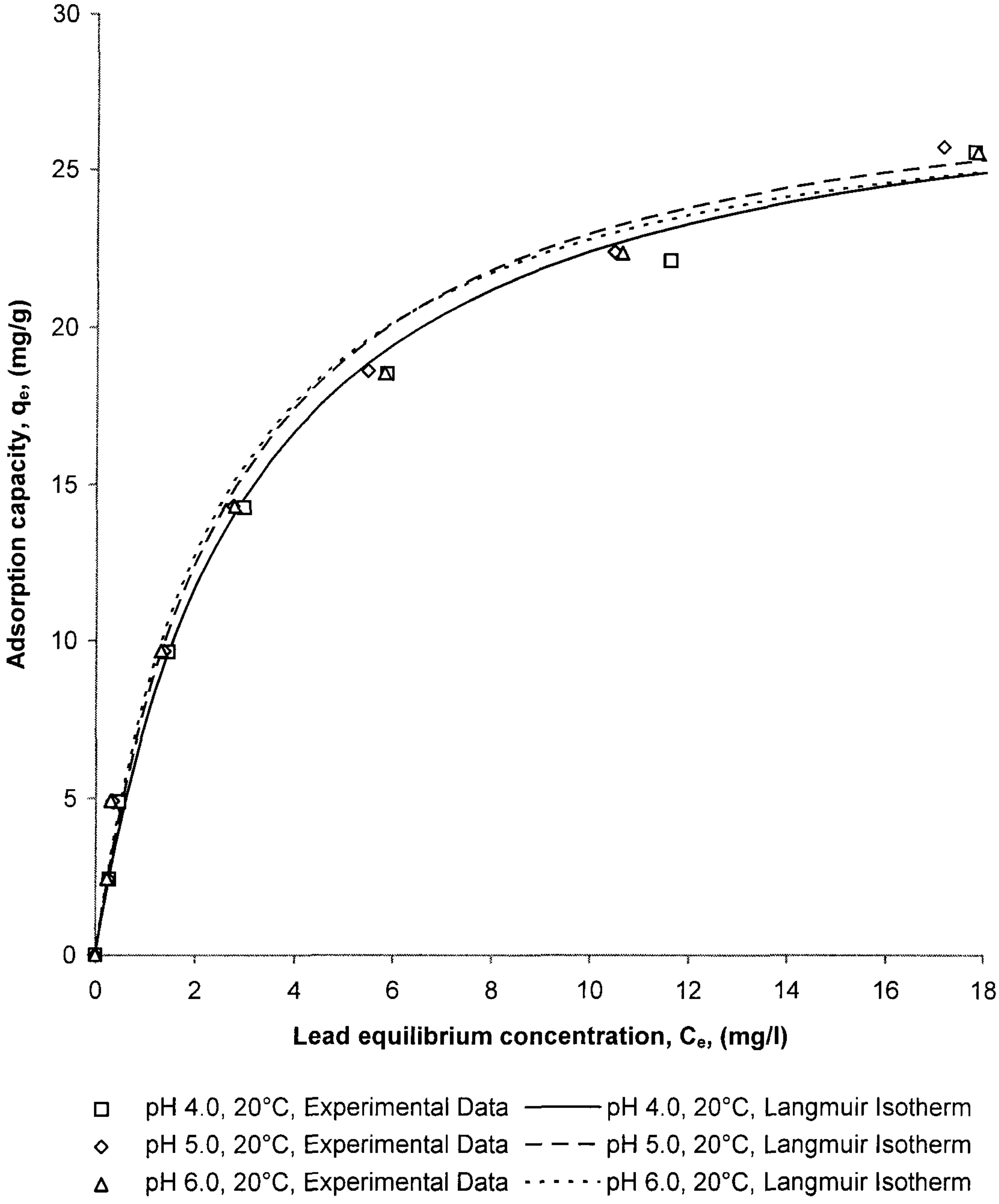
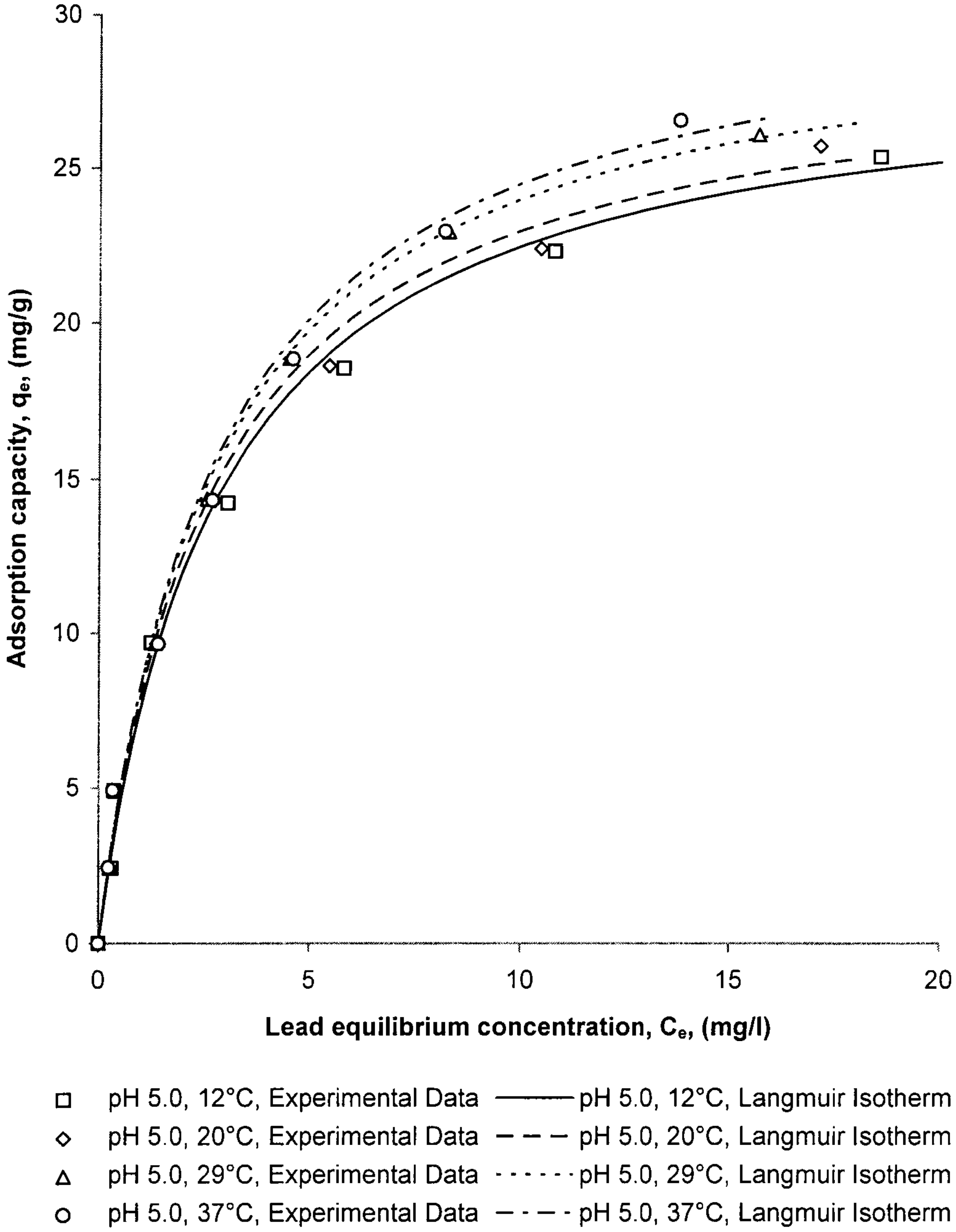


Figure 3.3.1-2: Typical adsorption curves for the lead-peat system at initial pH 5.0 and various temperatures.



Langmuir Isotherms

The equilibrium data for the adsorption of the lead ion on moss peat, at pH 4.0, 5.0, and 6.0, as well as 12, 20, 29, and 37°C fitted well the Langmuir model (monolayer formation) for the present system. This was confirmed by linear plots of (C_e/q_e) versus (C_e). Typical Langmuir isotherms at various pH values and 20°C as well as for various temperatures at pH 5.0 are presented in **Figures 3.3.2-1** and **3.3.2-2**.

The Langmuir constants were determined (**Table 3.3.2-1**) from slopes and intercepts of linear plots at various temperatures and pH values respectively. The isotherms at three different pH values and various temperatures in the range 12 to 37°C are seen to be linear over the whole concentration range used (**Figures 3.3.2-1** and **3.3.2-2**), and the correlation coefficients were found to be between 0.987 and 0.997. These fairly high values of correlation coefficients indicate that there is a strong positive relationship for the data and the lead-peat adsorption data follow the Langmuir model of adsorption. However, significant differences exist in that lead ions adsorb more strongly on the peat than those of copper or nickel. Chen *et al.* (1990) have reported the same order of binding of metals to peat.

The metal removal efficiency has also been studied. Ansted and MacCarthy (1984) found that lead removal was higher than copper removal by the sulphuric acid treated peat at the pH range 2.0 to 8.0 and an ionic strength of 0.01. We therefore also tested a range of pH values to find if our system behaved similarly.

It can be seen that the maximum adsorption capacity, X_m, increases with increasing reaction temperature for all the given pH. The highest values of adsorption capacity was found to be 31.3 mg/g of peat at initial pH 5.0 and temperature 37°C. The result clearly shows that a high temperature favours lead removal by adsorption on moss peat at the various temperatures used in this experiment. **Table 3.3.2-2** compares the X_m values for these adsorptions at their optimum pH values.

Figure 3.3.2-1: Linearised Langmuir isotherms for the lead-peat system at 20°C and various initial pH values.

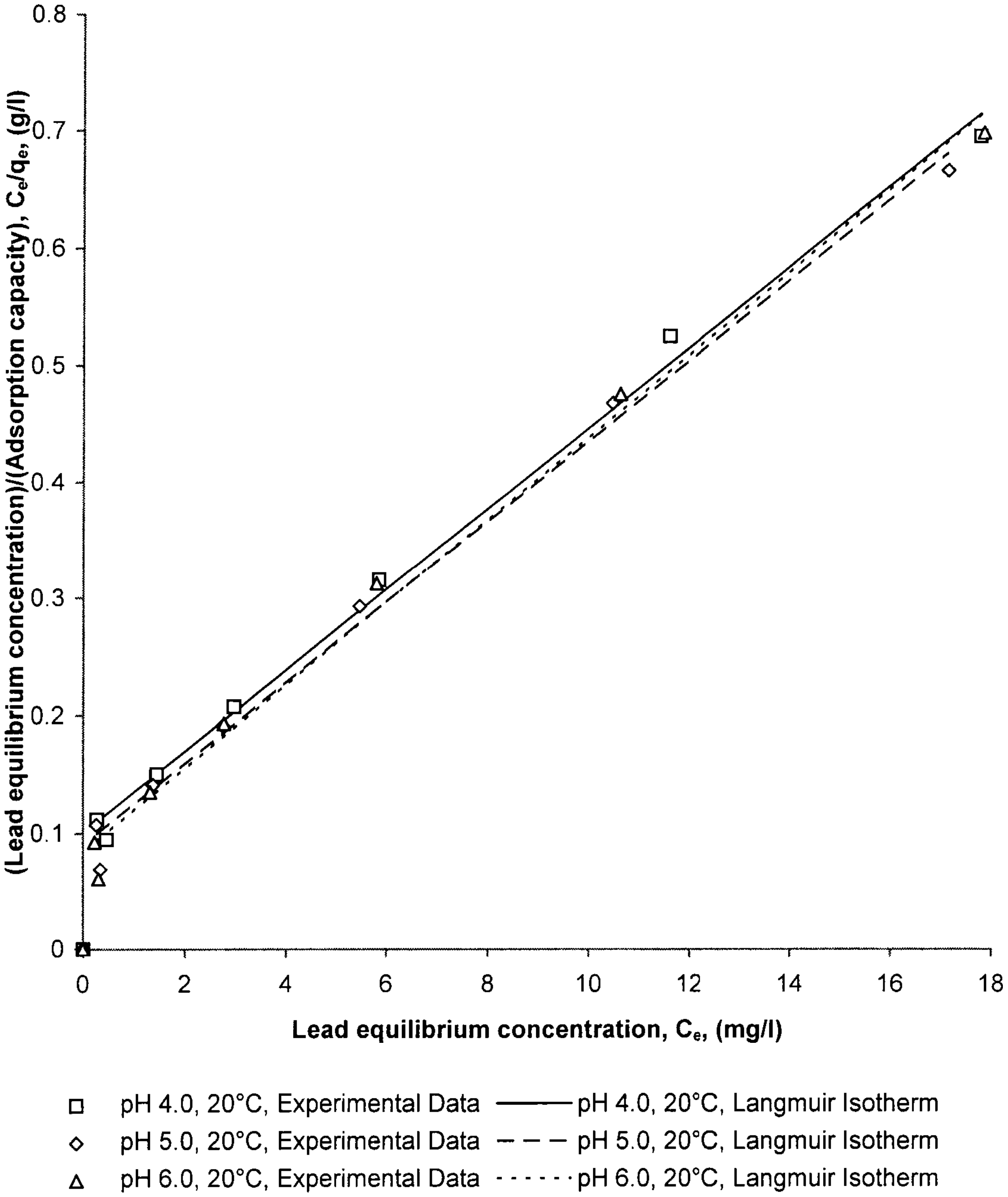


Figure 3.3.2-2: Linearised Langmuir isotherms for the lead-peat system at various temperatures; initial pH = 5.0.

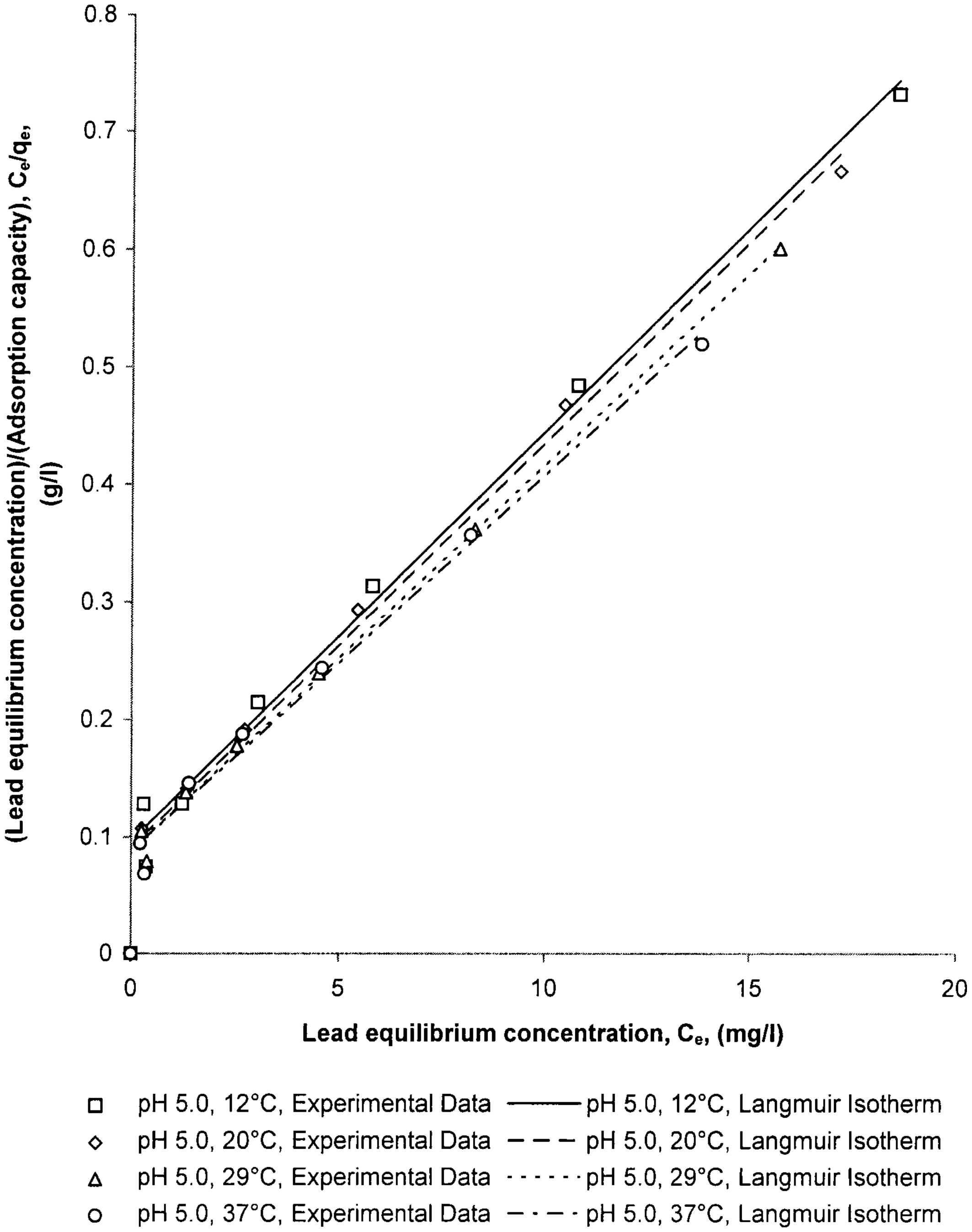


TABLE 3.3.2-1: Adsorption Isotherm Constants of Lead-Peat Binding.

		Langmuir Constants			Freundlich Constants		
pH_{in}	Temp. (°C)	Corr. Coeff. r^2	X_m (mg/g)	10×k (l/mg)	Corr. Coeff. r^2	K_F (mg/g)	10×(1/n)
4.00	12	0.992	27.3	3.64	0.994	7.97	4.95
4.00	20	0.995	28.9	3.43	0.992	7.62	5.33
4.00	29	0.996	29.5	3.44	0.997	7.61	5.34
4.00	37	0.991	30.3	3.45	0.997	7.95	5.11
5.00	12	0.993	28.7	3.61	0.994	8.23	4.81
5.00	20	0.993	29.0	3.80	0.997	8.37	4.88
5.00	29	0.997	30.4	3.72	0.999	8.30	5.56
5.00	37	0.990	31.3	3.63	0.997	8.47	5.16
6.00	12	0.993	28.3	3.93	0.986	8.51	4.89
6.00	20	0.993	28.3	4.17	0.997	8.60	4.56
6.00	29	0.996	29.7	4.03	0.999	8.53	5.31
6.00	37	0.987	30.7	3.87	0.997	8.76	4.75

TABLE 3.3.2-2: A Comparison of the Maximum Capacities of Peat (Langmuir X_m) for Chromium (VI), Copper(II), Nickel(II) and Lead(II) at the Peat Dose 4.0 g/l.

Metal	Optimum pH	Temp. (°C)	X_m (mg/g)	Source
Cr(VI)	1.5	25	119	Sharma and Forster (1993)
Pb(II)	5.0	40	31.3	This Study
Cu(II)	5.0	25	16.4	This Study
Ni(II)	7.0	25	9.18	This Study

Freundlich isotherms

The isotherm can be separated into three parts (**Figures 3.3.2-3** and **3.3.2-4**). The first part, at the low concentration range, 0 to 20 mg/l, is where the concentration affects adsorption capacity more than in the other ranges. Here, concentration is proportional to adsorption capacity. In this range, the process is almost wholly limited

Figure 3.3.2-3: Linearised Freundlich isotherms for the lead-peat system for various pH values; temperature = 20°C.

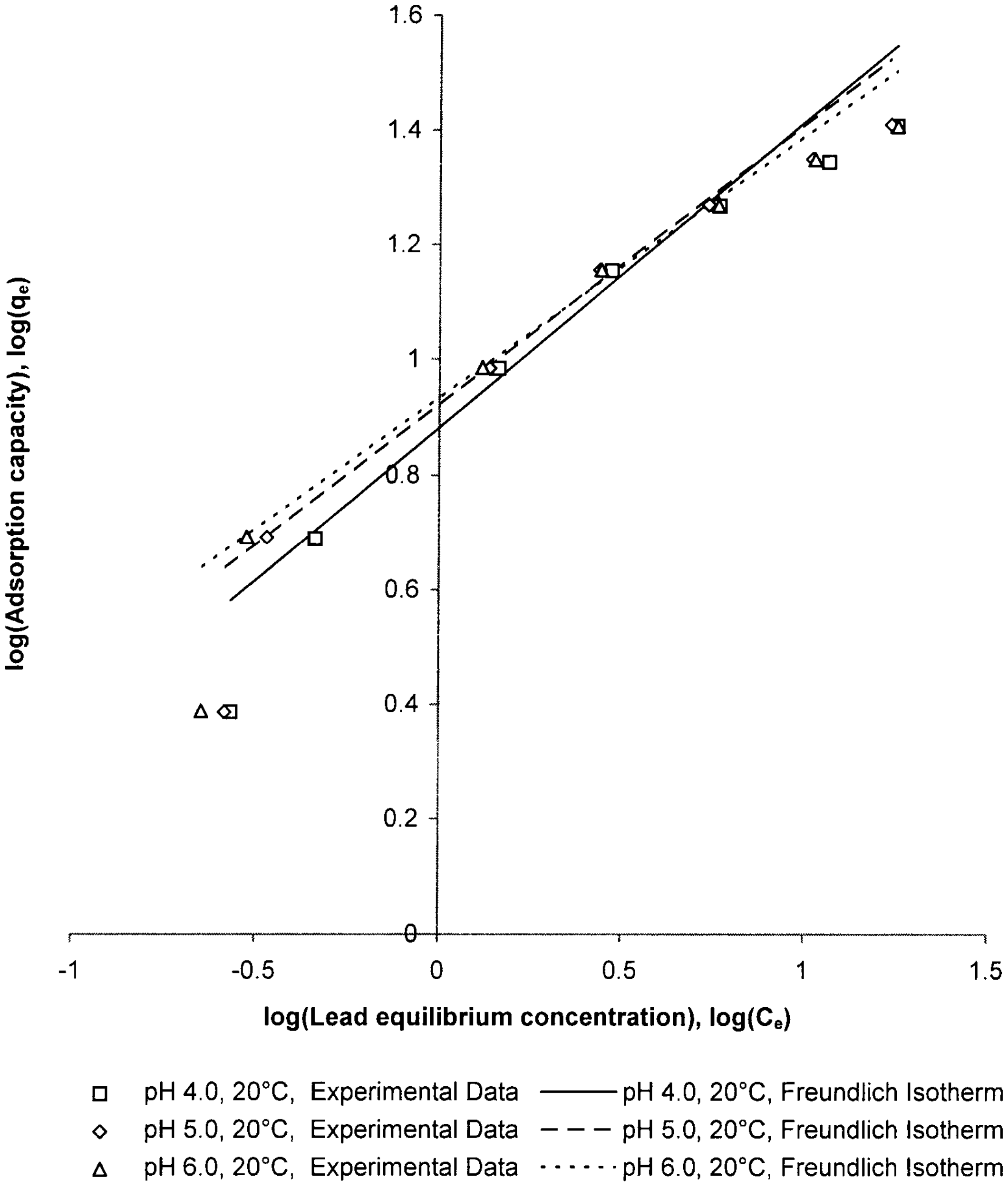
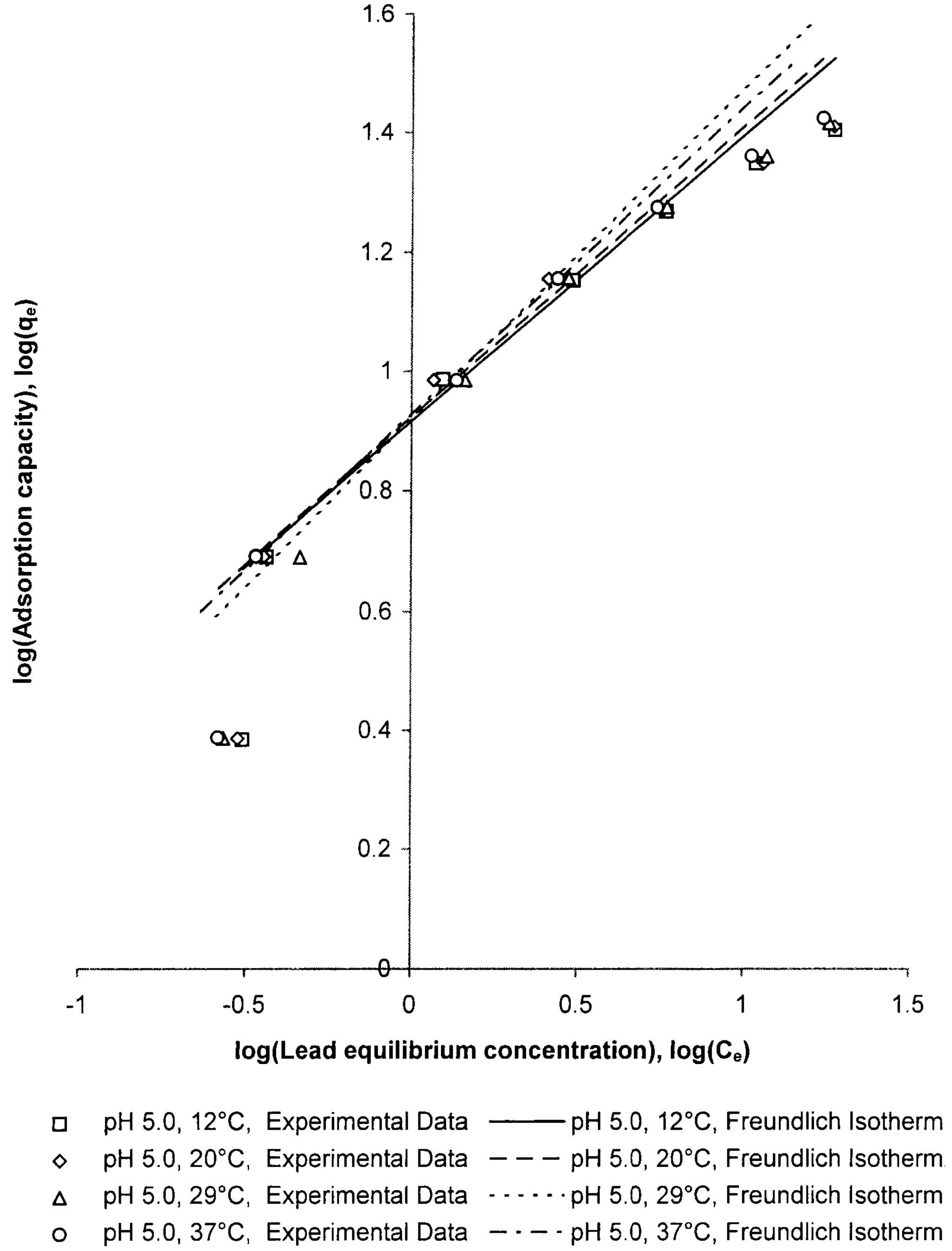


Figure 3.3.2-4: Linearised Freundlich isotherms for the lead-peat system at various temperatures; initial pH = 5.0.



by transport of adsorbate from solution to the particle-solution interface. The most simple isotherm is the linear model, which describes the accumulation of solute by the sorbent as directly proportional to the solution phase concentration (Weber *et al.*, 1991):

$$q_e = K_D \cdot C_e,$$

where q_e is the mass of solute sorbed per unit mass of sorbant at equilibrium with a solution of solute concentration C_e and K_D is the distribution coefficient.

In the second part, at a concentration from 20 to 80 mg/l, the effect of concentration on adsorption capacity is less than in the first part. In this range, the process is more complex, perhaps involving mass transfer, intraparticle diffusion of adsorbate and chemisorption. A Freundlich isotherm could be fitted in this range. The final range, is where the adsorption density is going to be saturating.

Equilibrium data for the adsorption of lead ions on moss peat have also been fitted by the Freundlich adsorption isotherm according to the equation:

$$q_e = K_F \cdot C_e^{1/n},$$

where q_e is the amount of lead ion per unit weight of peat (mg/g), K_F is a measure of adsorption capacity, 1/n defines adsorption intensity, and C_e is the equilibrium concentration of the lead ion solution. This system exhibits a monolayer coverage of the adsorption on the outer surface of the adsorbent. The constants of Freundlich K_F and 1/n were calculated from the intercepts and the slopes of the log-log plot (**Table 3.3.2-1**) for the range of the initial lead concentrations from 20 to 80 mg/l at the given temperatures and pH values. The validity of Freundlich isotherm was also tested by regression analysis of the equilibrium data at various temperatures and pH conditions (**Figures 3.3.2-3** and **3.3.2-4**). The validity of fitting the data to the Freundlich isotherm was tested by determining the general equation. The correlation coefficients were found to be between 0.986 and 0.999 (**Table 3.3.2-1**).

3.3.3. Effect of Lead on Equilibrium pH

The removal of lead ion from aqueous solution by adsorption is normally related to the pH of the solution which affects the surface charge, the degree of ionisation and the species of adsorbate. Historically, soluble lead has been removed, initially, by precipitation processes. A lead precipitation pH of 6.0, was suggested in one instance (Dean *et al.*, 1972). However, disposal of high-lead slurries can be difficult. As an alternative, Mittal and Venkobachar (1993) investigated lead removal by sorbents in the pH range 4.0 to 6.0. Metal uptake was maximal at pH 6.0. Huang *et al.* (1977) reported an abrupt increase in the adsorption of lead in the pH range of 5.0 to 6.0. Srivastava *et al.* (1989) also pointed out that the optimum pH for lead removal was almost the same, being in the pH range of 4.0 to 6.0.

In the present work, we therefore used the same experimental pH range; namely of 4.0 to 6.0. Lead ion removal from aqueous solution by adsorption with moss peat was at four different temperatures. With increase in solution pH from 4.0 to 6.0 the extent of removal increased from 86.1 to 88.7%, 88.4 to 89.4%, 89.9 to 91.6%, and 90.9 to 91.9% for the temperatures 12, 20, 29, and 37°C at an initial concentration of 100 mg/l (**Figure 3.3.3-1**). After a further increase in pH of the solution up to 6.0 the extent of lead removal decreased to 88.7, 89.4, 91.6, and 91.9% respectively. This result shows that adsorption by peat is not particularly sensitive to pH over the range 4.0 to 6.0.

Figures 3.3.3-2 and **3.3.3-3** shows that as the initial lead concentration increases, the resultant equilibrium pH is decreased. Typical equilibrium pH values at different initial lead concentrations are shown in **Figures 3.3.3-2** and **3.3.3-3**. When the reaction temperature is 37°C the resultant equilibrium pH values are lower than the others. It is indeed possible that an endothermic reaction could itself decrease the pH of the reaction mixture. Speculation aside, however, it is concluded that as more lead ions are adsorbed onto the peat, more hydrogen ions are released from the peat into the solution.

Figure 3.3.3-1: Effect of initial pH (pH_{in}) on percent removal (R) of lead by adsorption on peat at various temperatures.

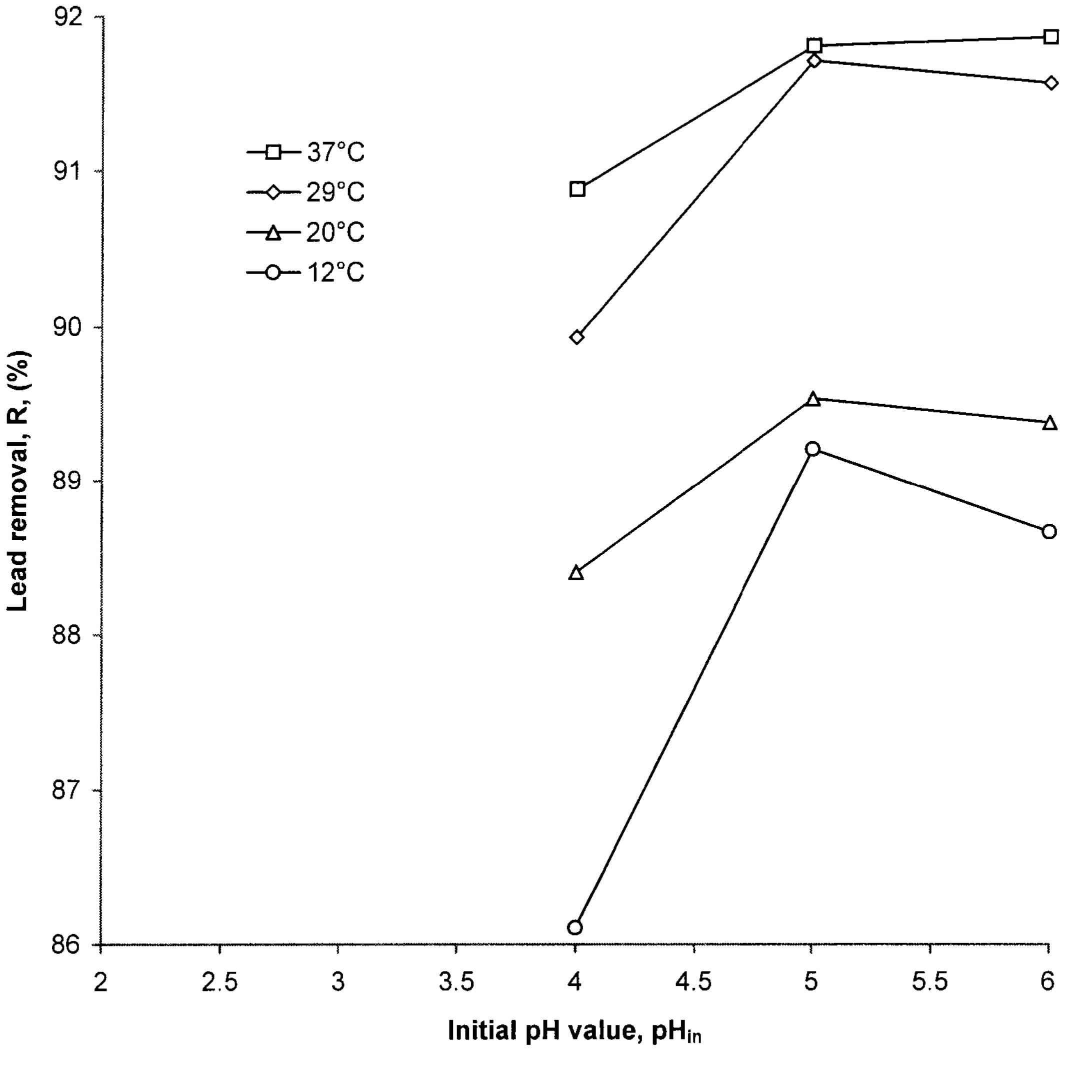


Figure 3.3.3-2: Typical equilibrium pH (pH_{fin}) values following adsorption of lead at various initial lead concentrations (C_0) on peat; temperature = 20°C, initial pH values.

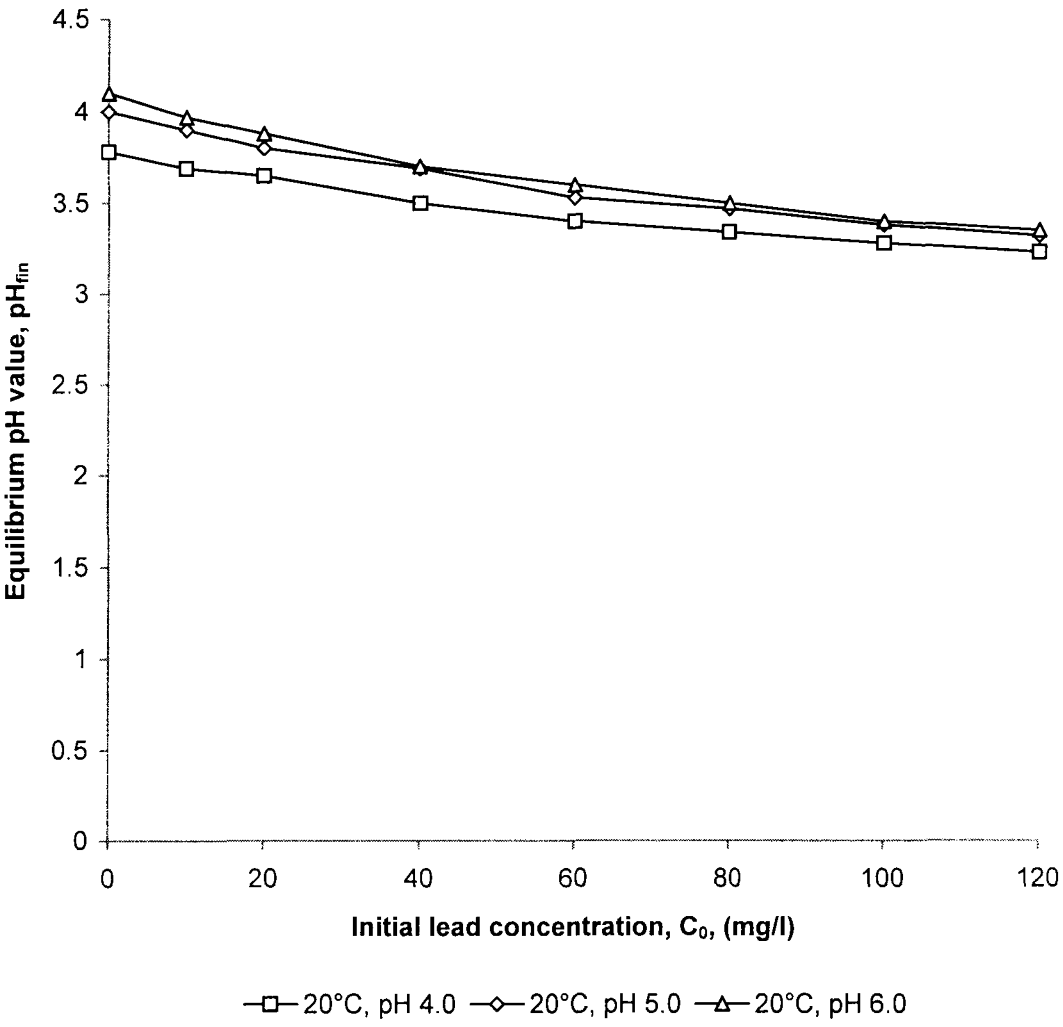
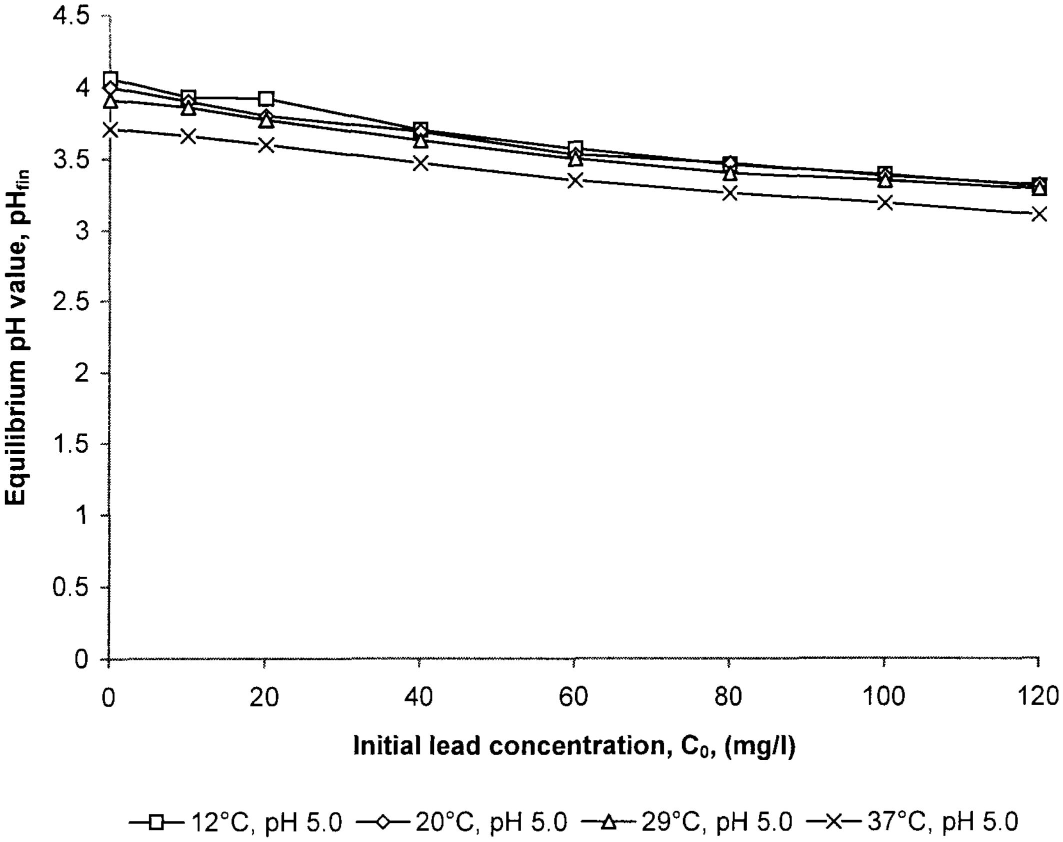


Figure 3.3.3-3: Typical equilibrium pH (pH_{fin}) values following adsorption of lead at various initial lead concentrations (C_0) on peat; initial pH = 5.0; temperature various.



3.3.4. Lead Removal

The removal of lead by adsorption has been studied on various adsorbents (**Table 3.3.4-1**). Yadava *et al.* (1989) reported that the Langmuir maxima for adsorption of lead ions by fly-ash was 0.368 mg/g at 20°C at a fly-ash dose of 20 g/l. Also, they reported (1991) that the Langmuir maxima for adsorption of lead ions by china clay and wollastonite were 0.415 mg/g and 0.308 mg/g at 20°C for an adsorbant dose of 20 g/l. The amounts of lead adsorbed clearly varied widely according to the source of the china clay. Farrah *et al.* (1980) pointed out that the Langmuir maximum adsorption of lead ion by three different Na^+-form clays were 3.93 mg/g for kaolin, 14.1 mg/g for illite and 71.8 mg/g for montmorillonite at 25°C and pH 5.0. This variation also occurs for peats. McLellan and Rock (1988) noted that lead removal by sphagnum moss peat was 19.9 mg/g for an initial ion concentration of 50 mg/l and 40.0 mg/g for an initial ion concentration of 500 mg/l. The moss, *Calymperes delessertii* Besch had a maximum sorption capacity of 49.9 mg/l at a moss dose of 10 g/l; higher than the resultant peats (Low and Lee, 1987). In contrast, Tummavuori and Aho (1980) investigated adsorption of lead ions by peat, noting that the capacity was 20.0 mg/g for the Rastunsuo peat at a dose of 26.6 g/l. These figures vary quite widely. A comparison with the adsobents (**Table 3.3.4-1**) shows up these variation.

The efficiency of lead removal by peat depended only very slightly on the initial pH of the reaction solution and temperature in the conditions of experiment. The result demonstrates that for lower initial lead concentrations, all of the lead removals were close to 100%: i.e. these adsorptions are close to saturation. However, a comparison of lead removal showed that when initial lead concentration was 120 mg/l and reaction temperature was at 12°C, lead removals were: 82.9% at pH 4.0, 84.5% at pH 5.0, and 84.6% at pH 6.0; at 20°C the lead removals were: 85.2% at pH 4.0, 85.7% at pH 5.0, and 85.1% at pH 6.0; at 29°C the lead removals were: 85.6% at pH 4.0, 86.9% at pH 5.0, and 86.4% at pH 6.0; and at 37°C the lead removals were: 86.9% at pH 4.0, 88.5%

TABLE 3.3.4-1: A Comparison of Maximum Adsorption Capacities for Lead of Various Materials With Those of Peats.

Capacity (mg/g)	X_m (mg/g)	Material	Reference
-	3.93	Kaolin Clay	Farrah *et al.* (1980)
-	14.1	Illite Clay	
-	71.8	Montmorillonite Clay	
10.2	-	Treated Bagasse	Kumar and Dara (1982)
10.4	-	Treated Acacia Bark	
10.9	-	Treated Laurel Bark	
10.8	-	Treated Techtona Bark	
0.269	-	Waste Type Rubber	Rowley *et al.* (1984)
8.90	-	Rice Hulls	Suemitsu *et al.* (1986)
12.0	-	Dyestuff-Treated (Red) Rice Hulls	
12.0	-	Dyestuff-Treated (Yellow) Rice Hulls	
-	49.9	Moss (*Calymperes delessertii* Besch)	Low and Lee (1987)
-	78.7	Tea Leaves	Tan and Abd. Rahman (1988)
-	0.368	Fly-Ash	Yadava *et al.* (1989)
-	1380	Waste Slurry	Srivastava *et al.* (1989)
19.0	-	*Aspergillus oryzae*	Huang *et al.* (1991)
114	-	Treated *Aspergillus oryzae*	
90.9	-	Sludge Solid	Tien and Huang (1991)
-	0.415	China Clay	Yadava *et al.* (1991)
-	0.308	Wollastonite	
-	61.8	Sphagnum Peat Moss	Allen *et al.* (1992)
0.08	-	Oil-Palm Fibres	Low *et al.* (1993)
-	116	Penicillium Biomass	Niu *et al.* (1993)
149	-	Titanium(IV) Oxide	Suzuki *et al.* (1994)
41.4	-	Yeast Biomass	Brady *et al.* (1994)
1860	-	Lignin	Srivastava *et al.* (1994)
-	251	Algae	Özer *et al.* (1994)
20.0	-	Peat (Rastunsuo)	Tummavuori and Aho (1980)
40.0	-	Sphagnum Moss Peat	McLellan and Rock (1988)
-	30.7	Sphagnum Moss Peat	This Work

at pH 5.0, and 88.3% at pH 6.0. Overall than, when the pH was increased from 4.0 to 6.0 and the temperature from 12 to 37°C, removal increased slightly.

3.3.5. Effect of Peat Dose on Adsorption

The percentage of lead ion removal at equilibrium with various peat doses at 25°C, is presented in **Table 3.3.5-1**.

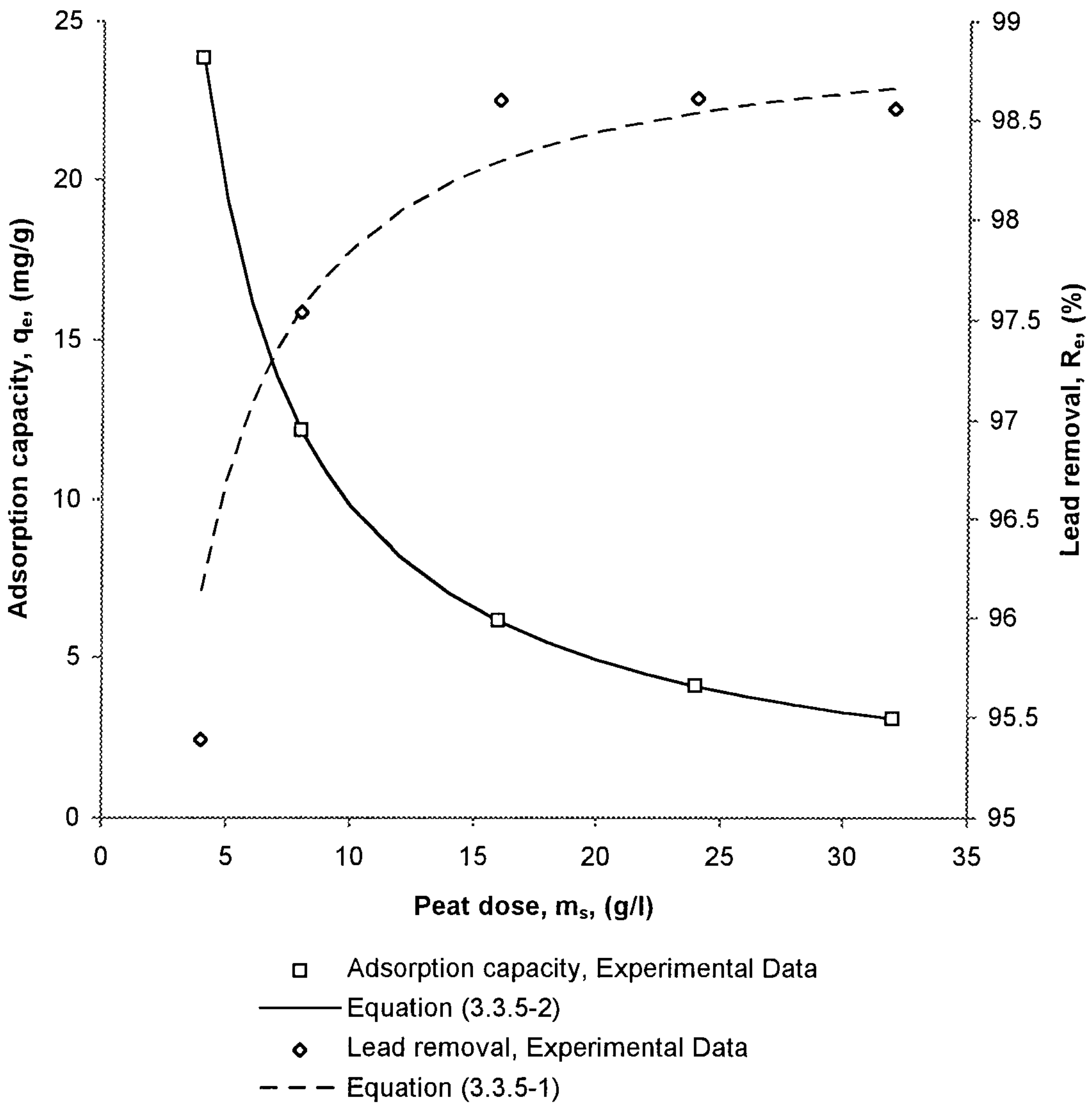
TABLE 3.3.5-1: Effects of Variations in Peat Dose on Adsorption Data an Initial Lead Ion Concentration, C_e; Percent Lead Ion Removal at Equilibrium, R_e; and Lead Ion Removal Capacity at Equilibrium, q_e; at a Temperature of 25°C.

m_s (g/l)	C_e (mg/l)	R_e (%)	q_e (mg/g)	pH_{fin}
4	4.61	95.4	23.8	3.28
8	2.46	97.5	12.2	3.37
16	1.40	98.6	6.16	3.38
24	1.39	98.6	4.11	3.28
32	1.44	98.6	3.08	3.21

A plot of the percentage of lead ion removal at equilibrium, R_e, and peat dose, m_s, is shown in **Figure 3.3.5-1**. The plots show that R_e increased with increasing peat doses. This is because adsorption is a function of active sites of peat, and more peat dose offered comparatively more sites and hence higher metal ion removal at equilibrium. A linear relation occurred between (m_s/R_e) and (m_s) with a correlation coefficient of 0.999 (**Figure 3.3.5-1**) for the following equation (**3.1.5-1**).

A predictive model for the percent lead ion removal for any peat dose within the test limits at pH of 5.0 and initial lead concentration of 100 mg/l can be presented as:

Figure 3.3.5-1: Variation of adsorption capacity (q_e) of the peat and lead removal (R_e) against peat dose (m_s).



$$R_e = \frac{m_s}{1.22 \times 10^{-3} + 1.01 \times 10^{-2} m_s}. \qquad (3.3.5\text{-}1)$$

The coefficients R_0 and S_1 in equation **(3.1.5-1)** are functions of adsorbent particle sizes (Bhargava and Sheldarkar, 1992 and 1993). The model of equation **(3.1.5-1)** has already been published for metal-peat adsorption systems (Ho *et al.*, 1994). Bhargava and Sheldarkar (1993) have also presented a model for predicting phosphate removal. Their model incorporates adsorbent particle size and adsorbent dose as follows:

$$R_e = \frac{m_s}{\left(4.4969 + 0.089961 d_p\right) + \left(\frac{\sqrt{d_p}}{386.8403 + 49.6774\sqrt{d_p}}\right) m_s},$$

where

d_p is geometric mean size of adsorbent particles, (μm).

Then, when the geometric mean particle size, d_p = 38.73 μm, the maximum percentage of phosphate removal was higher than 100% (1.12 times greater). This effect arose because of variations, due to poor suspension of the adsorbents; for instance, some remained stuck to the flask wall. This error arose not only because of the effect of contact between adsorbent and solution but also the value of C_0/m_s. In the present work, the result shows that the removal of lead at a peat dose ranging from 4.0 to 32 g/l is close to 100% **(Figure 3.3.5-1)**. Thus, the error of the maximum percentage of metal ion removal again appeared because the effect of contact is always lower than 100% in the process of suspending shaking.

The adsorption capacity curve on the **Figure 3.3.5-1** indicates that adsorption capacity decreased from 23.8 mg/g to 3.08 mg/g of peat when the doses were increased from 4.0 to 32 g/l. This leads to the conclusion that, in order to obtain an optimum peat dose, higher lead concentrations should be tested in conjunction with high doses.

The relationship between adsorption capacity and peat dose can be found using equation **(3.1.5-3)** where the correlation coefficient was as high as 0.999 (using the boundary m_s = 4.0 and 36 g/l).

$$q_e = \frac{1}{1.22 \times 10^{-3} + 1.01 \times 10^{-2} m_s}. \qquad (3.3.5\text{-}2)$$

Also, **Figure 3.3.5-2** shows variation of (C_e) against (m_s) for C_0 = 100 mg/l, which indicates a relationship shown in equation **(3.1.5-5)**. The linearised (m_s/C_e) and (m_s) plot showed a correlation coefficient as high as 0.992.

$$C_e = \frac{m_s}{7.87 \times 10^{-1} m_s + 2.32}. \qquad (3.3.5\text{-}3)$$

This above equation can be used to predict the equilibrium lead concentration for any given value of C_0 (here 100 mg/l) and m_s (in the range 4.0 to 32 g/l) for observed test conditions at pH 5.0. Values for the coefficient of correlation show the strength of the presented relationship. A similar empirical relationship can be obtained for different initial lead concentrations thus demonstrating the dependence of constants A_1 and A_2 on C_0.

3.3.6. Thermodynamics of Adsorption

Heat is always liberated when an adsorbate is adsorbed at a surface, which means that the enthalpy change ΔH is negative (Laidler, 1987). The reason is that the adsorption of an adsorbate inevitably involves an entropy decrease, because a molecule in the adsorbate phase (or indeed in solution) has more freedom than one attached to a surface. Hence any temperature increase through the adsorption process arises from this exothermic effect. However, in some cases, an increase in temperature due to this

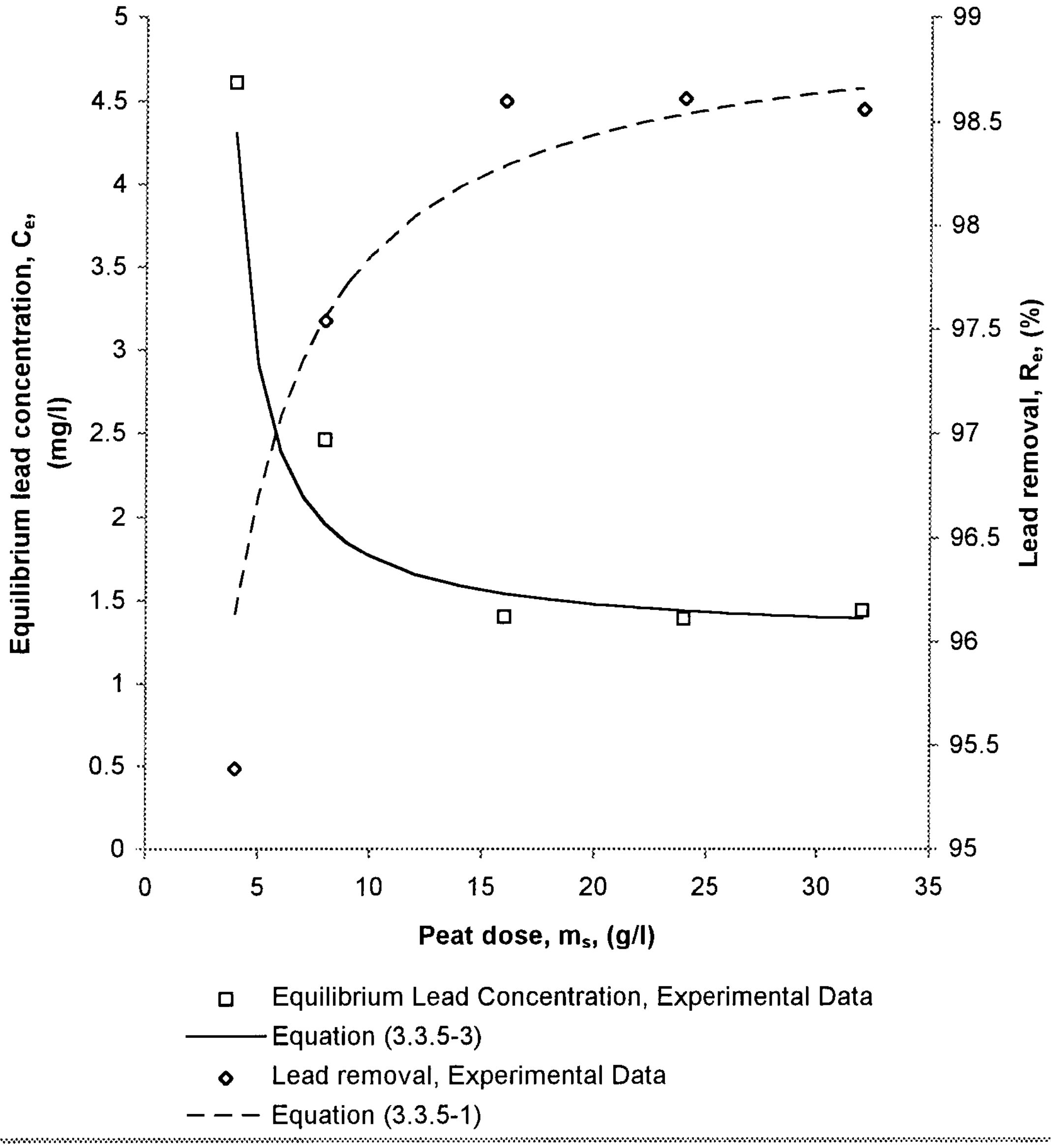


Figure 3.3.5-2: Equilibrium lead concentration (C_e) and lead removal (R_e) by peat as a function of peat dose (m_s).

exothermic adsorption causes a further effect. In such case, the temperature rises lead also to increased chemisorption effects, so leading to unanticipated overall increases in adsorption.

The change in apparent enthalpy of adsorption, ΔH, is related to the Langmuir constant, kX_m, using the Clausius-Clapeyron equation as given below (McKay *et al.*, 1987)

$$kX_m = A_c \exp\left(-\frac{\Delta H}{RT}\right),$$

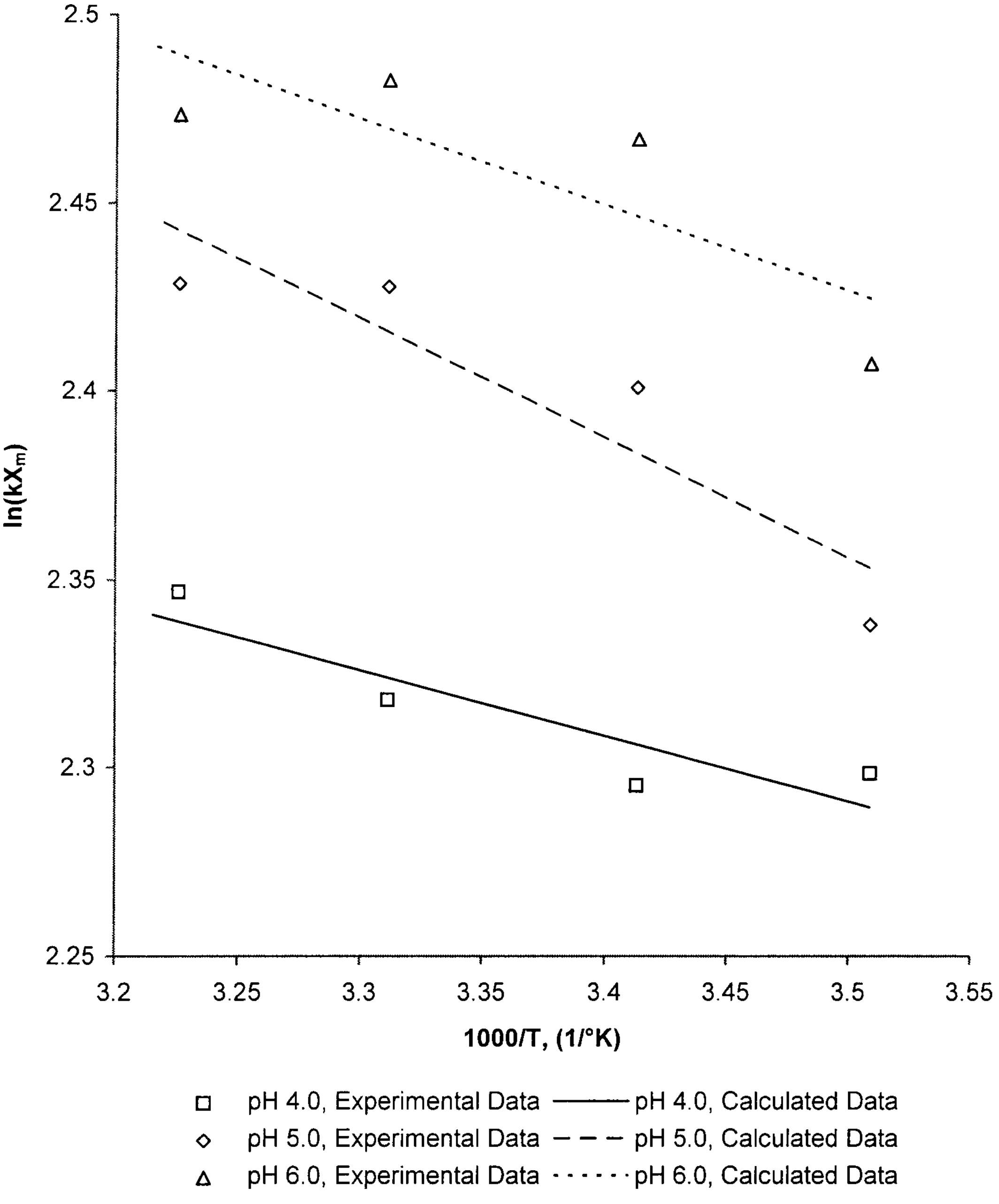
$$\ln(k \cdot X_m) = \ln A_c - \Delta H/RT,$$

where

A_c is constant.

The enthalpy change of adsorption of lead on peat at pH 4.0, 5.0, and 6.0 was in such case determined from the slope of the plot $\ln(kX_m)$ versus 1/T (**Figure 3.3.6-1**) and these values were found to be -1.46, -2.63, and -1.90 KJ/mol, respectively, which suggests the possibility of strong bonding between lead and peat. A similar phenomenon for the adsorption of lead ions on fly-ash, china clay, and wollastonite has also been reported (Yadave *et al.*, 1989 and 1991). They calculated ΔH by using the plot ln(k) versus 1/T. Their values of ΔH for fly-ash, china clay and wollastonite systems, respectively, were -7.269 Kcal/mol, -77.95, and -16.40 KJ/mol, which are very much larger than the figures we obtain. We suggest this is due to the adsorption involving chemisorption and physical adsorption. In addition, to confuse the issue still further, Viraraghavan and Ganesh (1993) reported the adsorption of cadmium on sphagnum moss peat was exothermic, while the adsorption of chromium on sphagnum moss peat was endothermic. It is, therefore, clear that individual tests on waste waters containing metal are vital if plant is to be designed on a same basis.

Figure 3.3.6-1: Plot of $\ln(kX_m)$ against (1/T) for the adsorption of lead on peat.



3.4. MECHANISM OF ADSORPTION

The mechanism of adsorption can be one of physical adsorption due to Van der Waals forces of attraction, exchange adsorption due to electrostatic forces induced by charged functional groups on the peat surface, or chemisorption in which the adsorbate reacts with the peat surface and is chemically bound to the peat. The first two mechanisms are reversible in nature and represent rather weak energies of interaction, while chemisorption is an irreversible process and is characterised by high energies of interaction.

Adsorption equilibria can be explained by species charges and peat surface charge chracteristics. The surface chracteristics are functions of solution pH and types of surface oxide groups present on the peat. The polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids phenolic hydroxides and ethers in the peat surface can influence adsorption of organic compounds. These groups may interact with the chelated heavy metals by promoting the formation of an electron donor-acceptor complex of the chelate and the active sites (such as polar functional groups). Possible hydrogen bonding between the surface groups and the chelated metals or free ligands could also enhance adsorption. Although the exact mechanism of adsorption of heavy metal chelates is quite complex, the charge barrier between the peat surface and solute species plays a predominant role during adsorption.

The net interaction energy of solute species with the peat surface may result from long-range forces (electrostatic and van der Waals attraction) and short-range chemical forces (hydrophobic bonding, orientation effects, etc.). The adsorption capacity of metal ions could be a function of pH, temperature, species charges, activated site of peat etc.

The assumption that the bonding between metal ions and humic acids is not only physical but also of chemical character is supported, among others, by the following facts (Lakatos *et al.*, 1972):

1. the capacity of metal ions of great affinity closely approaches the total acidity;

2. the capacity values of different kinds of humic acids, with respect to one metal ion are, in general, approximately equal, and finally;
3. the capacity values are, by order of magnitude, in agreement with the total acidity.

3.4.1. pH Dependence of Adsorption

The solubility of the metal hydroxide is defined by solubility products (K_S) and by equations relating the metal hydroxide solid species in equilibrium with soluble free metal ion or metal-hydroxide species. The following generalised equations may be used to describe the solubility of a divalent metal hydroxide (Bard, 1966).

$$M(OH)_{2(S)} \Leftrightarrow M^{2+} + 2OH^- \qquad K_{S0}$$

$$M(OH)_{2(S)} \Leftrightarrow M(OH)^+ + OH^- \qquad K_{S1}$$

$$M(OH)_{2(S)} \Leftrightarrow M(OH)_2^0 \qquad K_{S2}$$

$$M(OH)_{2(S)} + OH^- \Leftrightarrow M(OH)_3^- \qquad K_{S3}$$

$$M(OH)_{2(S)} + 2OH^- \Leftrightarrow M(OH)_4^{2-} \qquad K_{S4}$$

Each equation describes an equilibrium reaction between the solid phase, $M(OH)_{2(S)}$, and a soluble species of the metal, M. The equilibrium position for each reaction is described by a solubility product constant, K_S, as follows:

$$K_{S0} = \left[M^{2+}\right]\left[OH^-\right]^2,$$

$$K_{S1} = \left[M(OH)^+\right]\left[OH^-\right],$$

$$K_{S2} = \left[M(OH)_2{}^0\right],$$

$$K_{S3} = \left[M(OH)_3{}^-\right]/\left[OH^-\right],$$

$$K_{S4} = \left[M(OH)_4{}^{2-}\right]/\left[OH^-\right]^2.$$

The concentrations of soluble species are calculated by taking the logarithmic form and rearranging, when the following equations are obtained:

$$\log\left[M^{2+}\right] = \log K_{S0} - 2pH + 28,$$

$$\log\left[M(OH)^+\right] = \log K_{S1} - pH + 14,$$

$$\log\left[M(OH)_2{}^0\right] = \log K_{S2},$$

$$\log\left[M(OH)_3{}^-\right] = \log K_{S3} + pH - 14,$$

$$\log\left[M(OH)_4{}^{2-}\right] = \log K_{S4} + 2pH - 28.$$

In each above equation, the term for log hydroxyl activity is substituted by the expression (pH - 14), based upon the self-ionisation of water.

There are many possibilities for metal-hydroxide complexes. In order to know the species of metal complex, metal hydroxide solubility product constants are necessary **(Table 3.4.1-1)** (Feitknecht and Schindler, 1963).

The concentrations of metal species (i.e. MOH^+, $M(OH)_2$, $M(OH)_3{}^-$, and $M(OH)_4{}^{2-}$) are too small to affect the concentrations of M^{2+} within this study. Although many metal species can be viewed as potential adsorbates in the uptake of M^{2+} from solution, the data presented in this study suggest that, under experimental conditions, the species responsible for the adsorptive removal of M^{2+} is the predominant one in the species distribution (**Figures 3.4.1-1** to **3.4.1-3**), namely, the M^{2+}. Thus, adsorption can be explained by elucidating the mechanism whereby the M^{2+} molecules are accommodated by the sphagnum moss peat surface.

TABLE 3.4.1-1: Metal Hydroxide Solubility Product Constants (Information From Feitknecht and Schindler, 1963).

	Log of Stability Product Constant				
Metal	K_{S0}	K_{S1}	K_{S2}	K_{S3}	K_{S4}
Copper	-18.8	-12.2	-20.6	-3.6	-2.7
Nickel	-17.2	-13.8	-7.0	-4.2	-
Lead	-15.3	-9.5	-4.5	-1.4	-0.7

The plateau on each isotherm corresponds to monolayer coverage of the surface by the ion and this value is the ultimate sorptive capacity at high concentrations can be used to estimate the specific surface area, S, of the peat using the following equation:

$$S = \frac{X_m \cdot N \cdot A}{M},$$

where

S is specific surface area, m^2/g peat;

X_m is monolayer adsorption capacity, g solute/g sorbent;

N is Avogadro number, 6.02×10^{23};

A is cross sectional area of solute, $Å^2$;

M is molecular weight of solute.

For Cu^{2+}, Ni^{2+}, and Pb^{2+} ions, the molecular weights are 63.5, 58.7, and 207 and the cross sectional areas of Cu^{2+}, Ni^{2+}, and Pb^{2+} have been determined to be 1.63 $Å^2$, 1.91 $Å^2$, and 5.47 $Å^2$ (Cu^{2+}, Ni^{2+}, and Pb^{2+} radius is 0.72 Å, 0.78Å, and 1.32Å,

Figure 3.4.1-1: Distribution of copper(II) species at various of pH values (Information from Feitknecht and Schindler, 1963).

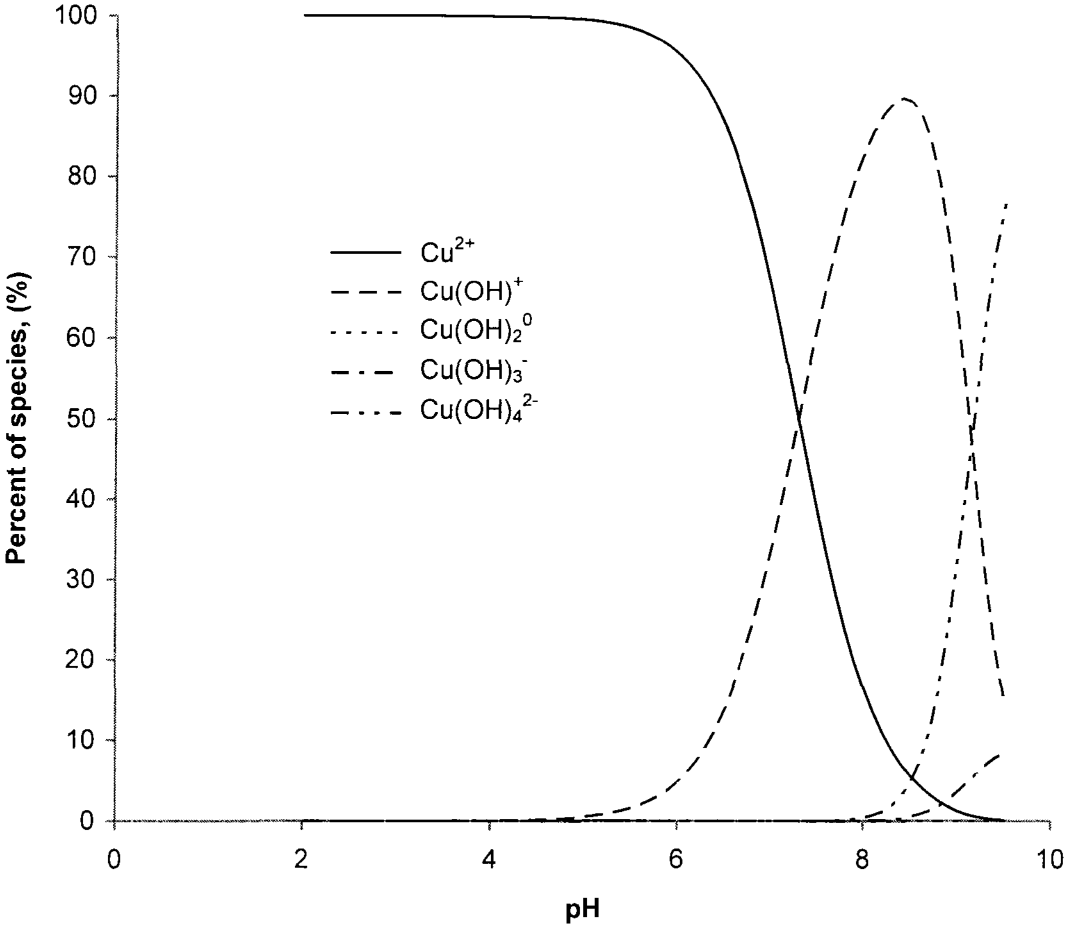


Figure 3.4.1-2: Distribution of nickel(II) species at various of pH values (Information from Feitknecht and Schindler, 1963).

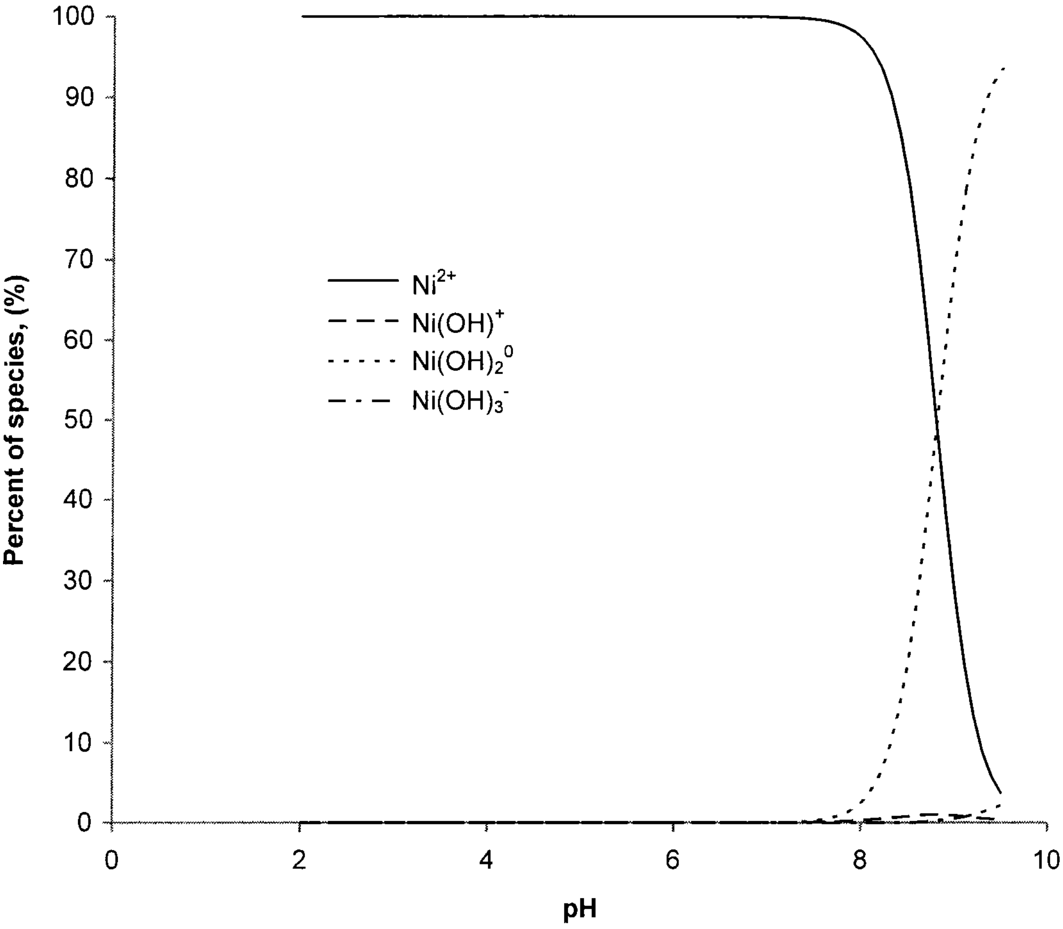
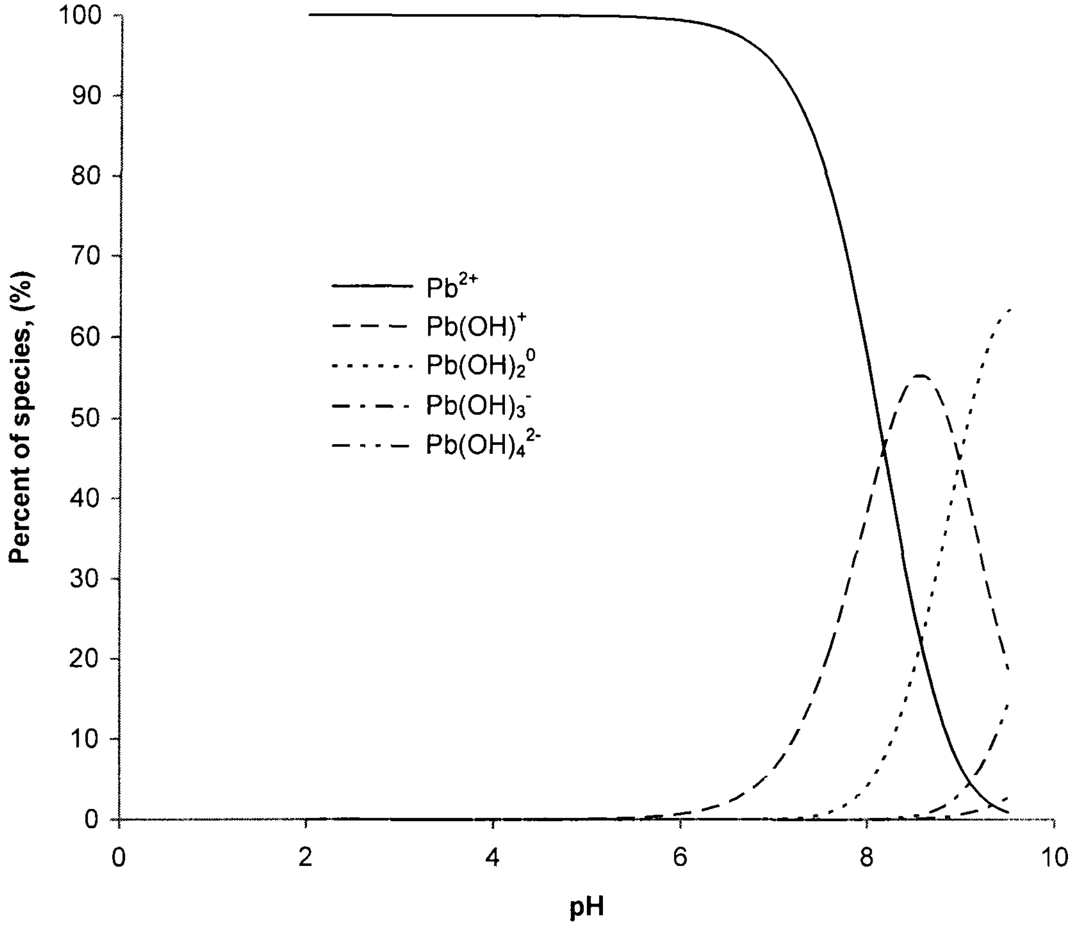


Figure 3.4.1-3: Distribution of lead(II) species at various of pH values (Information from Feitknecht and Schindler, 1963).



Mauahan, 1991) in a close packed monlayer. Therefore, the specific surface areas can be calculated for various pH values and are shown in **Tables 3.4.1-2** to **3.4.1-4**. The maximum specific surface area of peat towards Cu^{2+} binding at pH 5.0 and 25°C is 2.53 m^2/g; Ni^{2+} binding at pH 7.0 and 25°C is 1.80 m^2/g; Pb^{2+} binding at pH 5.0 and 37°C is 4.88 m^2/g.

TABLE 3.4.1-2: Specific Surface Areas for Various Initial pH Values for Copper at 25°C.

pH_{in}	Monolayer Coverage, X_m (mg Copper/g Peat)	Specific Surface (m^2/g Peat)
2.00	3.85	0.594
3.00	12.4	1.92
4.00	15.4	2.38
4.50	15.8	2.44
5.00	16.4	2.53

TABLE 3.4.1-3: Specific Surface Areas for Various Initial pH Values for Nickel at 25°C.

pH_{in}	Monolayer Coverage, X_m (mg Nickel/g Peat)	Specific Surface, S (m^2/g Peat)
2.00	1.23	0.240
3.00	5.53	1.08
4.00	7.84	1.54
5.00	8.13	1.59
6.00	8.52	1.67
7.00	9.18	1.80

TABLE 3.4.1-4: Specific Surface Areas for Various Initial pH Values Over a Range of Temperature for Lead.

pH_{in}	Temp. (°C)	Monolayer Coverage, X_m (mg Lead/g Peat)	Specific Surface, S (m^2/g Peat)
4.00	12	27.3	4.35
4.00	20	28.9	4.61
4.00	29	29.5	4.69
4.00	37	30.3	4.83
5.00	12	28.7	4.56
5.00	20	29.0	4.61
5.00	29	30.4	4.84
5.00	37	31.3	4.97
6.00	12	28.3	4.50
6.00	20	28.3	4.50
6.00	29	29.7	4.72
6.00	37	30.7	4.88

3.5. ISOTHERM SHAPE FACTOR ANALYSIS

The effect of isotherm shape has been discussed with a view to predicting whether an adsorption system is "favourable" or "unfavourable" in a fixed-bed (Weber and Chakravorti, 1974) as well as in batch adsorption systems (Poots *et al.*, 1978; Poots and McKay, 1979). According to Hall *et al.* (1966) the essential features of the Languir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R which is defined by the following relationship:

$$K_R = \frac{1}{1 + k \cdot C_0}.$$

This parameter indicates the shape of the isotherm accordingly:

Values of K_R	Type of Isotherm
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

The constant k is the constant from the Langmuir isotherm when expressed in the following way:

$$q_e = \frac{X_m \cdot k \cdot C_e}{1 + k \cdot C_e},$$

where

C_e is the experimental concentration of metal ion in solution at equilibrium.

The Langmiur isotherm includes a description of the equilibrium between the concentration, C_s, and the saturation level, q_s,

$$q_s = \frac{X_m \cdot k \cdot C_s}{1 + k \cdot C_s}.$$

The relation for saturation conditions can be divided into the general relation, resulting in

$$\frac{q_e}{q_s} = \frac{C_e(1 + k \cdot C_s)}{C_s(1 + k \cdot C_e)}.$$

Dimensionless concentrations,

$$C = \frac{C_e}{C_s}, \qquad (3.5\text{-}1)$$

and

$$Q = \frac{q_e}{q_s}, \tag{3.5-2}$$

are introduced, each bounded by the values 0 and 1. The relation between these term and the Langmuir isotherm then becomes:

$$Q = \frac{C}{K_R + (1 - K_R) \cdot C}. \tag{3.5-3}$$

For a single solute adsorption system, C_s, is usually the highest fluid-phase concentration encountered and q_s is the equilibrium solid phase concentration coexisting with C_s. Substitution of equations of **(3.5-1)** and **(3.5-2)** into equation **(3.5-3)** yields:

$$K_R = \frac{C_e(q_s - q_e)}{q_e(C_s - C_e)}.$$

The values of K_R are shown in **Figures 3.5-1** to **3.5-3** for peat at different conditions though a plot of dimensionless solid-phase concentration, Q, against dimensionles liquid-phase concentration, C.

The values of K_R (**Figures 3.5-1** to **3.5-3**) at pH 4.0, 5.0, and 6.0, and 12, 20, 29, and 37°C for the adsorption of lead are between 0.1 and 0.15; at pH 2.0 to 5.0 for the adsorption of copper are between 0.05 and 0.2; and in the range of pH 2 to 7 for nickel are between 0.05 and 0.2. The K_R values indicate that adsorption is more favourable for higher initial metal ion concentrations then for lower but the effects of adsorption on pH are slight, especially at typical temperatures for the lead system. All three metal ion systems show favourable adsorption, that is, $0 < K_R < 1$.

Figure 3.5-1: Shape factor (K_R) plots for the copper-peat system at various initial pH values.

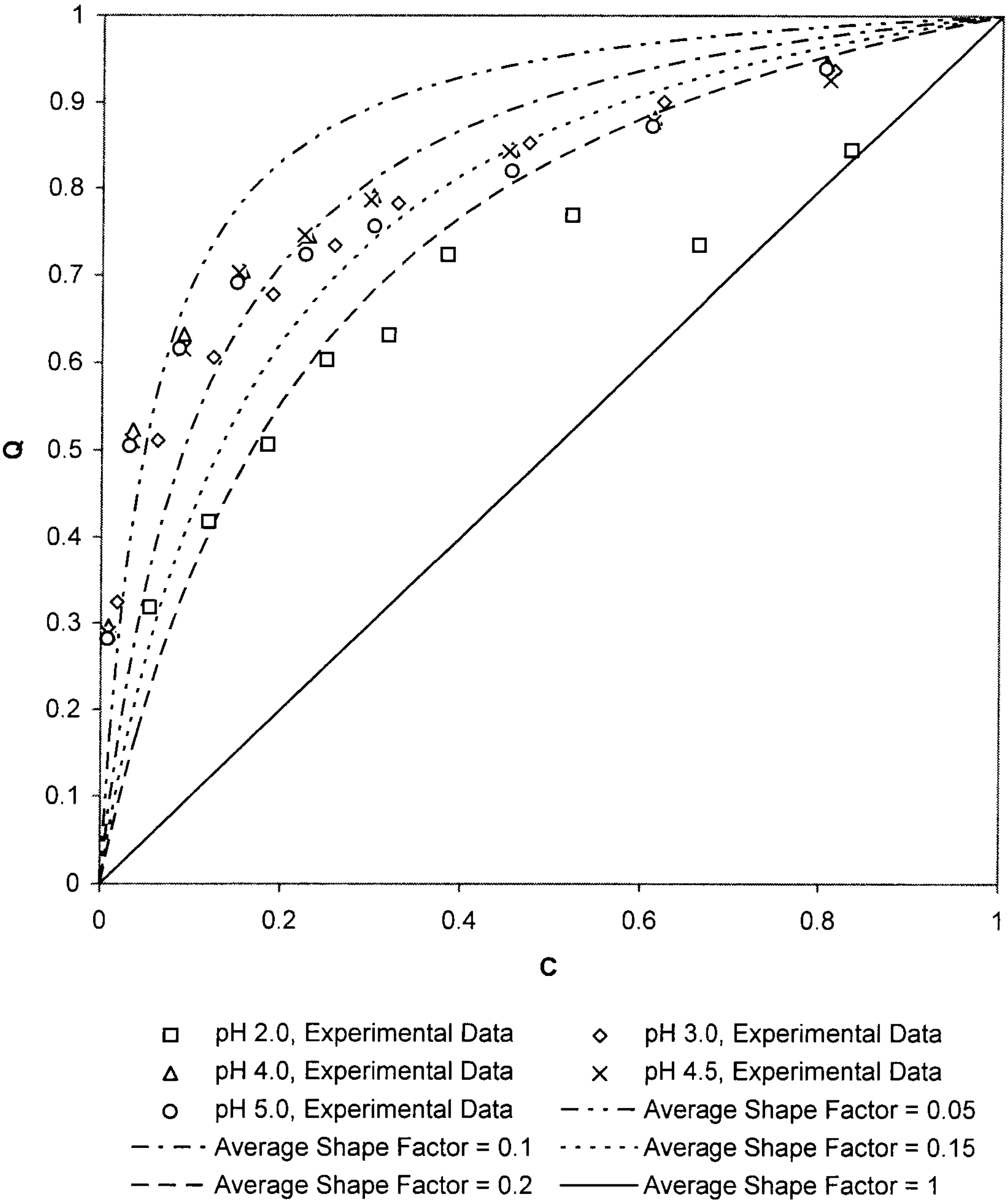


Figure 3.5-2: Shape factor (K_R) plots for the nickel-peat system at various initial pH values.

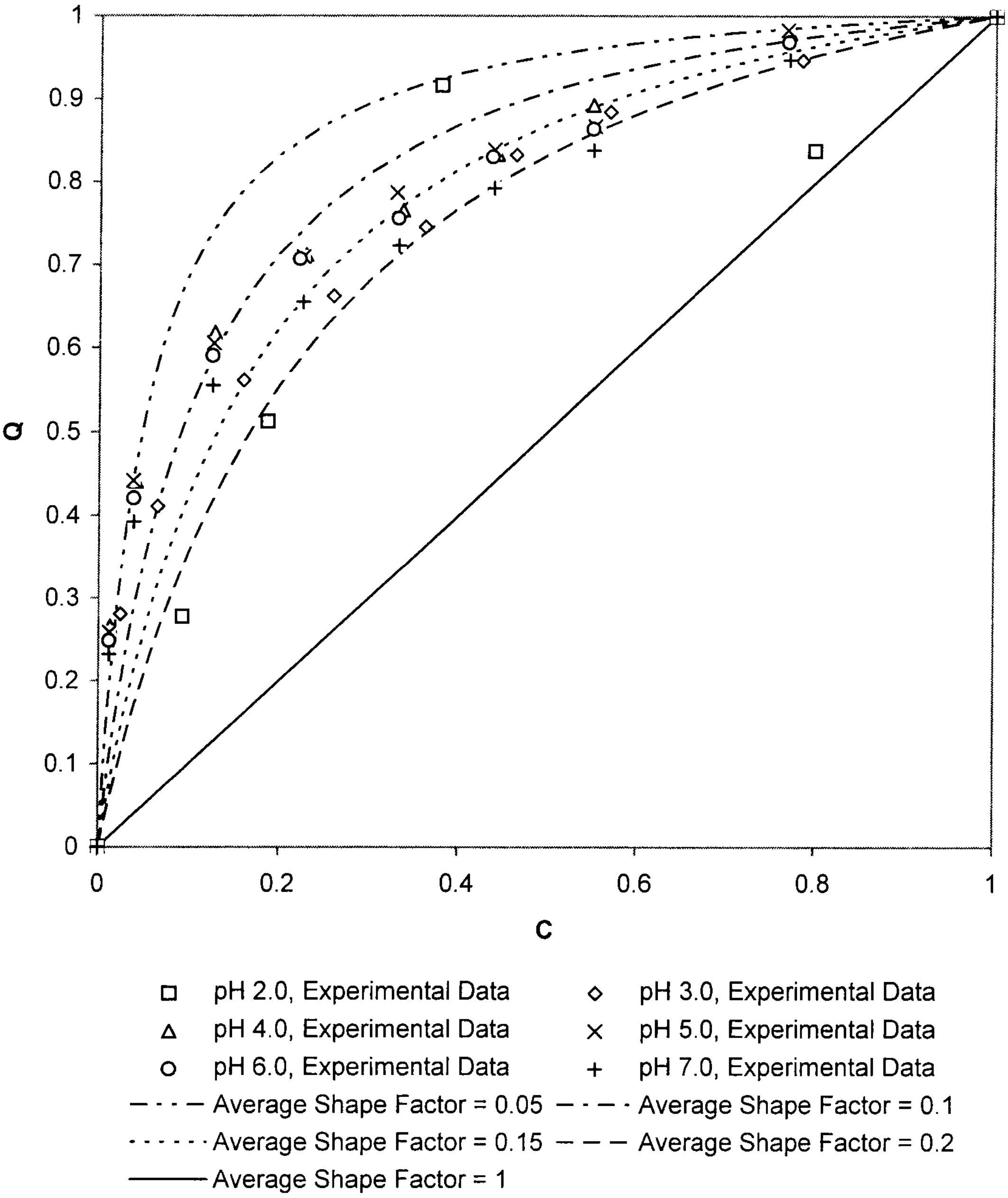
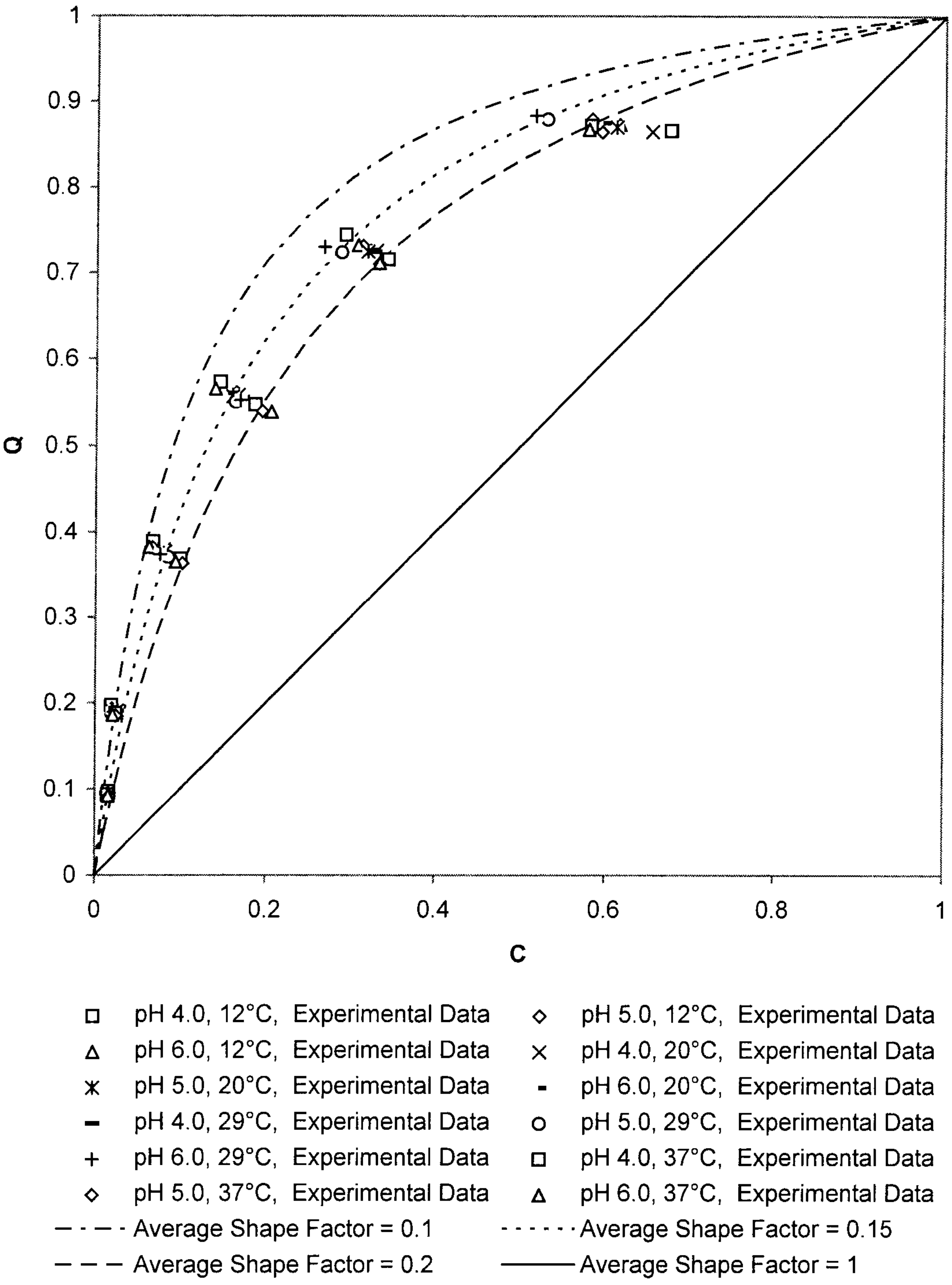


Figure 3.5-3: Shape factor (K_R) plots for the lead-peat system at various initial pH values.



3.6. HYDROXYL ION COMPETITION

Depending on the mode of proton interaction with the metal adsorption process, three modified forms of Langmuir adsorption equations that incorporate the effect of proton adsorption are possible: competitive, noncompetitive, and uncompetitive (Huang *et al.*, 1991). Competitive inhibition occurs when an agent other than the preferred one reversibly occupies the complexation site. Uncompetitive inhibition can be the result of chemical transformations that cannot be reversed by increasing the solute concentration. If the inhibition is caused by a combination of the above mechanisms then the inhibition is defined as noncompetitive (Gould and Genetelli, 1978). The linearized adsorption isotherm is described below.

1. Competitive Mode

The general form of the Langmuir adsorption isotherm is

$$\frac{C_e}{q_e} = \frac{1}{X_m} \cdot C_e + \frac{1}{X_m \cdot k}.$$

For proton-competitive adsorption, the slope is modified to include the effect of pH, and then the Langmuir isotherm becomes:

$$\frac{C_e}{q_e} = \frac{1}{X_m} \cdot C_e + \frac{1}{X_m \cdot k} \cdot \left(1 + \frac{[H^+]}{K_i}\right),$$

where

$[H^+]$ is proton concentration, (M);

K_i is the reaction constant between protons and the surface of peat.

2. Uncompetitive Mode

For uncompetitive proton inhibition, the metal ions are adsorbed on the peat directly prior to the formation of M-H-peat complexes. The lineralized Langmuir adsorption isotherm then takes the form:

$$\frac{C_e}{q_e} = \frac{1}{X_m} \cdot \left(1 + \frac{[H^+]}{K_i}\right) \cdot C_e + \frac{1}{X_m \cdot k}.$$

3. Noncompetitive Mode

For noncompetitive proton inhibition, the interaction of metal ions with surface sites is independent of proton interaction. Either metal or proton ions can be adsorbed independently at different sites on the peat and/or proton ions can react with M-peat complexes. The Langmuir adsorption isotherm is then modified as:

$$\frac{C_e}{q_e} = \frac{1}{X_m} \cdot \left(1 + \frac{[H^+]}{K_i}\right) \cdot C_e + \frac{1}{X_m \cdot k} \cdot \left(1 + \frac{[H^+]}{K_i}\right).$$

Figures 3.6-1 to **3.6-3** summarise the linearized plots of the modified Langmuir adsorption isotherms.

To determine reaction constants:

- plot (C_e/q_e) versus (C_e) for various [H^+] and obtain $\frac{1}{X_m} \cdot \left(1 + \frac{[H^+]}{K_i}\right)$ from slope and $\frac{1}{X_m k} \cdot \left(1 + \frac{[H^+]}{K_i}\right)$ from intercept **Figures 3.1.2-1** and **3.2.2-1**;
- plot $\frac{1}{X_m} \cdot \left(1 + \frac{[H^+]}{K_i}\right)$, which is the slope of (C_e/q_e) and (C_e) lines, versus [H^+] and determine $1/X_m$ from intercept at ordinate of the line shown in **Figures 3.6-4** and **3.6-5**;
- determine K_i from intercept at abscissa of the line shown in **Figures 3.6-4** and **3.6-5**;

Figure 3.6-1: Graph illustrating the effect of competitive inhibition on adsorption of a metal by peat (Huang *et al.*, 1991).

Figure 3.6-2: Graph illustrating the effect of uncompetitive inhibition on adsorption of a metal by peat (Huang *et al.*, 1991).

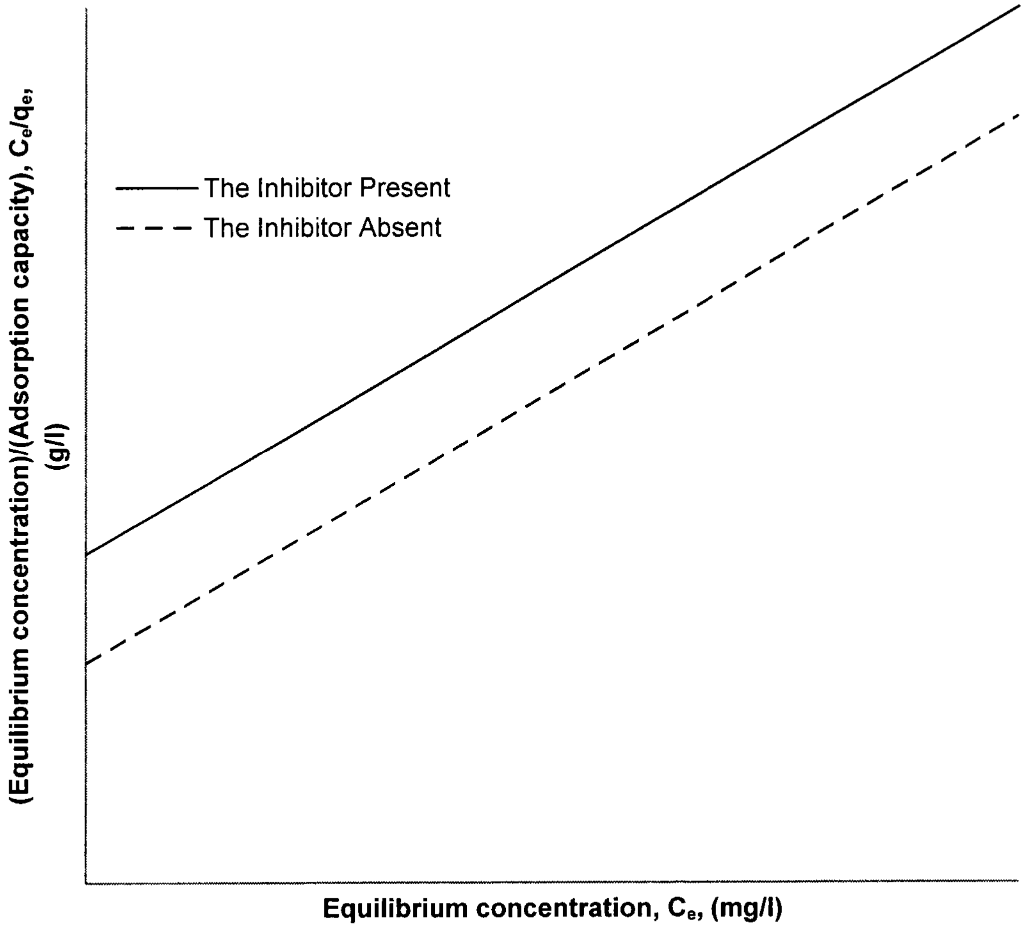


Figure 3.6-3: Graph illustrating the effect of noncompetitive inhibition on adsorption of a metal by peat (Huang *et al.*, 1991).

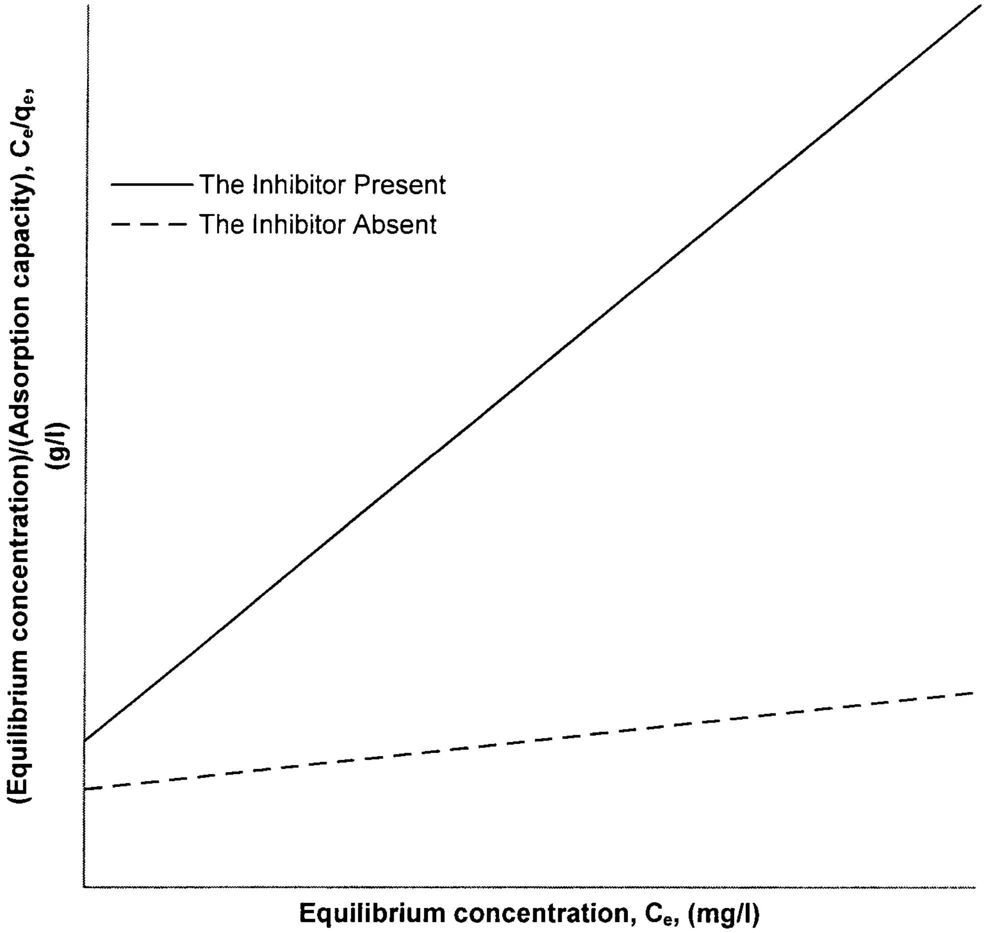


Figure 3.6-4: Linearised Langmuir plots for noncompetitive adsorption in the copper-peat system.

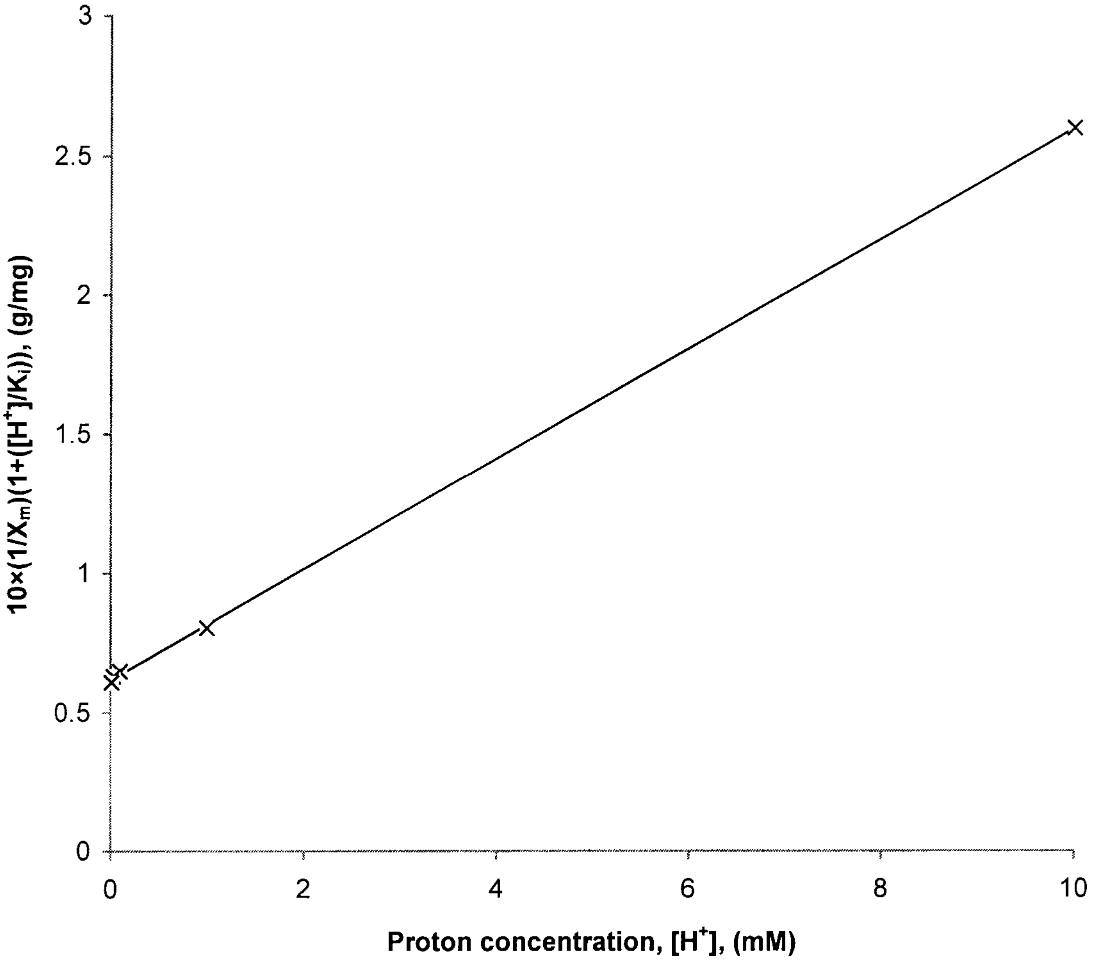
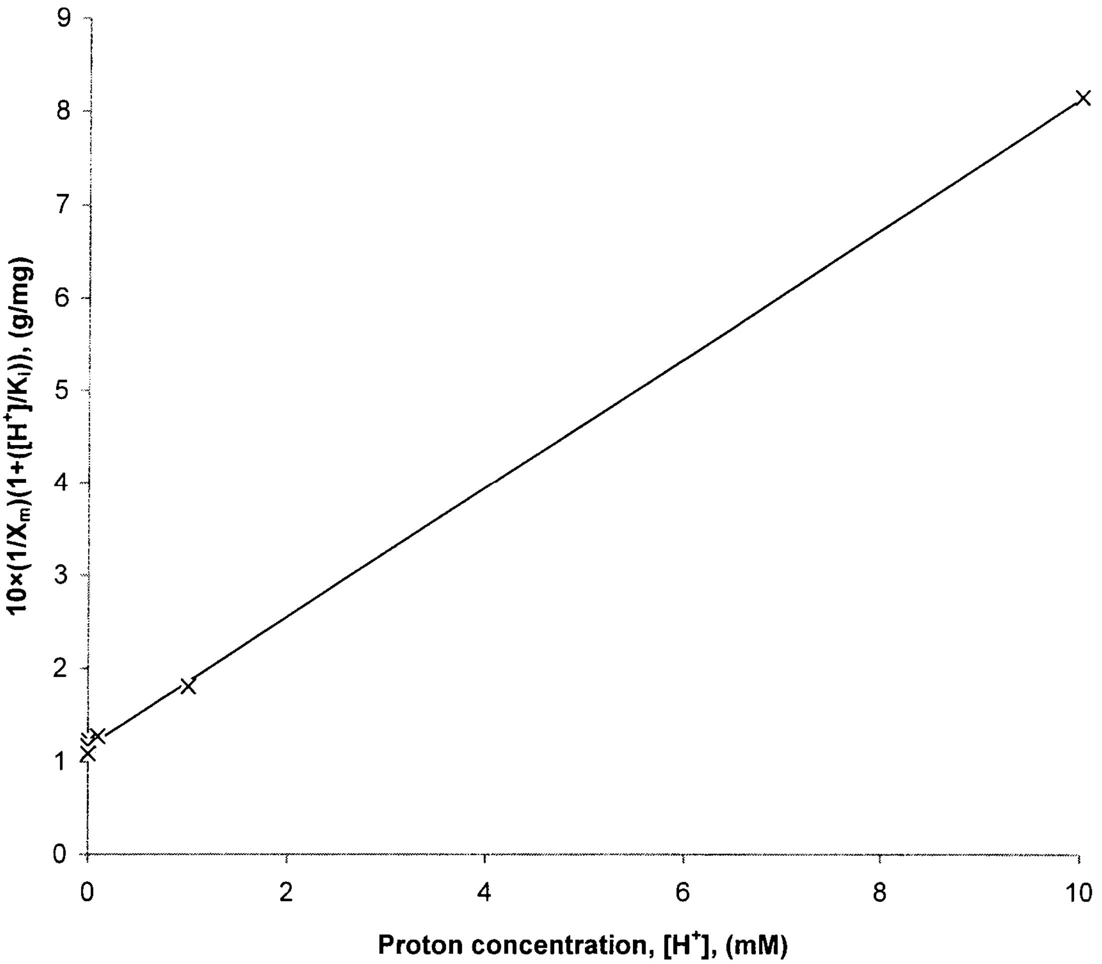


Figure 3.6-5: Linearised Langmuir plots for noncompetitive adsorption in the nickel-peat system.



- plot $\frac{1}{X_m k} \cdot \left(1 + \frac{[H^+]}{K_i}\right)$, which is the intercept of (C_e/q_e) and (C_e) lines, versus $[H^+]$ and determine $1/X_m k$ from intercept at ordinate of the line shown in **Figures 3.6-6** and **3.6-7**.

By examining the linear plots of the (C_e/q_e) versus (C_e) diagram (**Figures 3.1.2-1** and **3.2.2-1**), it is concluded that the hydrogen ion acts as a noncompetitive inhibitor over the pH range 2.0 to 5.0 for the copper-peat system and 2.0 to 7.0 for the nickel-peat system. The hydrogen ion in a similar chromium-peat adsorption system has been described as noncompetitive (Sharma, 1994). For copper, the value of the various adsorption constants obtained were X_m is 16.2 mg/g, k is 0.0836 l/mg, and K_i is 3.12 mM. Similarly the value of various adsorption constants for nickel-peat were X_m is 8.61 mg/g, k is 0.0601 l/mg, and K_i is 1.66 mM.

Figure 3.6-6: Linearised Langmuir plots for noncompetitive adsorption in the copper-peat system.

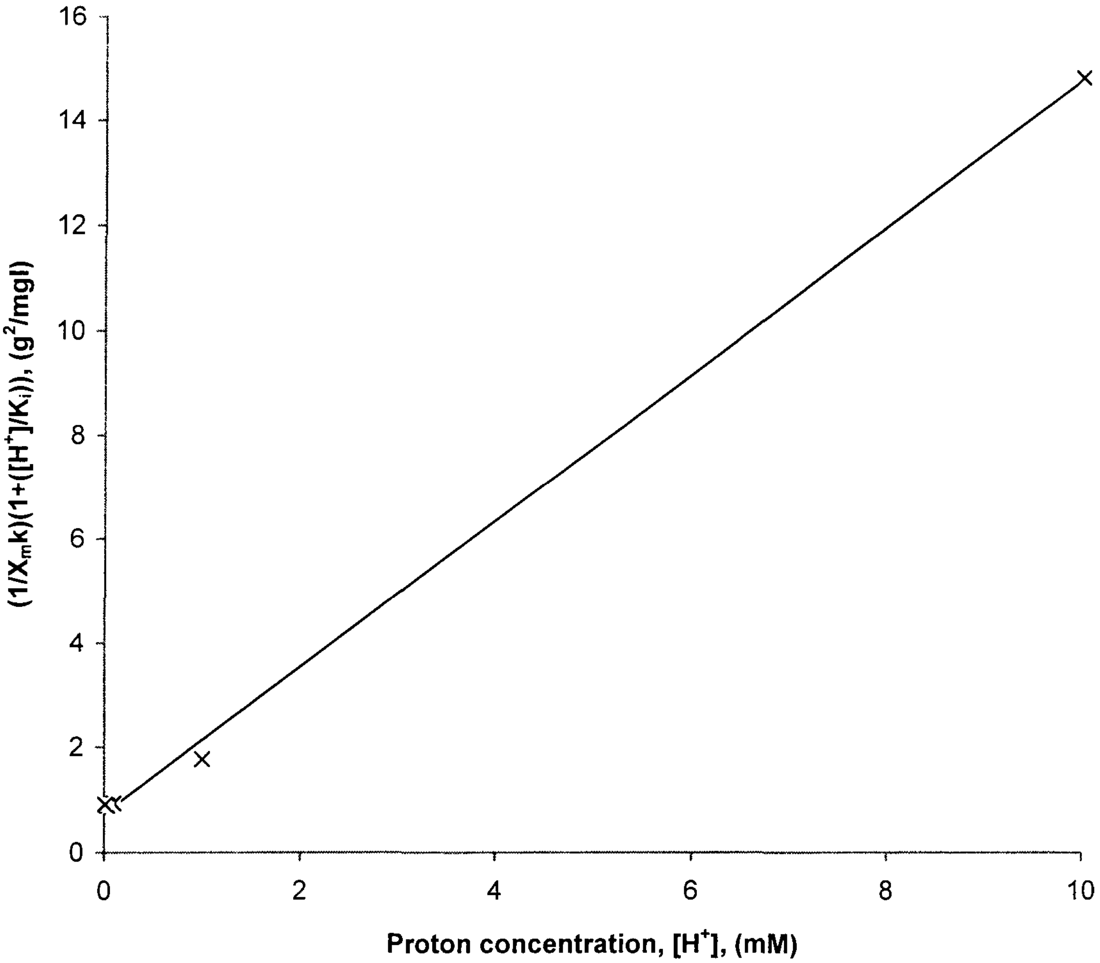
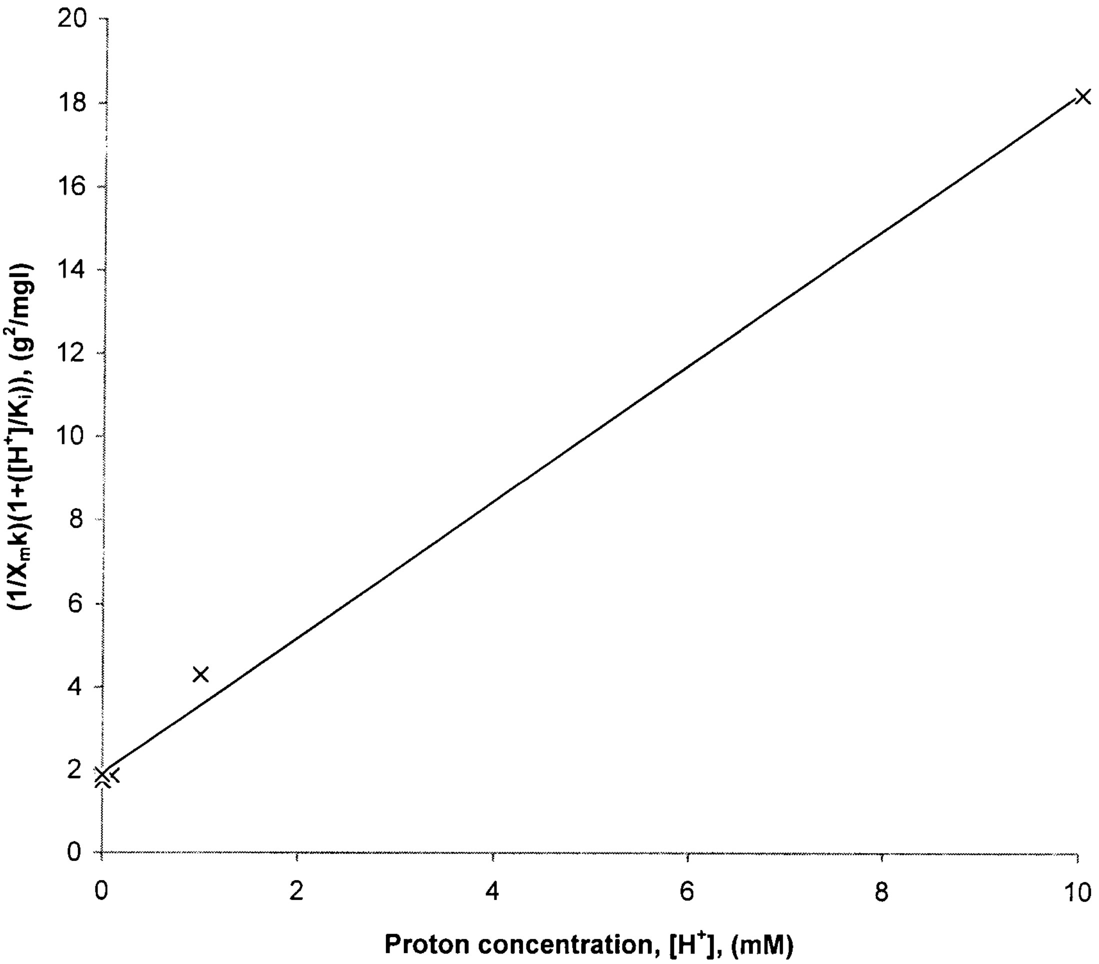


Figure 3.6-7: Linearised Langmuir plots for noncompetitive adsorption in the nickel-peat system.



CHAPTER FOUR

RESULTS AND DISCUSSION SORPTION KINETICS

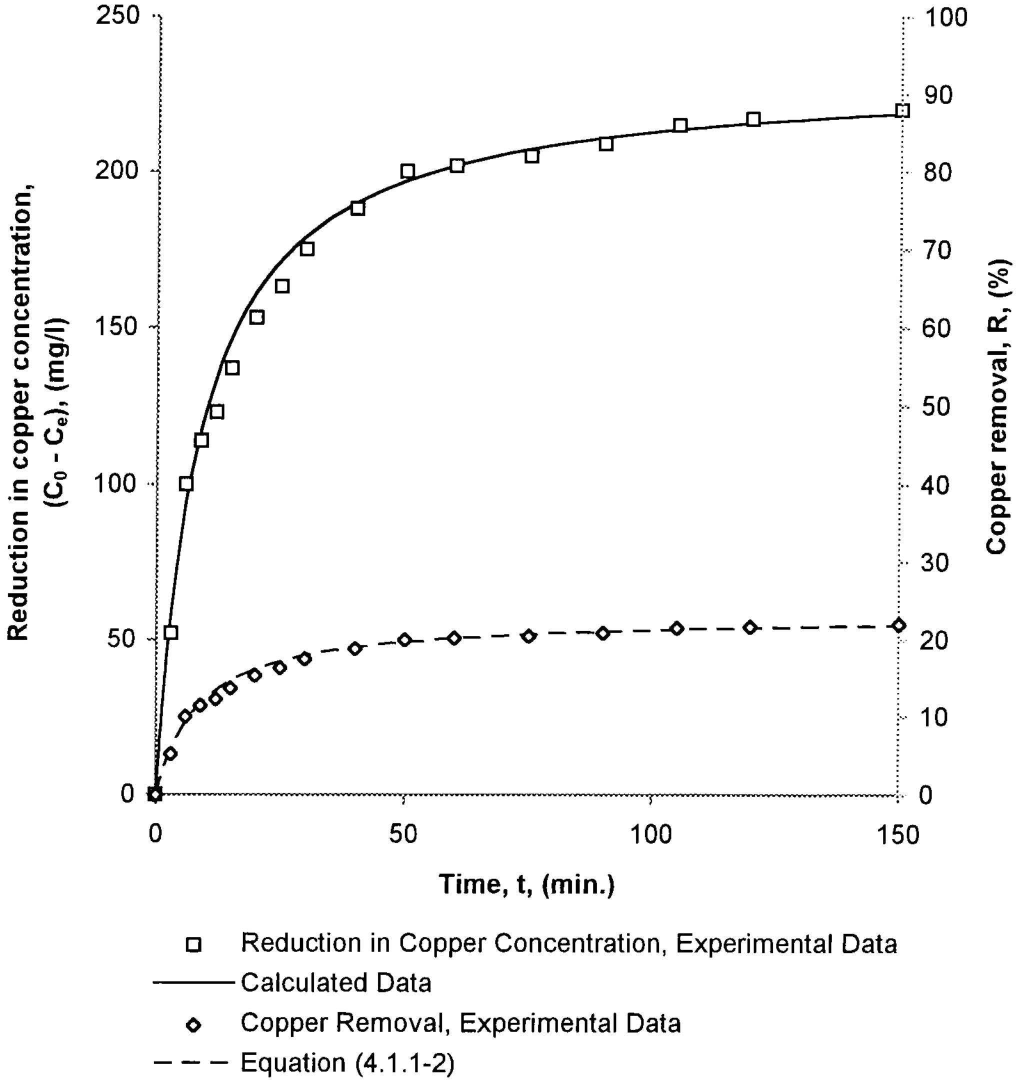
4.1. ADSORPTION KINETICS

4.1.1. Kinetics of Copper Removal

The effect of contact time on the copper(II) removal was investigated using initial copper concentrations of 1000 mg/l and a solution pH of 5.0. The results are presented in **Figure 4.1.1-1**. The sorption of copper(II) on peat was noted to consist of a rapid initial uptake step followed by a slow approach to equilibrium. This rapid initial step may be physical adsorption and the slow prolonged period may be chemical adsorption, with possibly pore diffusion as well.

It is clear from this figure that the removal of copper also attained an equilibrium condition in approximately 50 minutes. The decreasing removal rate, particularly towards the end, indicates a possible monolayer of copper ions on the outer interface of the peat, and pore (interparticle) diffusion onto the inner surface of the adsorbent particles through the film due to the continuous agitation maintained during the experiments. The percent copper removal against the reaction time is shown in (**Figure**

Figure 4.1.1-1: Copper reduction (C_0 - C_e) in soluble copper and copper removal (R) by peat as a function of time (t).



4.1.1-1). It shows a comparison of experimental values with those obtained using equation (**4.1.1-1**); the correlation coefficient was 0.997.

$$R = \frac{t}{\frac{1}{\alpha} + \frac{t}{R_e}}, \qquad (4.1.1\text{-}1)$$

and linear form

$$\frac{t}{R} = \frac{1}{\alpha} + \frac{t}{R_e}.$$

where

R is the percentage of metal ion removal at any time, (%);

t is the reaction time, (min.);

R_e is the maximum percentage of metal ion removal at equilibrium, (%);

α is the metal ion removal of the unit of time at t = 0, (%/min.).

A predictive model for the percent copper ion removal, R, for any time, within the test limits at pH of 5.0 and initial copper concentration of 1000 mg/l can be presented as:

$$R = \frac{t}{3.75 \times 10^{-2} + 4.32 \times 10^{-3} t}, \qquad (4.1.1\text{-}2)$$

and

$$\frac{t}{R} = \frac{1}{2.67} + \frac{t}{2.31 \times 10}.$$

In the absence of stoichiometric data, the simplest way to describe metal removal by peat is:

$$P + M \Leftrightarrow PM,$$

with $K' = (PM)/(P)(M) = k_b/k_r$

where

(P) is the concentration of peat binding sites, (mg/l);

(M) is the concentration of free metal in solution, (mg/l);

(PM) is the concentration of metal bound to peat, (mg/l);

K′ is the apparent conditional stability constant, (l/mg).

k_b (l/mgmin.) and k_r (1/min.) are the forward and reverse kinetic constants respectively. Based on this equation, Gosset *et al.* (1986) developed a technique for obtaining the binding kinetic constant k_b. This required the following assumptions:

- reverse reaction, k_r, is negligible;
- peat metal anion stoichiometry was constant for all experimental conditions and equal to one metal ion per binding site;
- overall kinetics were limited by the binding reaction itself and not the diffusion of species.

Gosset *et al.* (1986) then developed an expression to describe these reactions:

$$k_b t = \frac{1}{(PM)_{\lim} - (M)_{in}} \cdot \ln \frac{(M)_{in}}{(PM)_{\lim}} \cdot \frac{(PM)_{\lim} - (PM)}{(M)_{in} - (PM)}, \qquad (4.1.1\text{-}3)$$

where

(PM) and $(PM)_{\lim}$ are the variable and equilibrium bound metal concentration, (mg/l);

$(M)_{in}$ is the initial free metal concentration, (mg/l).

Thus, by plotting ($k_b t$) against time, t, values of k_b can be calculated. Such a plot is shown in **Figure 4.1.1-2**. With the current data, the relationship was found to be linear with a correlation coefficient of 0.969 (**Table 4.1.1-1**). The quality of this correlation supports the set of assumptions concerning the kinetics and especially the assumption of a chemical rate limiting step.

TABLE 4.1.1-1: Kinetic Constants of Adsorption.

C_0 (mg/l)	Corr. Coeff. r^2	k_b (l/mgmin.)	Saturation Time (min.)	Removal (%)
1000	0.969	5.58×10^{-5}	50	20.0

The equation can be rearranged as:

$$(PM) = (M)_{in} \cdot \frac{\exp\{[(M)_{in} - (PM)_{\lim}] \cdot k_b \cdot t\} - 1}{\frac{(M)_{in}}{(PM)_{\lim}} \cdot \exp\{[(M)_{in} - (PM)_{\lim}] \cdot k_b \cdot t\} - 1}. \qquad (4.1.1\text{-}4)$$

Thus, it can be used to calculate the concentration of copper adsorbed at any given time in a batch reactor. However, it does not take into account the effect of peat dose and the pH, although a similar relationship could be developed by evaluating k_b values as a function of pH and adsorbent dosing rate. **Figure 4.1.1-3** shows a comparison of experimental values with the values obtained using the equation (**4.1.1-4**). It is seen from this figure that the agreement is generally good, differences between experimental and calculated data being insignificant. Such agreement supports the set of assumptions concerning the kinetics and especially the assumption of a chemical rate limiting step.

Figure 4.1.1-2: Kinetic plots showing $k_b t$ against time (t).

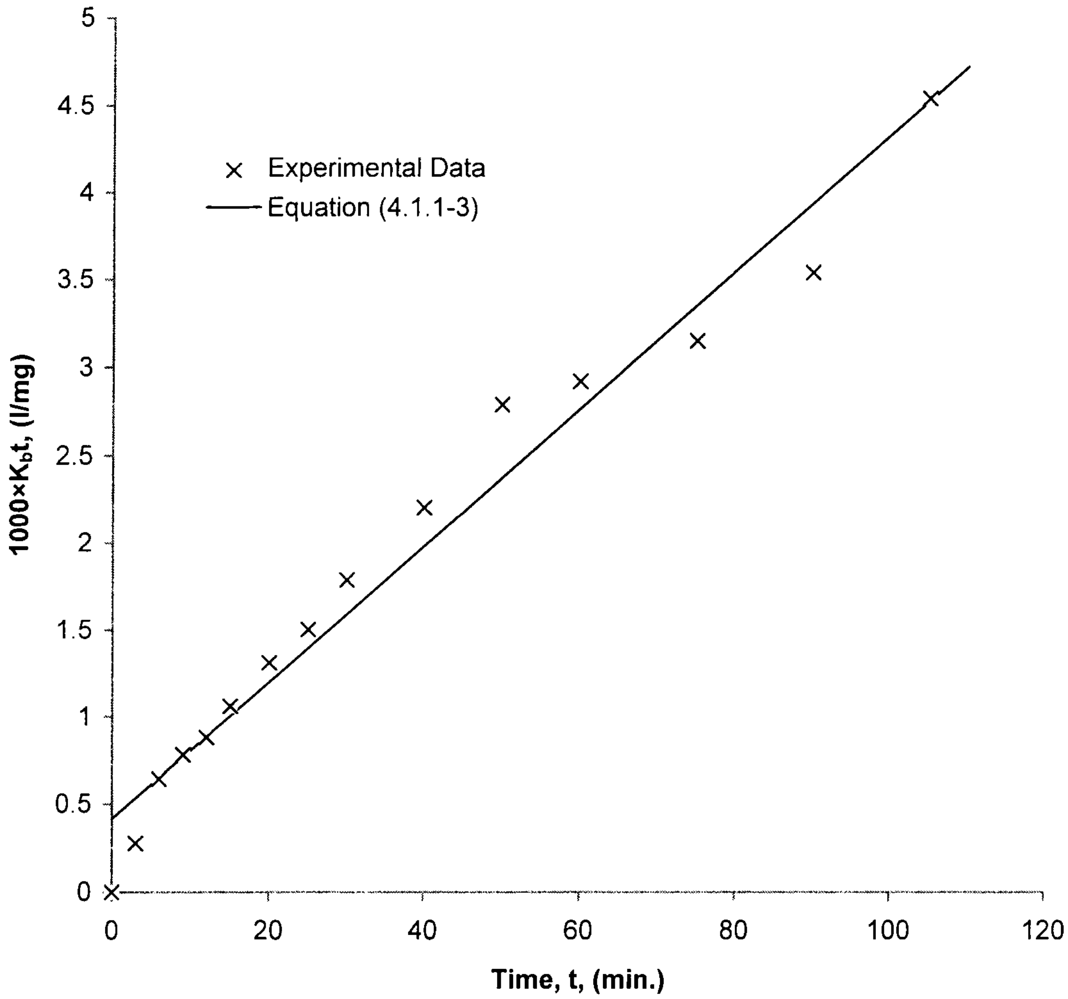
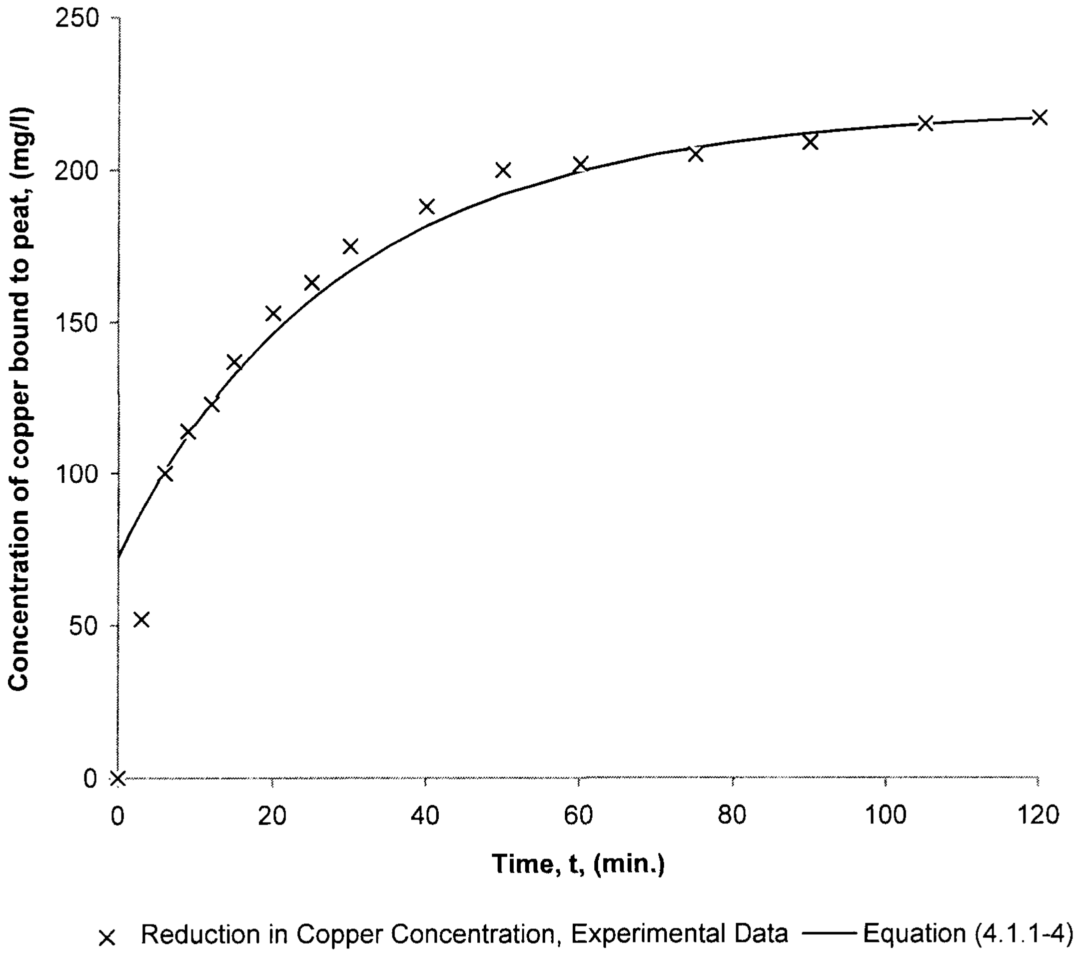


Figure 4.1.1-3: Kinetic plots showing a comparison of experimental values with those obtained using equation (4.1.1-4) in the copper-peat system.



4.1.2. Kinetics of Nickel Removal

The effect of contact time on nickel(II) removal was investigated at initial nickel concentrations of 50 to 400 mg/l, to optimise the residence time of the waste water treatment units. The results are presented in **Figure 4.1.2-1** and show how the amount of nickel bound to the peat changed with time. In this experiment, the nickel solutions in contact with peat were initially at pH 5.0. The relation between nickel reduction (C_0 - C_e) and reaction time can be found with a correlation coefficient as high as 0.999 when the nickel concentrations were 50 to 200 mg/l, and 0.996 at 400 mg/l. The relation can be expressed as:

at C_0 = 50 mg/l,

$$(50-C_e)=\frac{t}{7.68\times10^{-2}+2.64\times10^{-2}t}; \qquad (4.1.2\text{-}1)$$

at C_0 = 100 mg/l,

$$(100-C_e)=\frac{t}{7.29\times10^{-2}+1.60\times10^{-2}t}; \qquad (4.1.2\text{-}2)$$

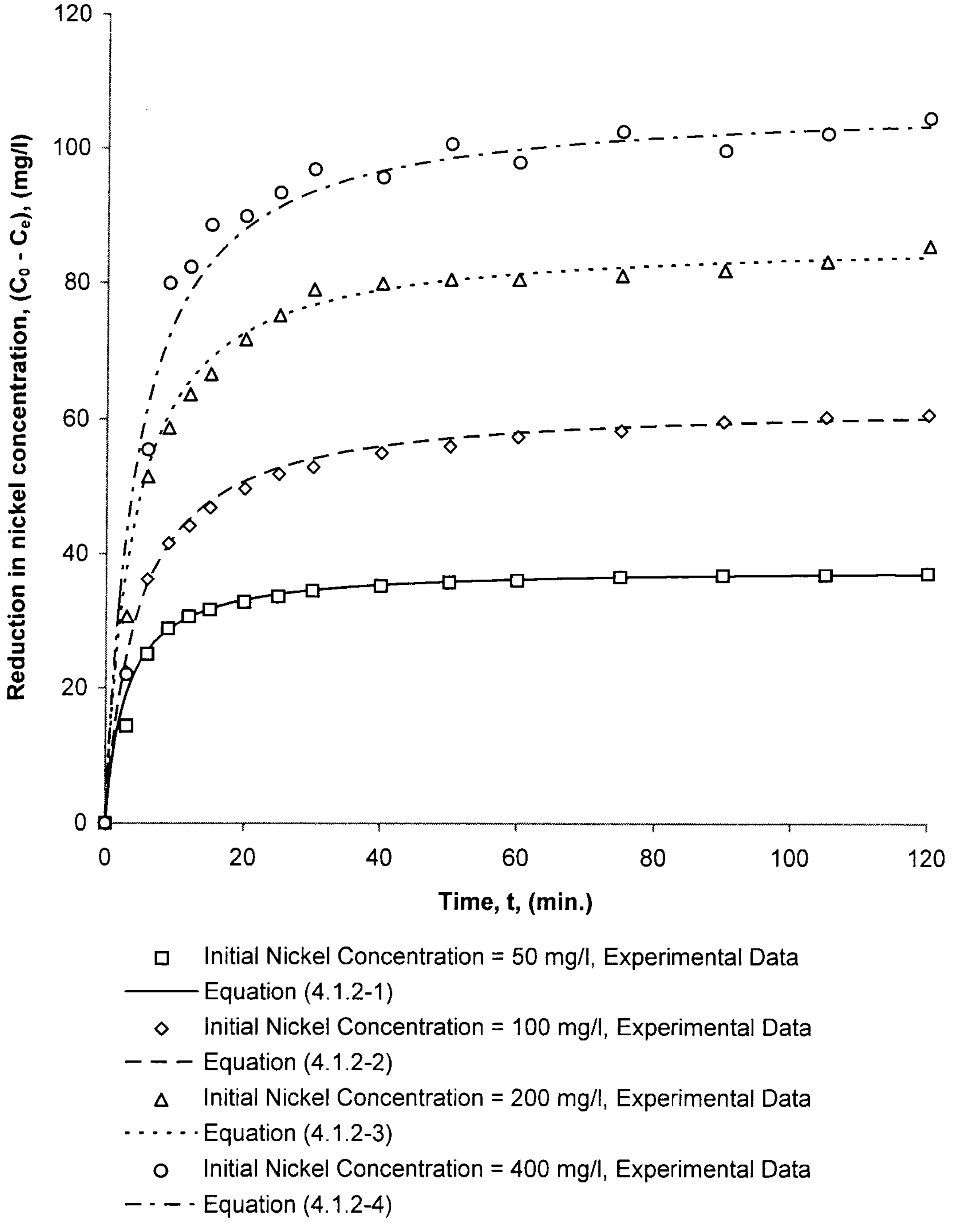
at C_0 = 200 mg/l,

$$(200-C_e)=\frac{t}{4.40\times10^{-2}+1.16\times10^{-2}t}; \qquad (4.1.2\text{-}3)$$

at C_0 = 400 mg/l,

$$(400-C_e)=400-\frac{t}{4.03\times10^{-2}+9.34\times10^{-3}t}. \qquad (4.1.2\text{-}4)$$

Figure 4.1.2-1: Nickel reduction (C_0 - C_e) in soluble nickel by peat as a function of time (t) at various initial nickel concentrations.



The percent nickel(II) removal for different contact times were done using the same data and are shown in **Figure 4.1.2-2**. It shows the comparison of experimental values with those obtained using equation (**4.1.1-1**).

A predictive model for the percent nickel ion removal, R, for any time, within the test limits at pH of 5.0 and initial nickel concentration of 50 to 400 mg/l can be presented as:

$$R = \frac{t}{3.84 \times 10^{-2} + 1.32 \times 10^{-2} t}, \tag{4.1.2-5}$$

$$R = \frac{t}{7.29 \times 10^{-2} + 1.60 \times 10^{-2} t}, \tag{4.1.2-6}$$

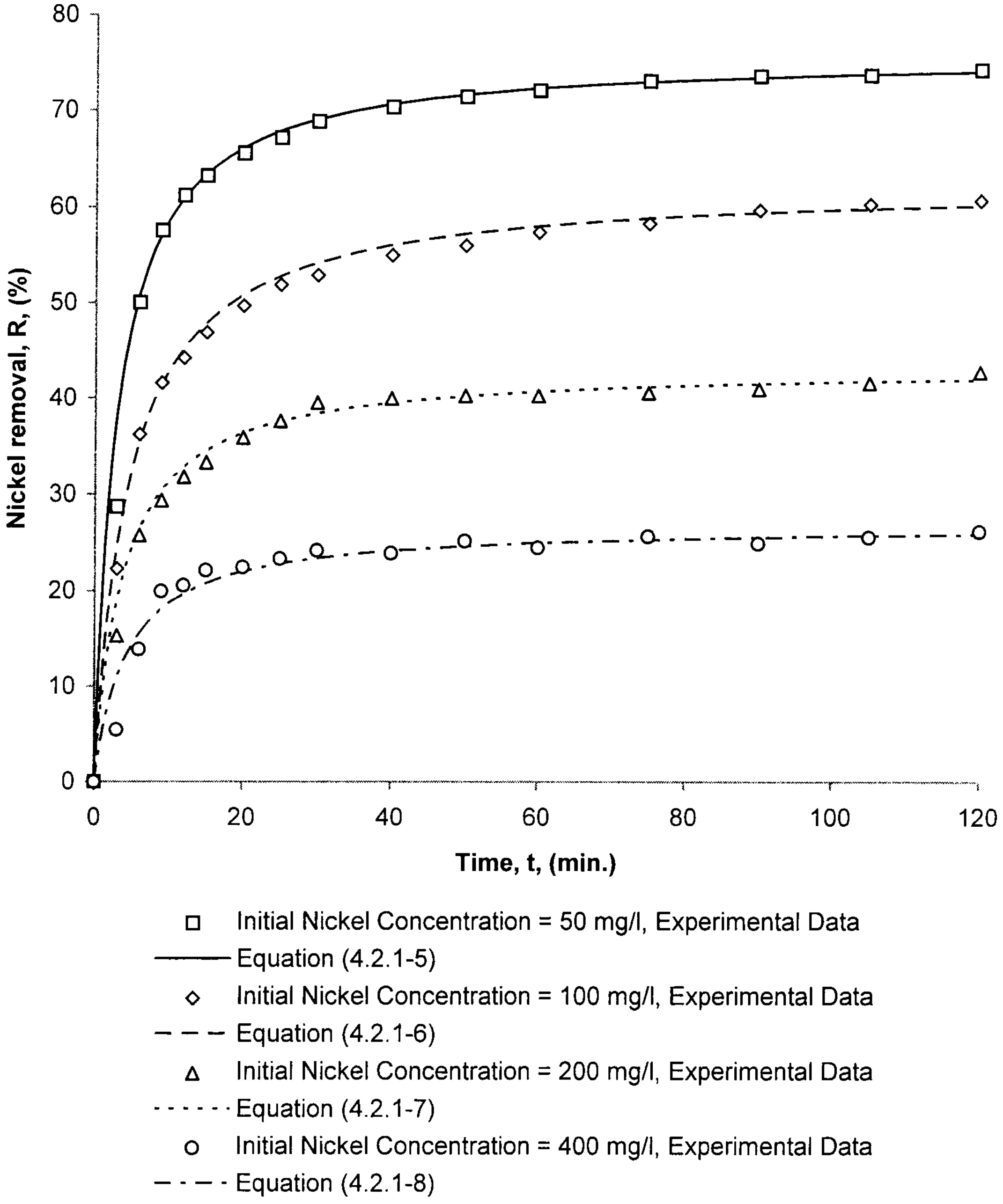
$$R = \frac{t}{8.79 \times 10^{-2} + 2.31 \times 10^{-2} t}, \tag{4.1.2-7}$$

$$R = \frac{t}{1.16 \times 10^{-1} + 3.74 \times 10^{-2} t}, \tag{4.1.2-8}$$

Figure 4.1.2-2 also shows that removal of nickel increased and attained almost an equilibrium condition in approximately 25, 40, 60, and 75 minutes for initial concentrations of 50, 100, 200, and 400 mg/l respectively. This indicates that the equilibrium time is not independent of the initial concentration, probably because the adsorption sites adsorbed the available nickel more quickly at low solute concentrations. However, for higher concentrations, interparticle diffusion or creation of new sites were predominant adsorption mechanisms. This decreasing removal rate, particularly towards the end, suggests formation of a monolayer of nickel ions on the outer surface of the peat and pore (interparticle) diffusion onto the inner surface of the adsorbent particles through the film due to continuous agitation maintained during the experiments.

Several hypotheses have been advanced to explain the variations in pH which arise when peat is added to a metal cation solution. These include: the acidic properties

Figure 4.1.2-2: Nickel removal (R) of peat as a function of time (t) at various initial nickel concentrations.



of carboxylic and phenolic functional groups present in humic substances (Bloom and McBride, 1979; and Boyd *et al.*, 1981); some ion exchange reactions, such as proton release when metal cations bind to peat (Bunzl *et al.*, 1976; Bloom and McBride, 1979; and Aho and Tummavuori, 1984).

Gosset *et al.* (1986) have developed an expression for the kinetic constant, k_b, for the binding of metal ion to peat (equation **4.1.1-3**). It has been examined (Sharma and Forster, 1993) for the binding of chromium ion to peat.

Kinetic plots of the data for nickel removal are presented in **Figure 4.1.2-3**. The relationship is linear, and the correlation coefficients (**Table 4.1.2-1**), suggest a strong relationship between the parameters. The kinetic constant k_b increased with decreasing nickel concentration **Figure 4.1.2-4**.

TABLE 4.1.2-1: Kinetic Constants of Adsorption of Nickel to Peat.

C_0 (mg/l)	Corr. Coeff. r^2	k_b (l/mgmin.)	Saturation Time (min.)	Removal (%)
50	0.982	3.51×10^{-3}	25	67.9
100	0.974	9.84×10^{-4}	40	56.1
200	0.843	3.22×10^{-4}	60	40.7
400	0.785	1.37×10^{-4}	75	25.3

The linearised k_b and C_0 values on a double logarithmic plot showed a correlation coefficient of 0.992 and the relationship between k_b and C_0 being of the type:

$$k_b = a \cdot C_0^{\,b}.$$

The values of a and b were found to be 1.44 and -1.56 respectively; and so the equation can be written as:

$$k_b = 1.44 C_0^{-1.56}. \qquad (4.1.2\text{-}9)$$

Figure 4.1.2-3: Kinetic plots showing K_bt against time (t) at various initial nickel concentrations.

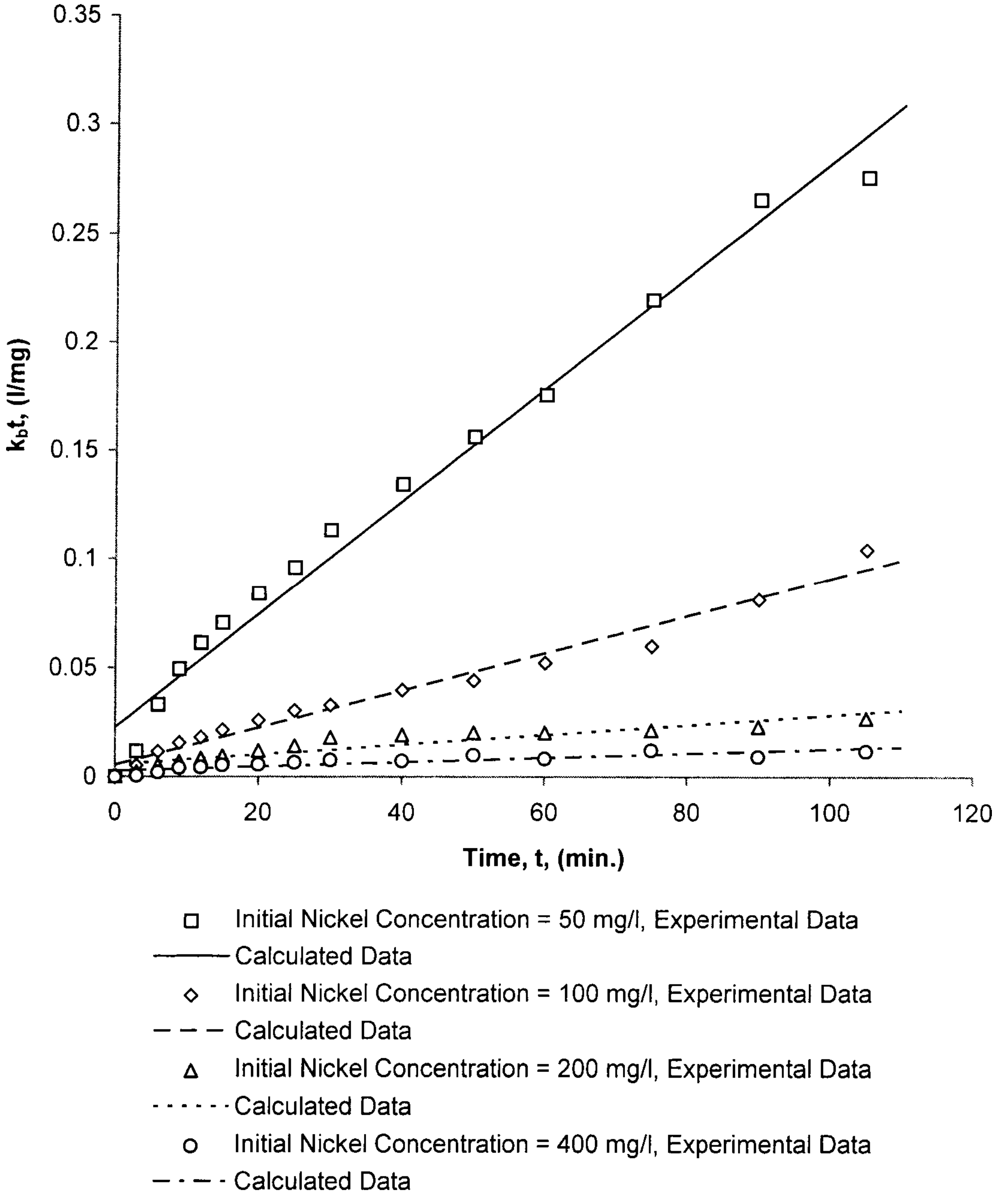
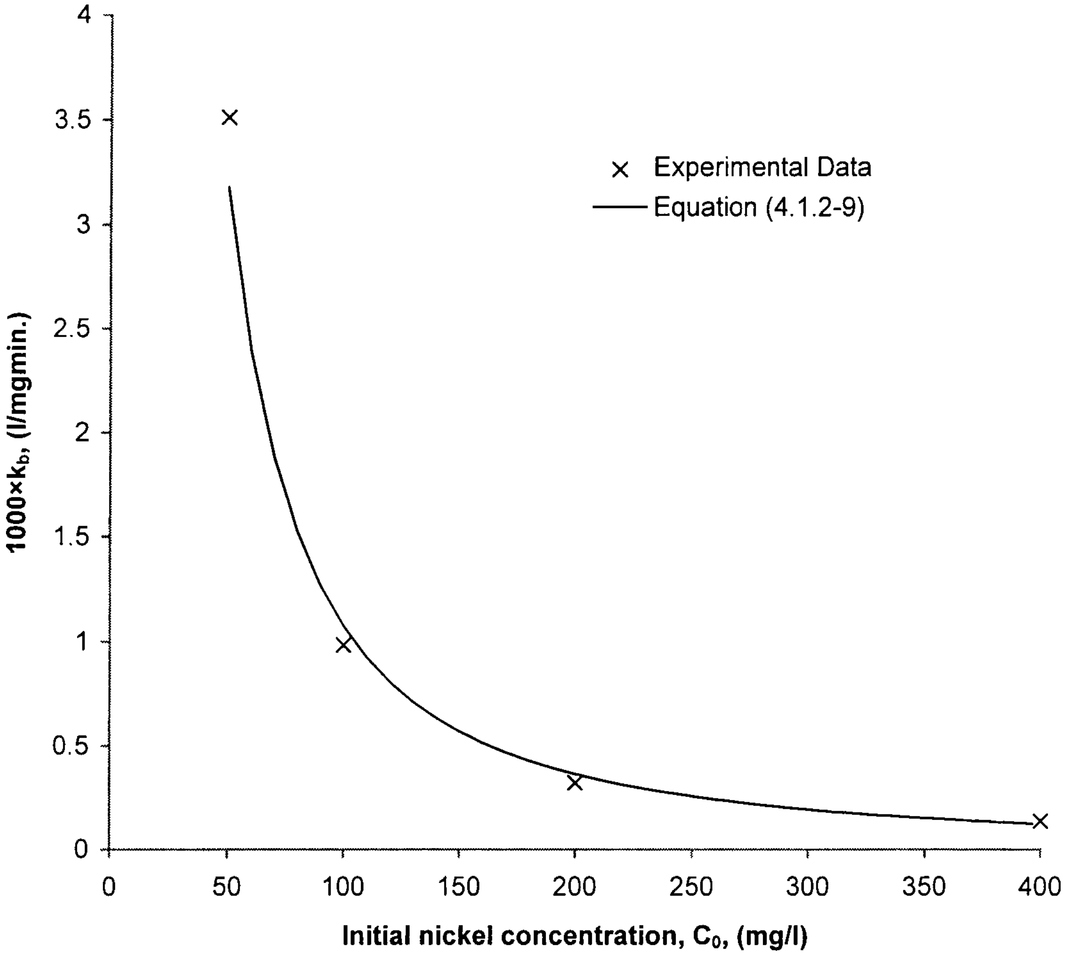


Figure 4.1.2-4: Variation of k_b against initial nickel ion concentration (C_0).



This equation would be useful to calculate reaction constants given the initial nickel concentration under the test conditions. The equation can be rearranged as:

$$(PM) = (M)_{in} \cdot \frac{\exp\{[(M)_{in} - (PM)_{\lim}] \cdot k_b \cdot t\} - 1}{\frac{(M)_{in}}{(PM)_{\lim}} \cdot \exp\{[(M)_{in} - (PM)_{\lim}] \cdot k_b \cdot t\} - 1}. \qquad (4.1.2\text{-}10)$$

Substituting the value of k_b from above equations:

$$(PM) = (M)_{in} \cdot \frac{\exp\{[(M)_{in} - (PM)_{\lim}] \cdot 1.44(M)_{in}^{-1.56} \cdot t\} - 1}{\frac{(M)_{in}}{(PM)_{\lim}} \cdot \exp\{[(M)_{in} - (PM)_{\lim}] \cdot 1.44(M)_{in}^{-1.56} \cdot t\} - 1},$$

or

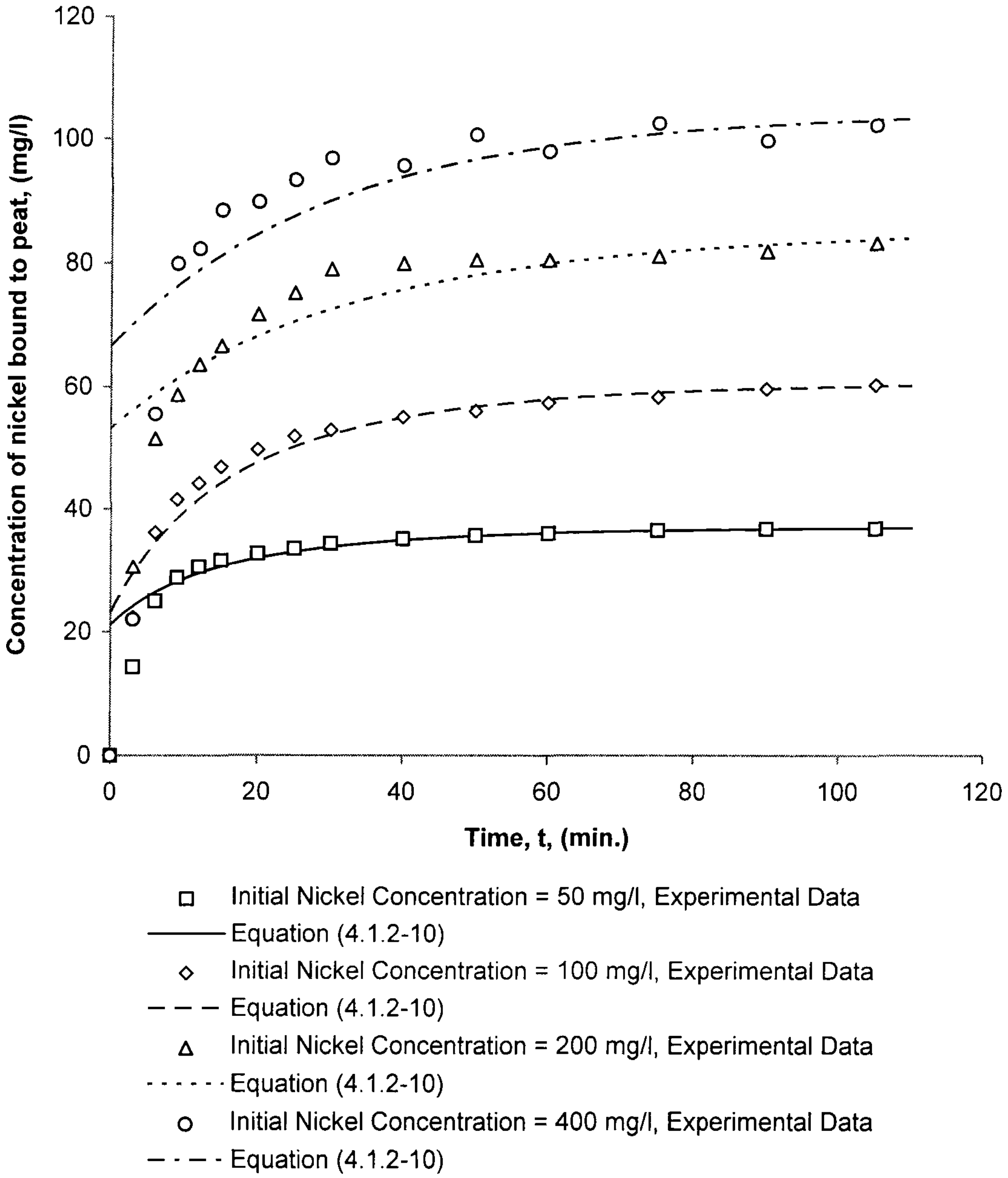
$$(PM) = (M)_{in} \cdot \frac{\exp[(M)_e \cdot 1.44(M)_{in}^{-1.56} \cdot t] - 1}{\frac{(M)_{in}}{[(M)_{in} - (M)_e]} \cdot \exp[(M)_e \cdot 1.44(M)_{in}^{-1.56} \cdot t] - 1},$$

where

$(M)_e$ is equilibrium residual free metal concentration in solution, (mg/l).

Therefore, the above equation can be used to calculate the concentration of nickel adsorbed at any given time and for any initial nickel concentration in a batch reactor. This equation does not take into account the effect of peat dose and the pH, as the equation is valid at pH 5.0 and peat dose of 20 g/l only. However, a similar relationship can be developed by evaluating k_b values as a function of pH and adsorbent dosing rate. **Figure 4.1.2-5** shows the comparison of experimental values with those values obtained using equation **(4.1.2-10)**. The quality of this correlation supports the assumptions concerning the kinetics; particularly the assumptions concerning these kinetics and especially the assumption of a chemical rate limiting step.

Figure 4.1.2-5: Kinetic plots showing the comparison of experimental values with those obtained using the equation.



4.1.3. Kinetics of Lead Removal

The removal of lead from water by adsorption on peat increased with time until equilibrium was accomplished and thereafter it becomes constant. The amount adsorbed increased from 22.0 (88.9% removal) to 22.7 mg/g (90.8% removal) by adsorption on peat, with an increase in solution temperature from 12 to 37°C, and at an initial lead concentration of 100 mg/l and a pH of 5.0 (**Figures 4.1.3-1** and **4.1.3-2**). However, the amount of lead removal by adsorption had only a very slight dependence on the reaction temperature between 20 to 37°C. The removal of lead suggests that from 22.5 (90.2% removal) to 22.7 mg/g (90.8% removal) by increasing the temperature from 20 to 37°C. The increase in the adsorption capacity of peat indicates the adsorption process is endothermic. Rodda *et al.* (1993) reported that there are at least two reasons why adsorption increases with temperature. The first is thermodynamic. Results of other workers (Tewari *et al.*, 1972) suggest that adsorption reactions for many divalent cations are endothermic. The equilibrium constants for such reactions increase with temperature, i.e. the reaction products (the adsorbed species) are favoured at higher temperatures. The second reason follows from the observations that the surface charge of the adsorbate (at a given pH) decreases, as the temperature increases. Thus an increase in temperature will reduce the electrostatic repulsion between the surface and the adsorbing species, allowing adsorption to occur more readily.

The increase in uptake of lead ion with temperature may be due to the desolvation of the adsorbing species, changes in the size of the porosities, and enhanced rate of intraparticle diffusion of adsorbate as well as chemisorption.

Figure 4.1.3-1: Effect of contact time (t) and temperature (T) on the adsorption capacity (q_t) by peat at an initial lead concentration of 100 mg/l and pH 5.0.

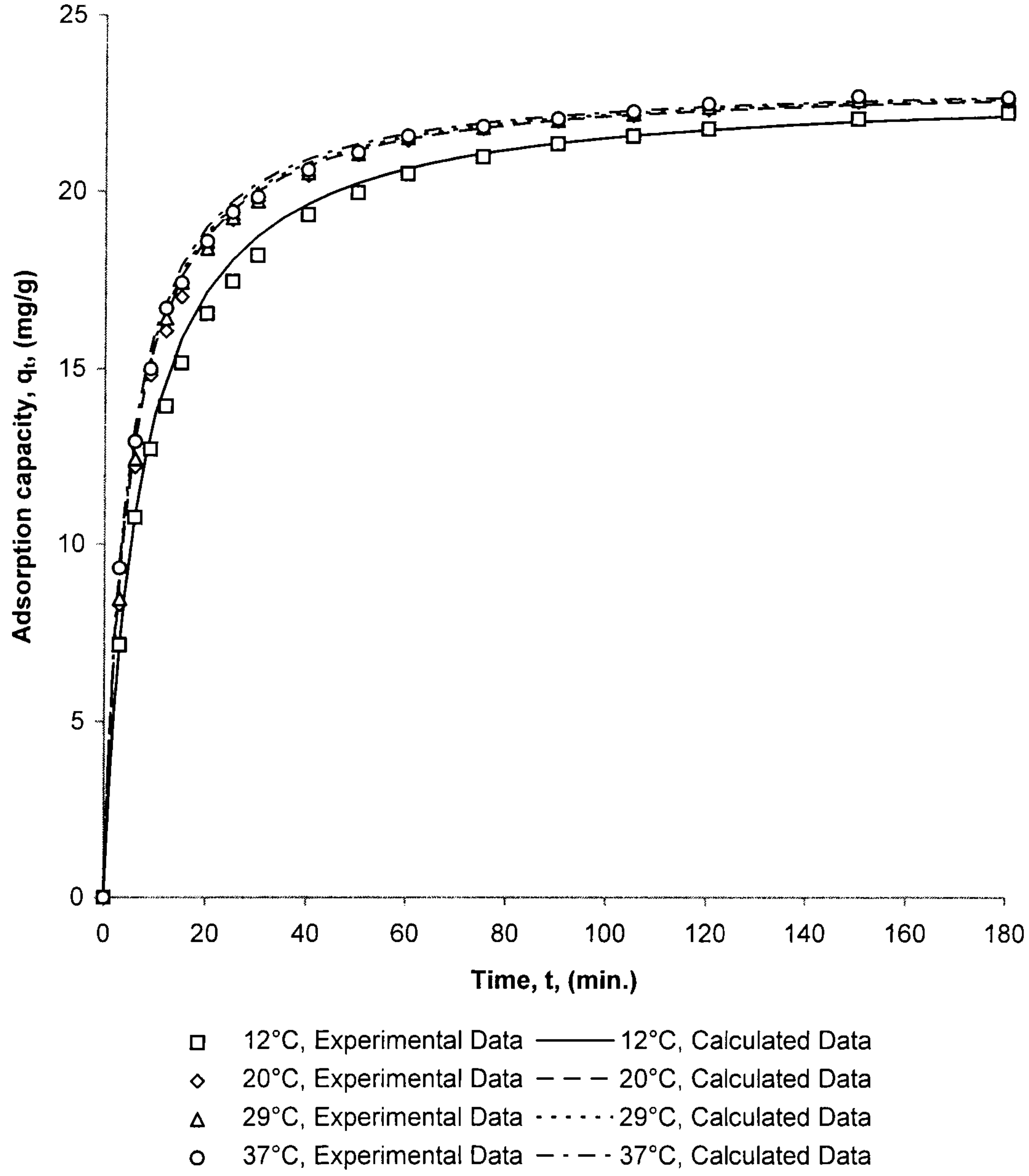
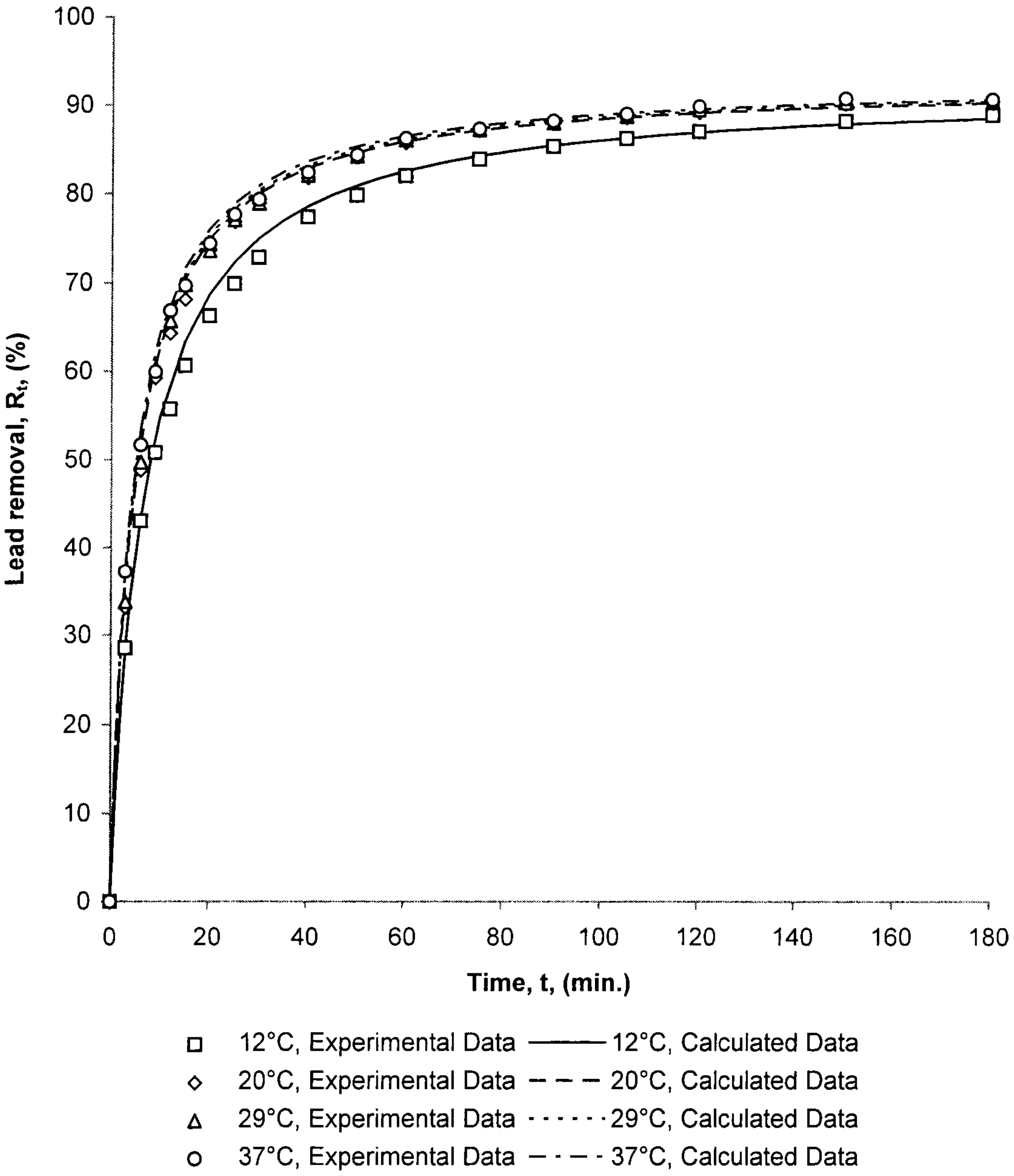


Figure 4.1.3-2: Effect of contact time (t) and temperature (T) on the percent removal (R_t) by peat at an initial lead concentration of 100 mg/l and pH 5.0.



4.2. PSEUDO SECOND-ORDER REACTION MODEL

The adsorption of metal ions onto peat is well documented (Tummavuori and Aho, 1980; Gosset *et. al.*, 1986; McLellan and Rock, 1988; and Viraraghavan and Dronamraju, 1993) but is not completely understood. Nevertheless, the adsorption of metal ions from aqueous solution plays an important role in water pollution control. It is therefore important to be able to predict the rate at which metal ion is removed from aqueous solutions in order to design appropriate adsorption treatment plant. Numerous attempts have been made to describe plots of the amount adsorbed against the time by simple analytical expressions, but the results have not been satisfactory. Dzombak and Morel (1987) reported that the kinetics of cadmium sorption on hydrous ferric oxide can be described by a second-order rate equation. In addition, Tien and Huang (1991) also reported that the rates of metal adsorption on sludge solids follows a second order expression. The sequence of equilibrium constants follows the order: Hg(II) > Pb(II) > Cd(II) > Cu(II) > Zn(II) > Ni(II) > Co(II).

In the present work, a simple kinetic approach to the adsorption of metal ions from aqueous solution onto sphagnum moss peat was evolved, and various adsorption parameters such as the equilibrium adsorption, percent metal ion removal, rate constants and initial rate adsorption have been calculated from the experimental data. A simple kinetics model has been reported which may be used to provide information on the progress of adsorption reaction. Unlike others we used a new equation expression to model the reaction. The empirical models of effects of the operating variables are also discussed.

Theoretical Background

Moss peat contains polar functional groups such as alcohol, aldehydes, ketone, acids, phenolic hydroxides and ethers. These groups can be involved in chemical bonding and are responsible for the cation exchange capacity. The peat-copper reaction may be presented in two way (Coleman *et al.*, 1956):

$2P^- + Cu^{++} \Leftrightarrow CuP_2$;

and

$2HP + Cu^{++} \Leftrightarrow CuP_2 + 2H^+$.

Assuming the reactions of the type are:

$2P^- + M^{++} \Leftrightarrow MP_2$;

and

$2HP + M^{++} \Leftrightarrow MP_2 + 2H^+$.

In an attempt to present the equation representing adsorption of divalent metals onto sphagnum moss peat during suspending shaking, an assumption can be made that the process may be second order. In order to clarify the process-specific approach, a "pseudo" second order process is introduced as follows:

The adsorption follows a Langmuir model in which adsorption leads to the deposition of a monolayer of metal ion on the surface of peat. The energy of adsorption for each ion is the same and independent of surface coverage. The adsorption occurs only on localised sites and involves no interactions between sorbed ions. The rate of adsorption is almost negligible in comparison with the initial rate of adsorption.

The rate of second order reaction may be dependent on the amount of divalent metal ion on the surface of sphagnum moss peat and amount of divalent metal ion adsorbed at equilibrium. The adsorption equilibrium, q_e, is a function of temperature, initial metal ion concentration, peat dose and nature of solute etc.

The rate expression for the adsorption in the above equations is:

$$\frac{-d(P)_t}{dt} = 2K\left[(P)_0 - (P)_t\right]^2,$$

or

$$\frac{-d(HP)_t}{dt} = 2K\left[(HP)_0 - (HP)_t\right]^2,$$

where

$(P)_t$ and $(HP)_t$ are active sites of peat at time t;

$(P)_0$ and $(HP)_0$ are total active sites of peat.

The kinetic rate equations above can be rewritten as follows:

$$\frac{-d(q_e - q_t)}{dt} = 2K(q_e - q_t)^2, \tag{4.2-1}$$

where

K is rate constant of adsorption, (g/mgmin.);

q_e is amount of divalent metal ion adsorbed at equilibrium, (mg/g);

q_t is amount of divalent metal ion on the surface of adsorbent at any time, t, (mg/g).

Separating equation **(4.2-1)** variables:

$$\frac{-d(q_e - q_t)}{(q_e - q_t)^2} = 2Kdt,$$

integrating with boundary conditions t = 0 to t and q_t = 0 to q_t,

$$\int_0^{q_t} \frac{-d(q_e - q_t)}{(q_e - q_t)^2} = \int_0^t 2Kt,$$

integrating

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + 2Kt, \qquad (4.2\text{-}2)$$

which is the integrated rate law for a "pseudo" second order reaction. Rearranging equation (**4.2-2**) we obtain:

$$q_t = \frac{t}{\frac{1}{2Kq_e^2} + \frac{t}{q_e}}, \qquad (4.2\text{-}3)$$

and linear form

$$\frac{t}{q_t} = \frac{1}{2Kq_e^2} + \frac{1}{q_e}t. \qquad (4.2\text{-}4)$$

If the initial adsorption rate is

$$h = 2Kq_e^2,$$

then equations (**4.2-3**) and (**4.2-4**) become

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}}, \qquad (4.2\text{-}5)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t. \qquad (4.2\text{-}6)$$

These equations **(4.2-3)** and **(4.2-5)** satisfying the adsorption kinetics and the parameters can be determined experimentally by fitting equation **(4.2-4)**, and plotting (t/q_t) against (t). The slope of the straight line is $1/q_e$. From the values of slope the equilibrium capacity of moss peat can be obtained. The initial adsorption rate is a reciprocal of the intercept. From the values of the intercept the rate constant, K, can be obtained.

There are many important features influencing adsorption, such as contact time, pH, temperature, adsorbent concentration, nature of solute, solute concentration and particle size, etc. The kinetic model is constructed so that the influence of the commonly used features on the overall kinetic rate is evident. Further parameters which affect it include initial metal ion concentration, temperature, peat dose and nature of solute.

4.3. USING NEW MODEL IN SINGLE-METAL SYSTEM

4.3.1. Effect of Initial Metal Ions Concentration and Nature of Solute

The results of the contact time experiments carried out at 25°C and pH 5.0 are shown in **Figures 4.3.1-1** to **4.3.1-3** for various initial metal ion concentrations and metal ions. It is clear from the plots that the amount of the adsorbed metal increases with time, initially quite sharply, but very slowly towards the end of the reaction. The plots also show that the adsorption capacity was higher for higher initial metal ion concentrations irrespective of time. In addition, the curves show that initial metal ion concentrations have an influence. Thus, this parameter has a major bearing on the time of contact necessary to reach equilibrium. The straight line plots of (t/q_t) against (t) **(Figures 4.3.1-4** to **4.3.1-6)** at various initial metal concentrations have correlation coefficients of 0.996 for lead, 0.995 for nickel, and 0.996 for copper, and this confirms the validity of the equations **(4.2-3)** and **(4.2-5)**. The process rate kinetics are likely to be second order.

Figure 4.3.1-1: Effect of initial lead concentration on a plot of the amount of lead adsorbed (q_t) versus time (t) onto peat at a temperature of 25°C, pH = 5.0 and peat dose = 8 g/l.

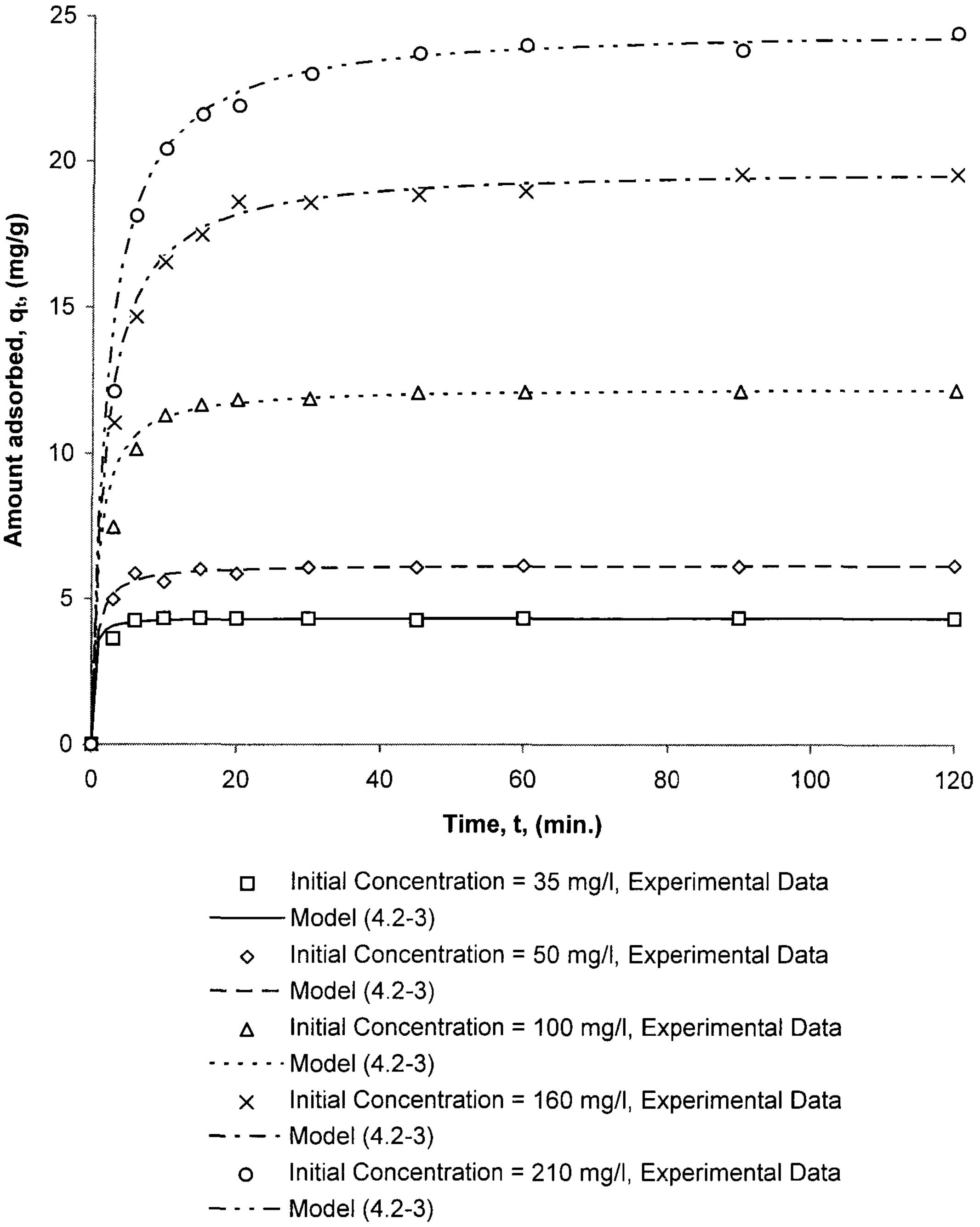


Figure 4.3.1-2: Effect of initial copper concentration on a plot of the amount of copper adsorbed (q_t) versus time (t) onto peat at a temperature of 25°C, pH = 5.0 and peat dose = 4 g/l.

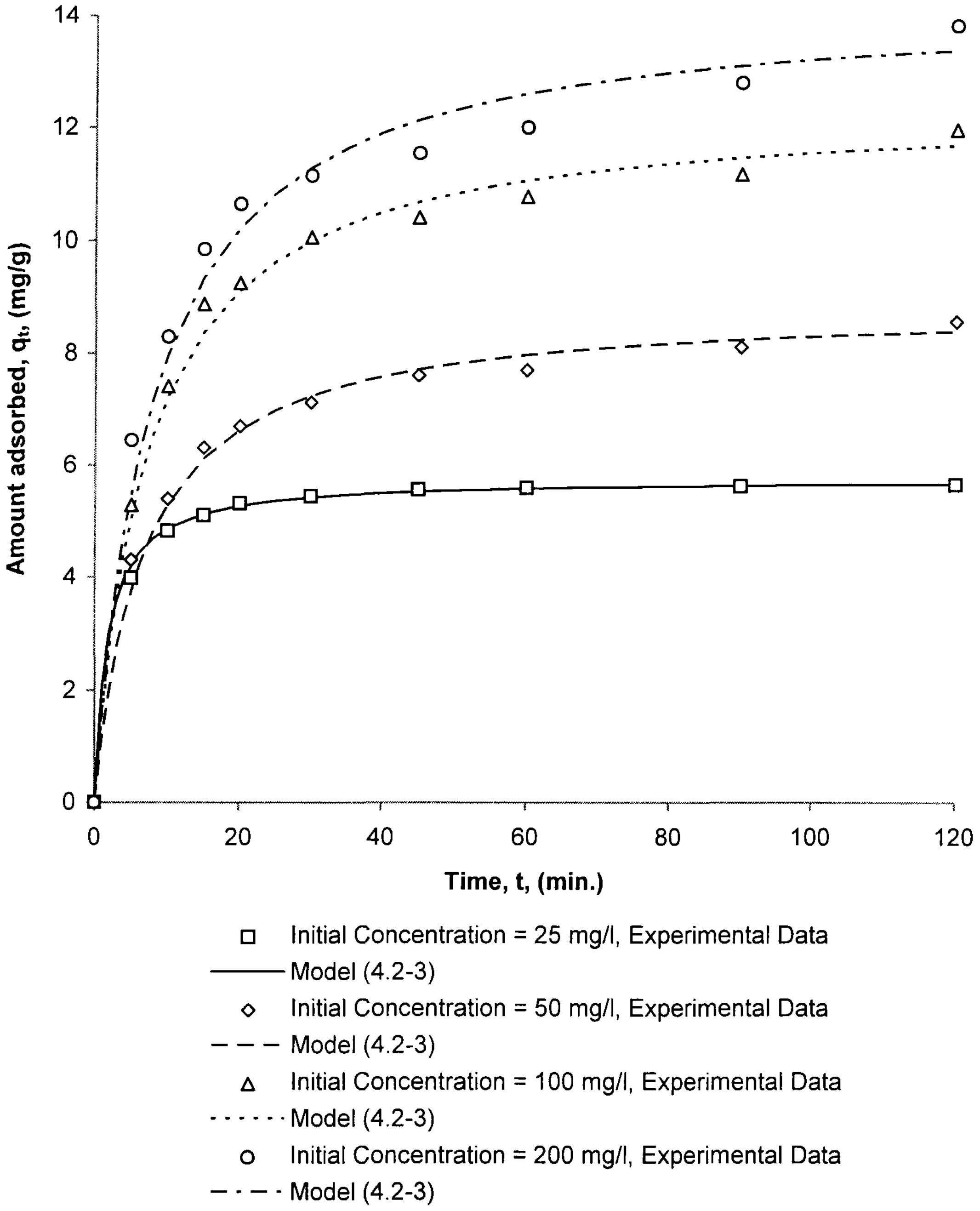
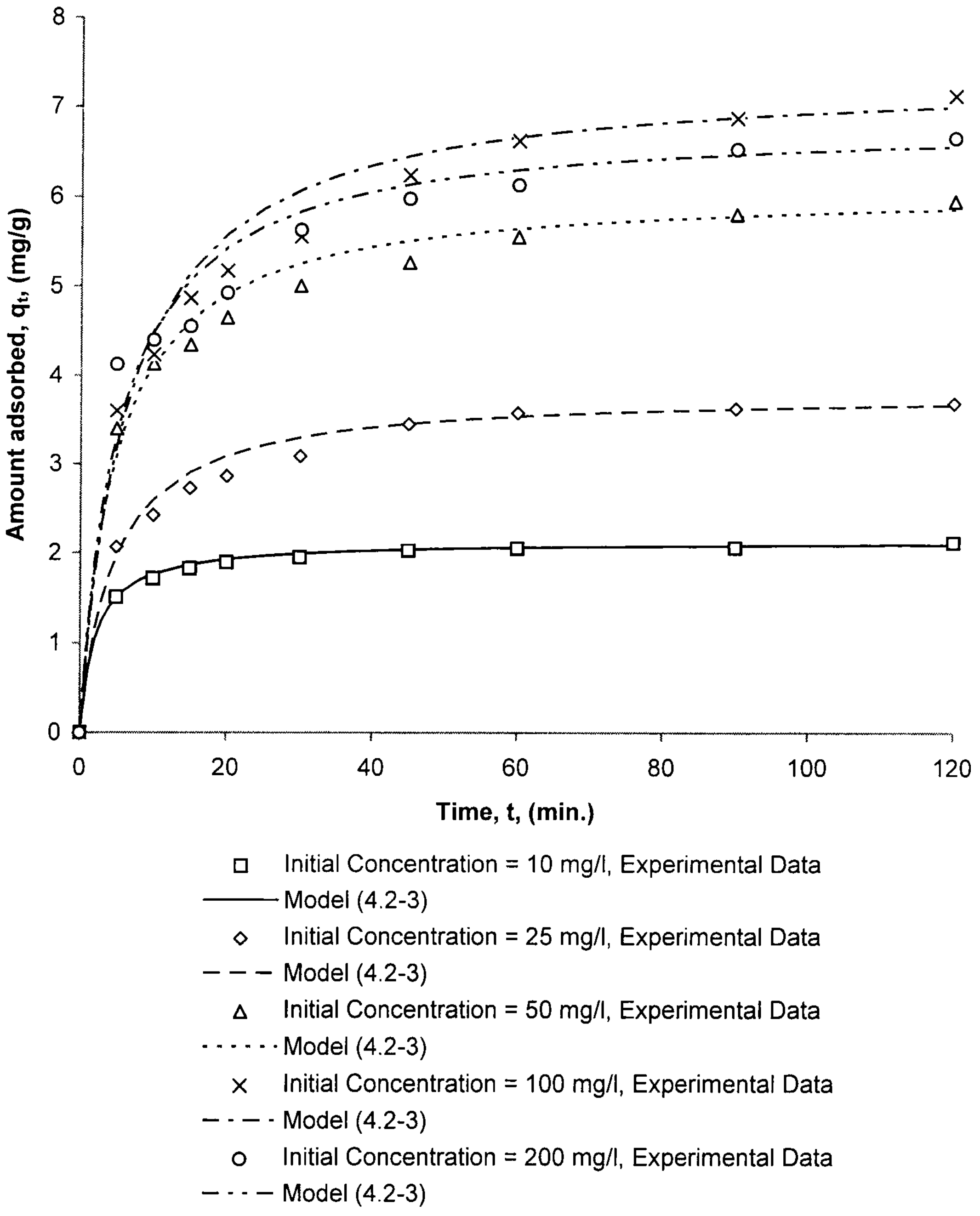


Figure 4.3.1-3: Effect of initial nickel concentration on a plot of the amount of nickel adsorbed (q_t) versus time (t) onto peat at a temperature of 25°C, pH = 5.0 and peat dose = 4 g/l.



The values of q_e, h and K, at various initial metal concentrations and metal ions calculated from these plots are shown in **Table 4.3.1-1**. Adsorption of metal ions increased with an increase in the concentration of the metal ion solution. Thus, on varying the initial lead concentration from 35 to 210 mg/l, equilibrium adsorption increased from 4.34 to 24.7 mg/g. The same effect applies to nickel which was varied from 10 to 200 mg/l, when equilibrium adsorption increased from 2.13 to 6.84 mg/g, whilst for copper ions, when initial concentration was increased from 25 to 200 mg/l, equilibrium adsorption rose from 5.75 to 14.3 mg/g, using sphagnum moss peat as an adsorbent. This shows that the equilibrium adsorption of a metal is highly dependent on the initial concentration of the metal solutions and metal ions.

An empirical model has been mentioned for predicting the percentage of metal ion removal by substituting the parameters q_t and q_e from R_t and R_e in all of the equations of q_t and q_e. The model manifested a high correlation coefficient, as indeed, all of the original equations had. Thus, the percentage of metal ion removal at equilibrium, R_t is a function of temperature, initial metal ion concentration, peat dose and nature of solute. An empirical model is therefore proposed as:

$$R_t = \frac{t}{\frac{1}{2KR_e^2} + \frac{t}{R_e}}.$$

The values of the initial adsorption rates, h, were determined by using the values from the intercepts of the straight lines (**Figures 4.3.1-4** and **4.3.1-6**) as mentioned above. Equilibrium results were measured as adsorbed metal ion per gram of peat, q_t, and unadsorbed metal ion concentration in solution, C_e, at equilibrium respectively. Overall the initial adsorption rate, h, increased with a decrease in the initial metal concentrations. For lead, when C_0 was varied between 210 to 35 mg/l, h was found to vary between 12.2 to 20.6 mg/gmin. For copper, C_0 was varied in a similar range; from 200 to 25 mg/l, but in this case the initial adsorption rate, h, was much less, at 1.81 to 3.20 mg/gmin. Finally, for C_0 values of 10 to 200 mg/l, the initial nickel adsorption rate

Figure 4.3.1-4: Effect of initial lead concentration on the adsorption kinetics of lead onto peat at 25°C, pH = 5.0 and peat dose = 8 g/l: plot of the amount adsorbed (t/q_t) versus time (t).

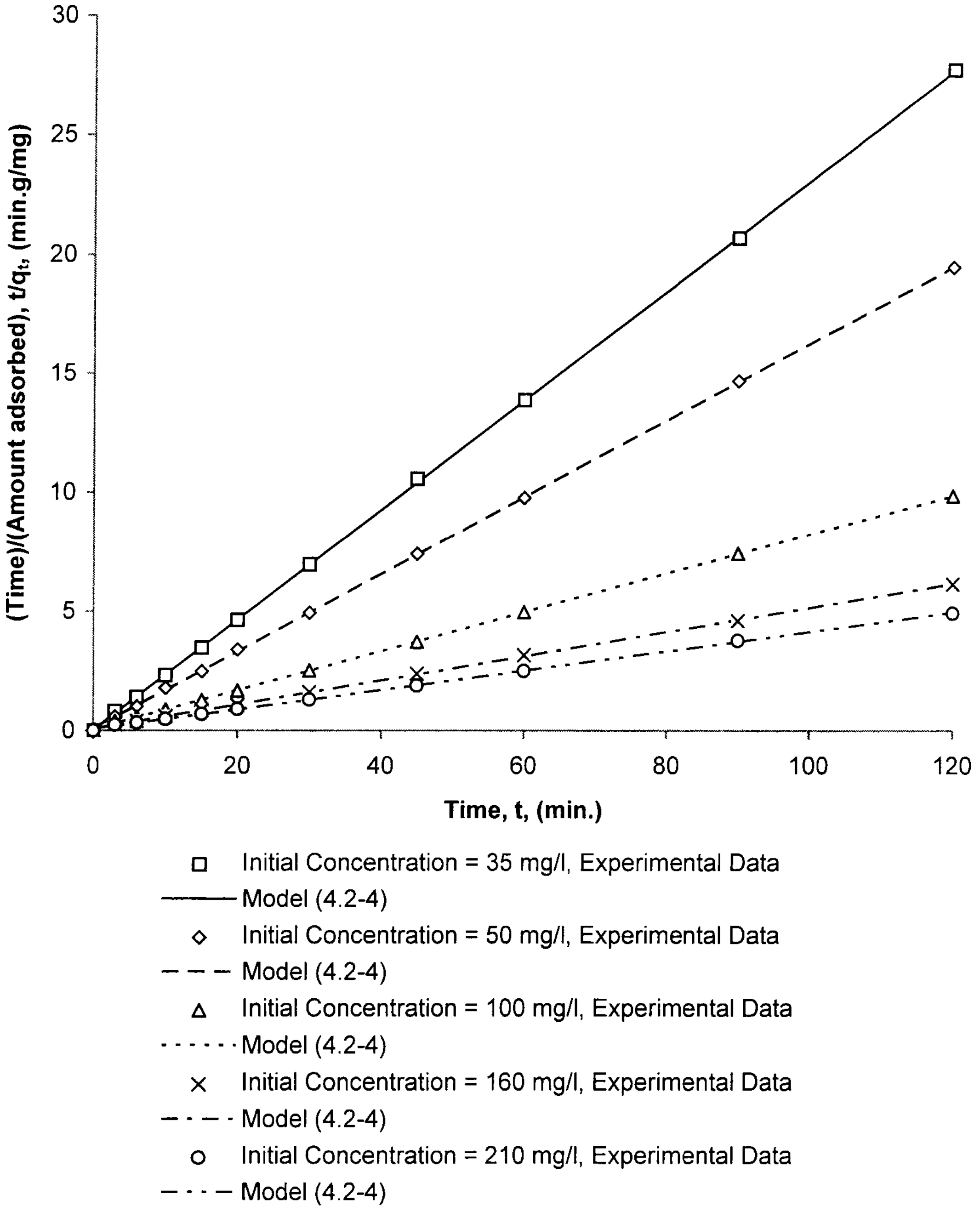


Figure 4.3.1-5: Effect of initial copper concentration on the adsorption kinetics of copper onto peat at 25°C, pH = 5.0 and peat dose = 4 g/l: plot of the amount adsorbed (t/q_t) versus time (t).

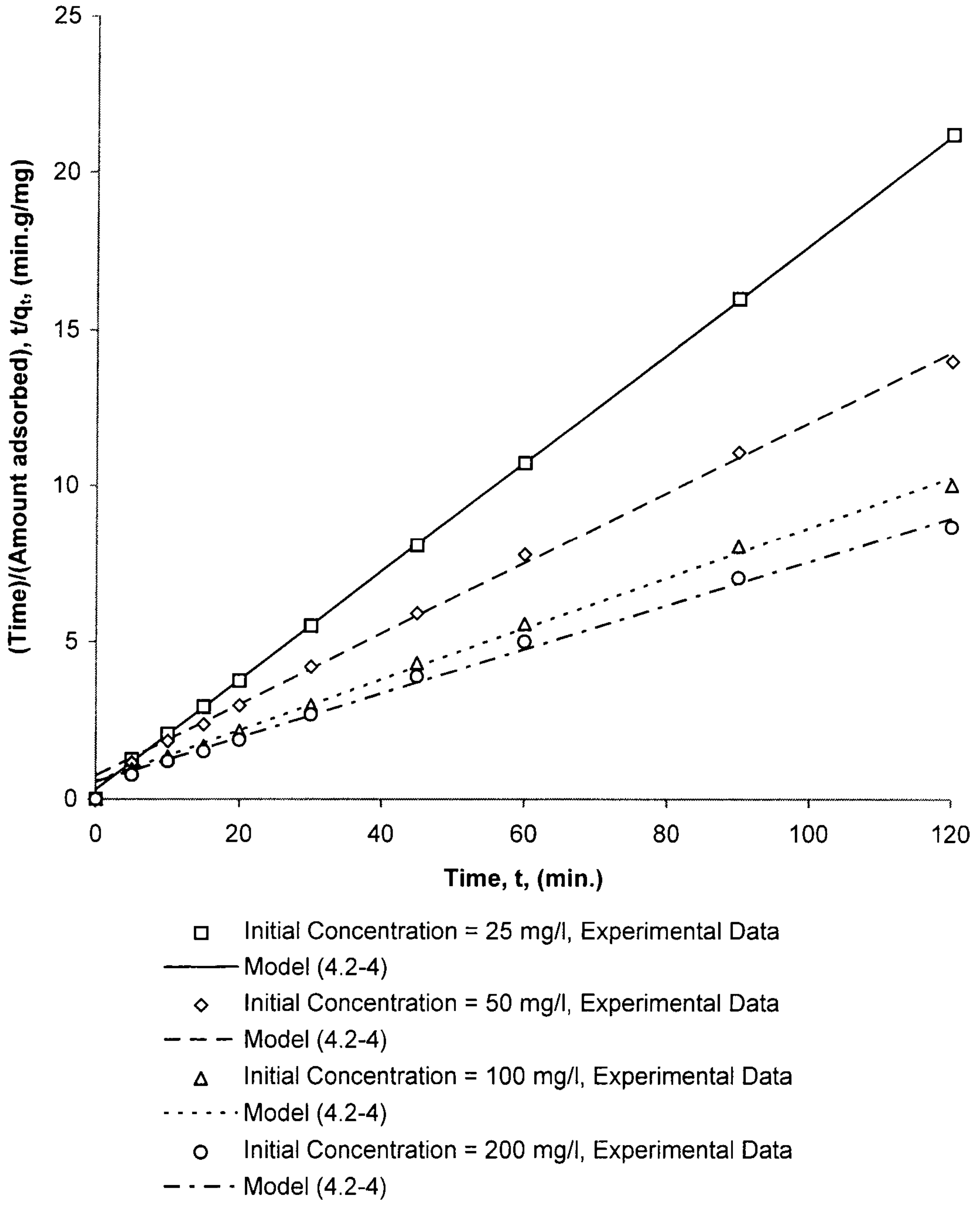


Figure 4.3.1-6: Effect of initial nickel concentration on the adsorption kinetics of nickel onto peat at 25°C, pH = 5.0 and peat dose = 4 g/l: plot of the amount adsorbed (t/q_t) versus time (t).

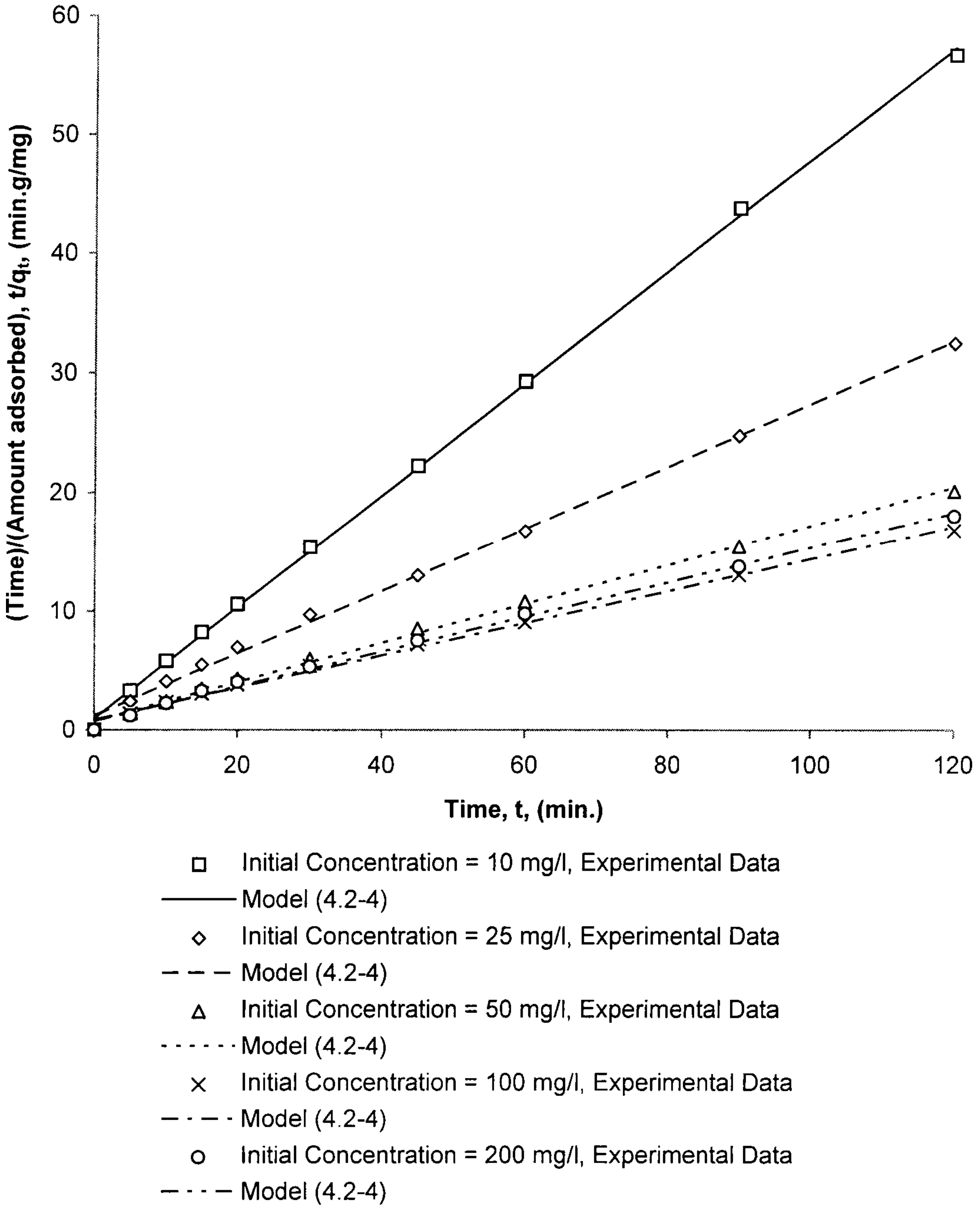


TABLE 4.3.1-1: Metal Ion Adsorption Data. Initial Concentration of Metal Ions, C_0; Metal Ion Removal Capacity at Equilibrium, q_e; Metal Ion Removed at Equilibrium, R_e; Initial Adsorption Rate, h; and Rate Constant, K; for Sphagnum Moss Peat in Respect of Various Initial Metal Ion Concentrations and Metal Ions at pH = 5, Temperature = 25°C and Peat Doses 8 g/l for Lead and 4 g/l for Copper and Nickel.

M^{2+} C_0, (mg/l)	q_e (mg/g)	R_e (%)	h (mg/gmin.)	K (g/mgmin.)
Pb, 35	4.34	99.3	20.6	0.546
50	6.18	98.9	10.5	0.137
100	12.3	98.2	13.4	0.0445
160	19.8	99.1	11.2	0.0142
210	24.7	94.0	12.2	0.0101
Cu, 25	5.75	91.5	3.20	0.0482
50	8.87	69.6	1.32	0.00838
100	12.4	48.6	1.73	0.00566
200	14.3	27.9	1.81	0.00445
Ni, 10	2.13	85.1	1.02	0.112
25	3.81	61.0	0.81	0.0280
50	6.09	48.7	1.28	0.0173
100	7.37	29.5	1.45	0.0105
200	6.84	13.7	1.32	0.0141

varied between only 1.02 to 1.32 mg/gmin. This of course, means that lead is easier to adsorb than copper, which is easier than nickel, and that low concentration of each are easier to adsorb than high concentrations. If this applies to other bio-adsorbents, then this would explain why only lead is such an accumulative poison.

The values of the rate constant, K, were found to increase from 0.0101 to 0.546 g/mgmin for lead, with a decrease in the initial concentration from 210 to 35 mg/l, from 0.0141 to 0.112 g/mgmin for nickel, with a decrease in the initial concentration from 200 to 10 mg/l, and from 0.00445 to 0.0482 g/mgmin for copper, with a decrease in the initial concentration from 200 to 25 mg/l, respectively.

The corresponding linear plots of the values of q_e, h and K against C_0 are displayed in **Figures 4.3.1-7** to **4.3.1-15** respectively, and were regressed to obtain expressions for these values in terms of the initial metal ion concentration with correlation coefficients of 0.998, 0.976 and 0.980 respectively for lead, 0.984, 0.991 and 0.959 respectively for nickel, and 0.998, 0.976 and 0.998 respectively for copper as follows:

for lead

$$q_e = 1.18\times10^{-1}C_0 + 3.74\times10^{-1}, \qquad (4.3.1\text{-}1)$$

$$h = \frac{1}{5.71\times10^{-1}C_0 - 2.31\times10}, \qquad (4.3.1\text{-}2)$$

$$K = 8.72\times10^{2}C_0^{-2.15}; \qquad (4.3.1\text{-}3)$$

for copper

$$q_e = \frac{C_0}{5.54\times10^{-2}C_0 + 2.83}, \qquad (4.3.1\text{-}4)$$

$$h = \frac{C_0}{5.51\times10^{-1}C_0 + 1.83}, \qquad (4.3.1\text{-}5)$$

$$K = \frac{C_0}{2.55\times10^{2}C_0 - 6.65\times10^{3}}. \qquad (4.3.1\text{-}6)$$

for nickel

$$q_e = \frac{C_0}{1.29\times10^{-1}C_0 + 2.56}, \qquad (4.3.1\text{-}7)$$

Figure 4.3.1-7: Effect of initial lead concentration on the adsorption of lead onto peat: plot of log(rate constant), log(K), versus log(initial lead concentration), log(C_0).

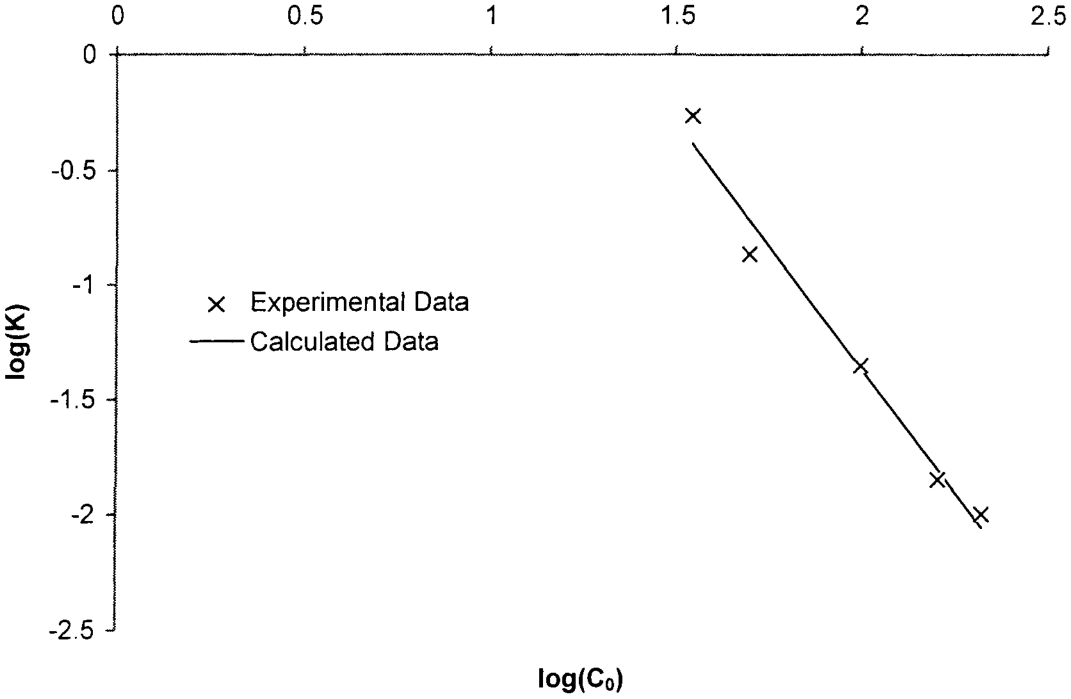


Figure 4.3.1-8: Effect of initial lead concentration on the adsorption of lead onto peat: plot of 1/(initial adsorption rate), (1/h), versus initial lead concentration (C_0).

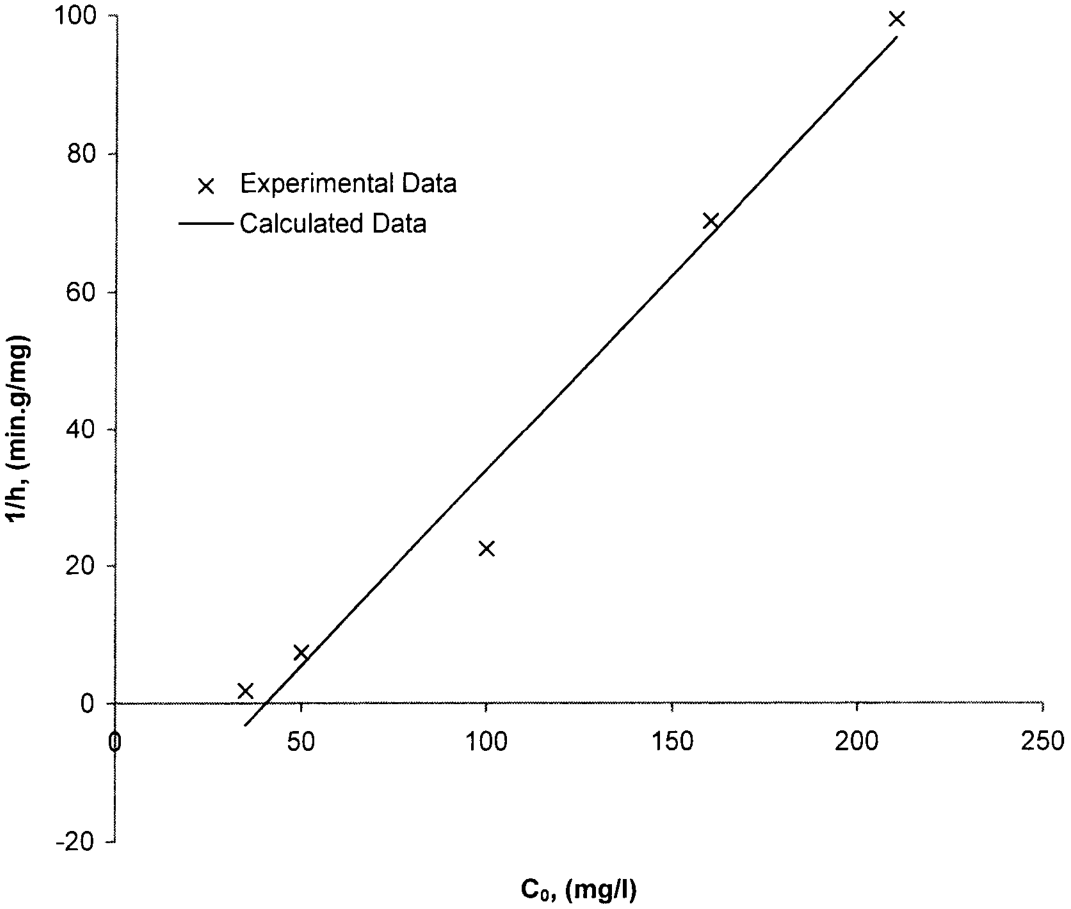


Figure 4.3.1-9: Effect of initial lead concentration on the adsorption of lead onto peat: plot of equilibrium adsorption (q_e) versus initial lead concentration (C_0).

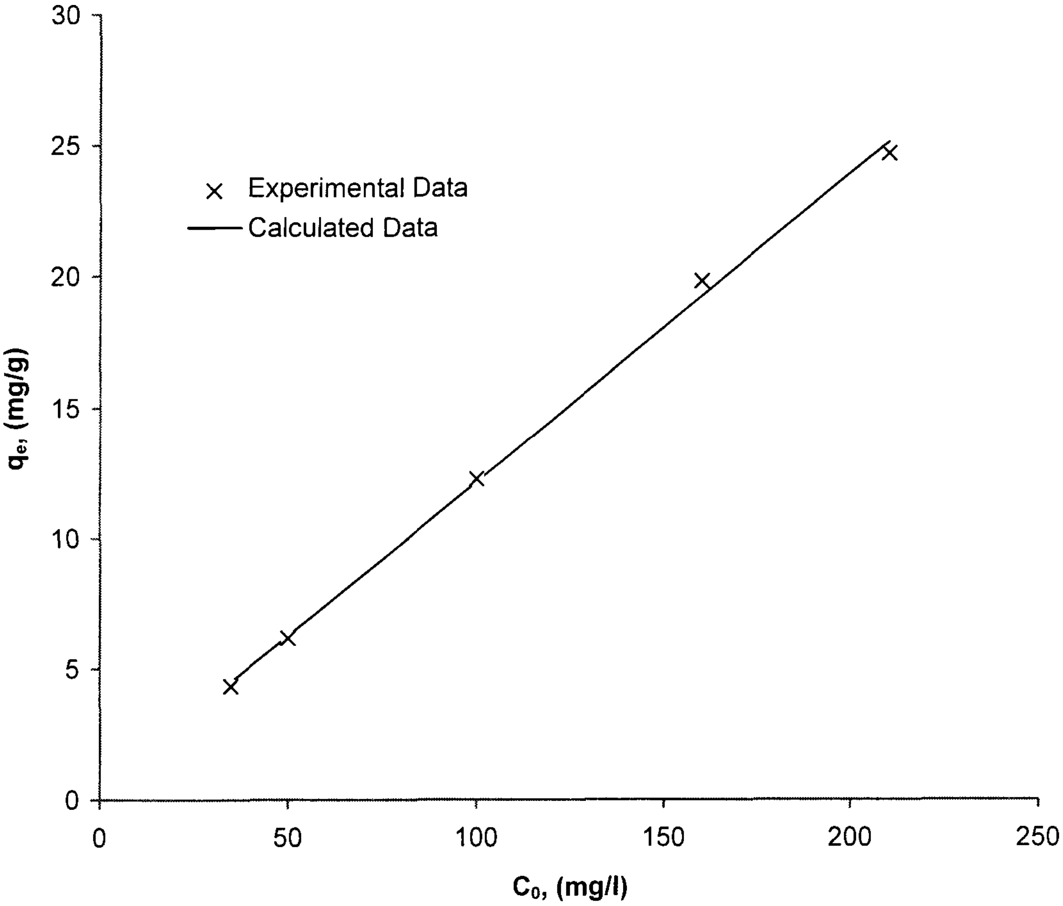


Figure 4.3.1-10: Effect of initial copper concentration on the adsorption of copper onto peat: plot of (initial copper concentration)/(rate constant), (C_0/K), versus initial copper concentration (C_0).

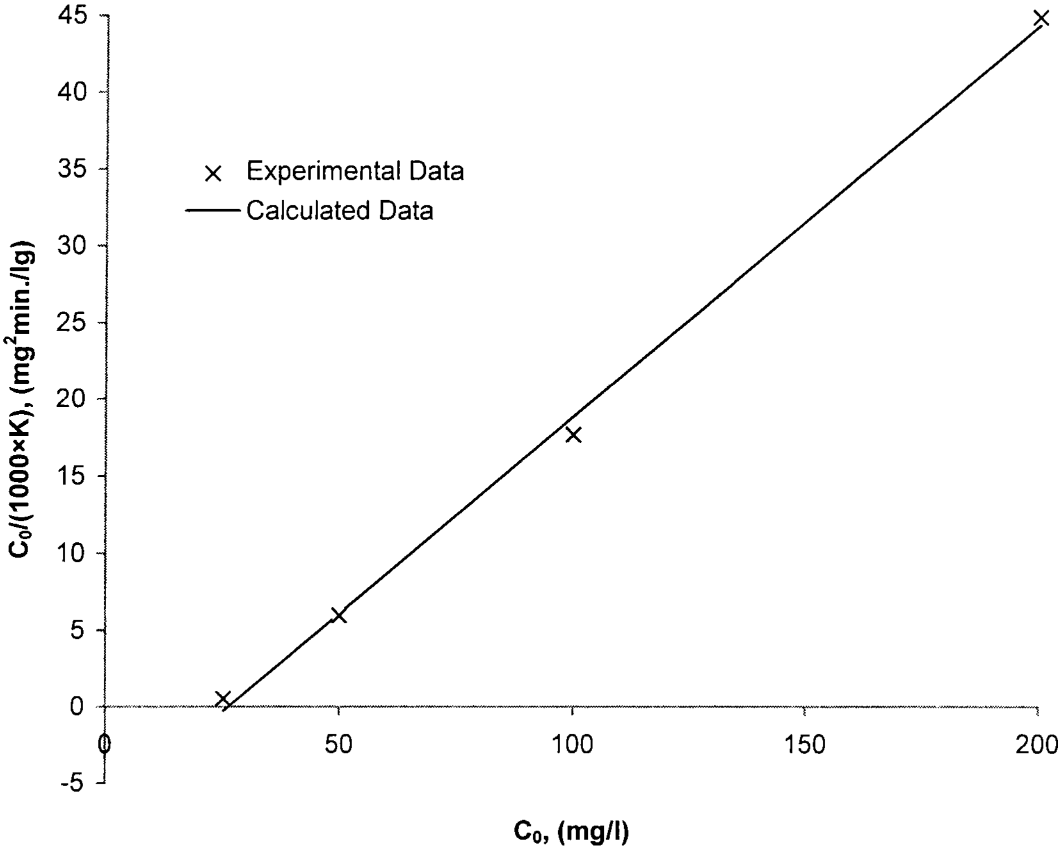


Figure 4.3.1-11: Effect of initial copper concentration on the adsorption of copper onto peat: plot of 1/(initial adsorption rate), (1/h), versus initial copper concentration (C_0).

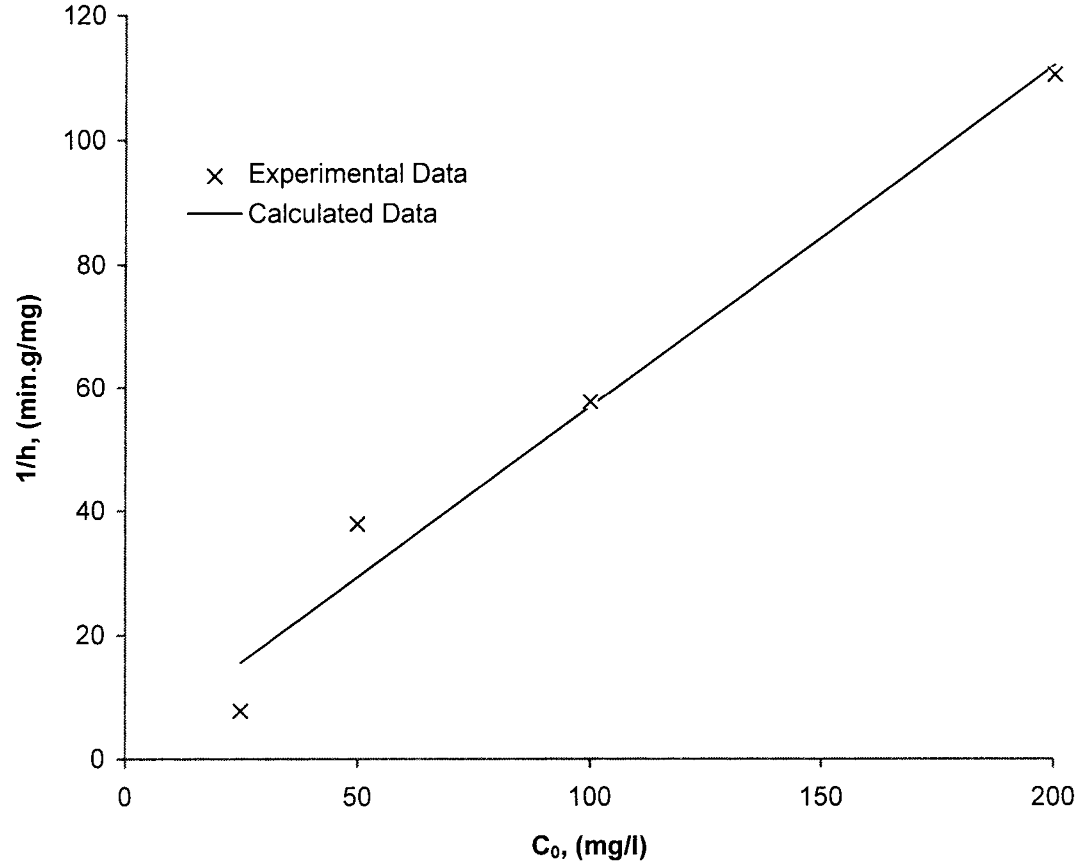


Figure 4.3.1-12: Effect of initial copper concentration on the adsorption of copper ion onto peat: plot of (initial copper concentration)/(amount adsorbed at equilibrium), (C_0/q_e), versus initial copper concentration (C_0).

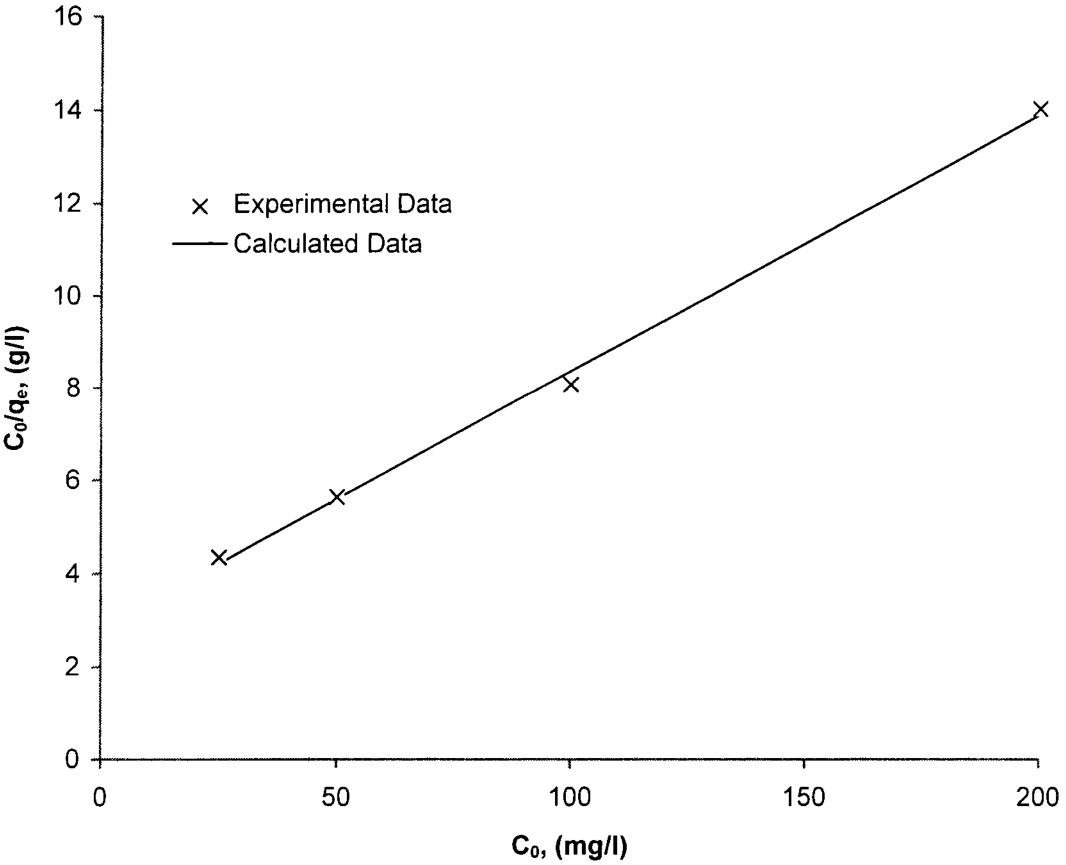


Figure 4.3.1-13: Effect of initial nickel concentration (C_0) on the adsorption of nickel onto peat: plot of (initial nickel concentration)/(rate constant), (C_0/K), versus initial nickel concentration (C_0).

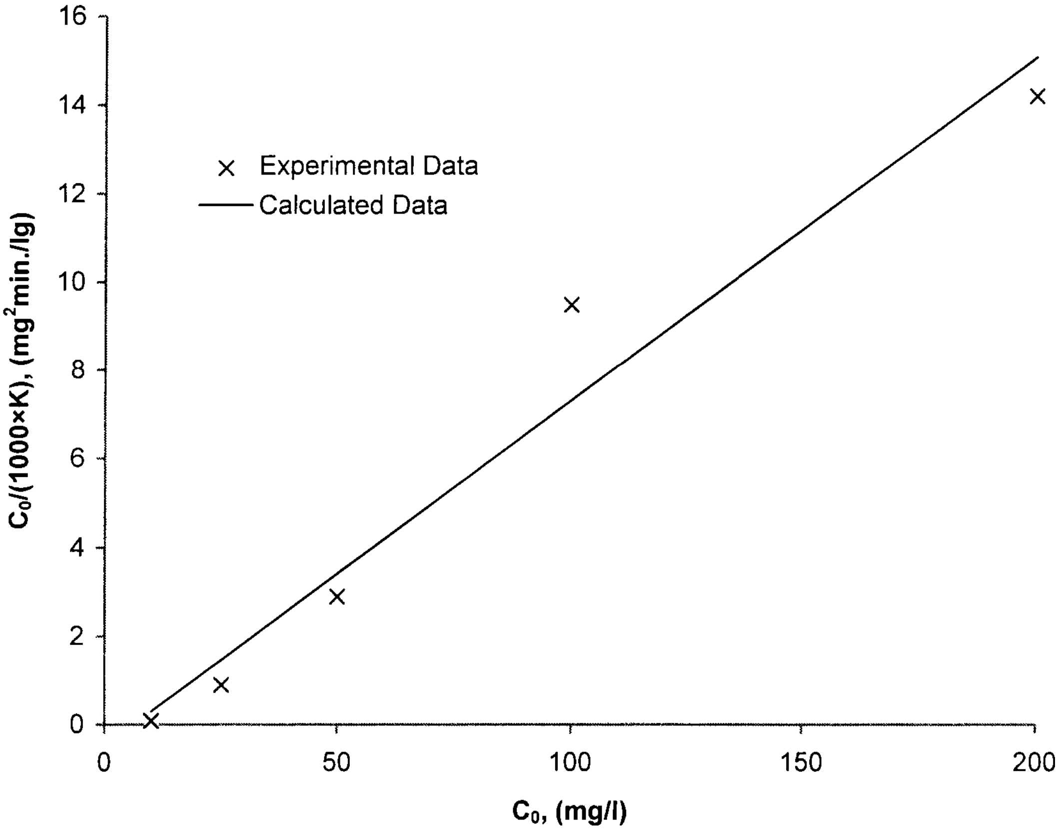


Figure 4.3.1-14: Effect of initial nickel concentration on the adsorption of nickel onto peat: plot of (initial nickel ion concentration)/(initial adsorption rate), (C_0/h), versus initial nickel concentration (C_0).

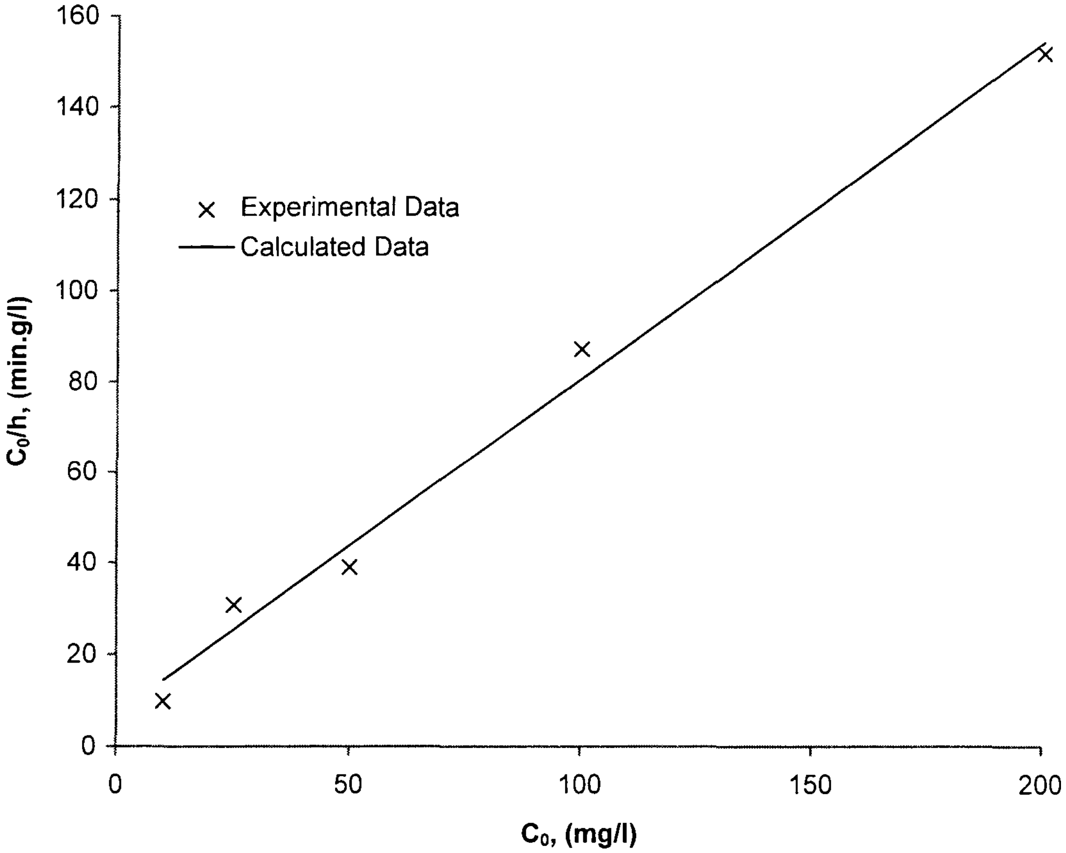
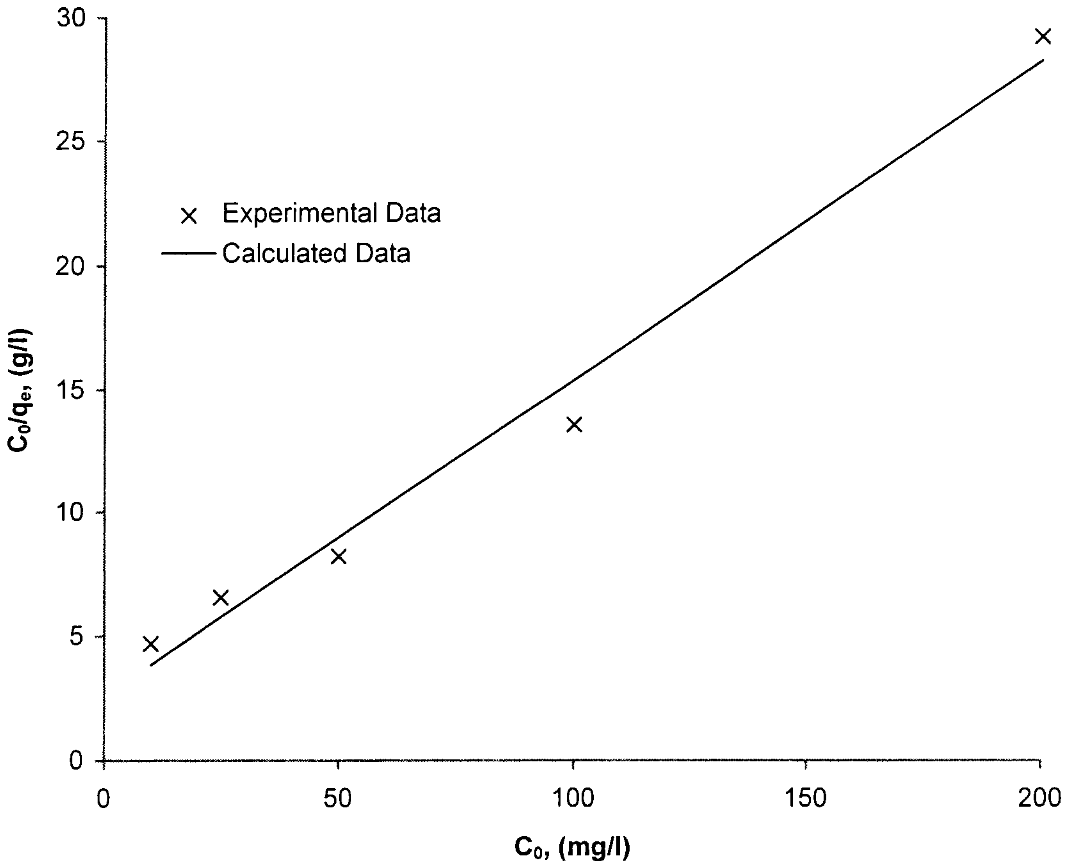


Figure 4.3.1-15: Effect of initial nickel concentration on the adsorption of nickel onto peat: plot of (initial nickel ion concentration)/(amount adsorbed at equilibrium), (C_0/q_e), versus initial nickel concentration (C_0).



$$h=\frac{C_0}{7.37\times10^{-1}C_0+6.99}, \tag{4.3.1-8}$$

$$K=\frac{C_0}{7.79\times10C_0-4.81\times10^2}. \tag{4.3.1-9}$$

Substituting the values of q_e and K from equations **(4.3.1-1)**, **(4.3.1-3)**, **(4.3.1-4)**, **(4.3.1-6)**, **(4.3.1-7)**, and **(4.3.1-9)** in equations **(4.2-2)**, and **(4.2-6)**, the rate law for a second-order and the relationship of q_t, C_0 and t can be represented as:

for lead:

the rate law for a second-order reaction is

$$\frac{1}{1.18\times10^{-1}C_0+3.74\times10^{-1}-q_t}=\frac{1}{1.18\times10^{-1}C_0+3.74\times10^{-1}}-1.74\times10^3C_0^{-2.15}\cdot t,$$

$$\frac{t}{q_t}=\frac{1}{5.71\times10^{-1}C_0-2.31\times10}+\frac{1}{1.18\times10^{-1}C_0+3.74\times10^{-1}}\cdot t; \tag{4.3.1-10}$$

for copper:

the rate law for a second-order reaction is

$$\frac{1}{\frac{C_0}{5.54\times10^{-2}C_0+2.83}-q_t}=\frac{5.54\times10^{-2}C_0+2.83}{C_0}+\frac{2C_0}{2.55\times10^2C_0-6.65\times10^3}\cdot t,$$

$$\frac{t}{q_t}=\frac{5.51\times10^{-1}C_0+1.83}{C_0}+\frac{5.54\times10^{-2}C_0+2.83}{C_0}\cdot t. \tag{4.3.1-11}$$

for nickel:

the rate law for a second-order reaction is

$$\frac{1}{\frac{C_0}{1.29\times10^{-1}C_0+2.56}-q_t}=\frac{1.29\times10^{-1}C_0+2.56}{C_0}+\frac{2C_0}{7.79\times10C_0-4.81\times10^2}\cdot t,$$

$$\frac{t}{q_t} = \frac{7.37 \times 10^{-1} C_0 + 6.99}{C_0} + \frac{1.29 \times 10^{-1} C_0 + 2.56}{C_0} \cdot t. \qquad (4.3.1\text{-}12)$$

Equations **(4.3.1-10)** to **(4.3.1-12)** represent generalised predictive models for the amount of metal ion adsorbed at any contact time and the involved initial metal ion concentration. They indicate that the metal ion adsorbed at any contact time is higher for greater initial metal ion concentrations. This is obvious for higher C_0 values, where more efficient utilisation of the adsorptive capacities of the adsorbent is expected due to the greater driving force of the higher concentration gradient (Bhargava and Sheldarkar, 1993).

Similarly, a predictive model for the removal of metal ion, R_t, at any contact time, t, and involved initial metal ion concentration, C_0, can be presented as follows:

for lead

$$R_t = \frac{t}{1.09 \times 10^{-4} C_0 - 7.10 \times 10^{-4} + \frac{\left(1.06 \times 10^{-2} C_0 - 3.22 \times 10^{-2}\right) \cdot t}{C_0}}, \qquad (4.3.1\text{-}13)$$

for copper

$$R_t = \frac{t}{\frac{2.51 \times 10^{-1} C_0 - 8.78}{C_0} + \frac{4.03 \times 10^{-2} C_0 - 1.22}{C_0} \cdot t}. \qquad (4.3.1\text{-}14)$$

for nickel

$$R_t = \frac{t}{\frac{4.07 \times 10^{-1} C_0 - 1.04 \times 10}{C_0} + \frac{7.72 \times 10^{-2} C_0 - 2.03}{C_0} \cdot t}. \qquad (4.3.1\text{-}15)$$

These equations can then be used to derive the percent metal removal at any given initial metal ion concentration and any reaction time. The three dimensional plots of the equations are shown in **Figures 4.3.1-16** to **4.3.1-18**.

4.3.2. Effect of Temperature

A series of contact time experiments were carried out at a constant initial lead ion concentration of 100 mg/l, peat dose 4.0 g/l and with various temperatures of the reaction. The results were evaluated using equation **(4.2-3)** and appropriate plots are shown in **Figure 4.3.2-1**. It indicates that for the lead-peat system, on increasing the temperature of the reaction from 12 to 37°C, the equilibrium adsorption, q_e, of the lead ion slightly increased from 22.9 to 23.2 mg/g (**Table 4.3.2-1**). The plots also show that, for any time, the equilibrium adsorptions were higher for higher temperatures. The values of rate constants, K, the initial adsorption rates, h, and the equilibrium adsorption at various temperatures, were determined from the intercept and slope of the straight line plots of t/q_t versus t in equation **(4.2-4)** (**Figure 4.3.2-2**), as the model of equations (**4.2-3**) and (**4.2-4**).

TABLE 4.3.2-1: Lead Ion Adsorption Data. Temperature, T; Lead Ion Removal Capacity at Equilibrium, q_e; Metal Ion Removed at Equilibrium, R_e; Initial Adsorption Rate, h; and Rate Constant, K; for Sphagnum Moss Peat in Respect of Various Temperatures at pH = 5, Initial Lead Ion Concentration of 100 mg/l and Peat Dose 4 g/l.

T (°C)	q_e (mg/g)	R_e (%)	h (mg/gmin.)	K (g/mgmin.)
12	22.9	91.8	3.41	0.00324
20	23.2	92.6	4.92	0.00459
29	23.2	92.7	5.07	0.00472
37	23.2	92.8	5.26	0.00489

Figure 4.3.1-16: Effect of initial lead concentration (C_0) on lead removal (R_t) at various reaction times (t).

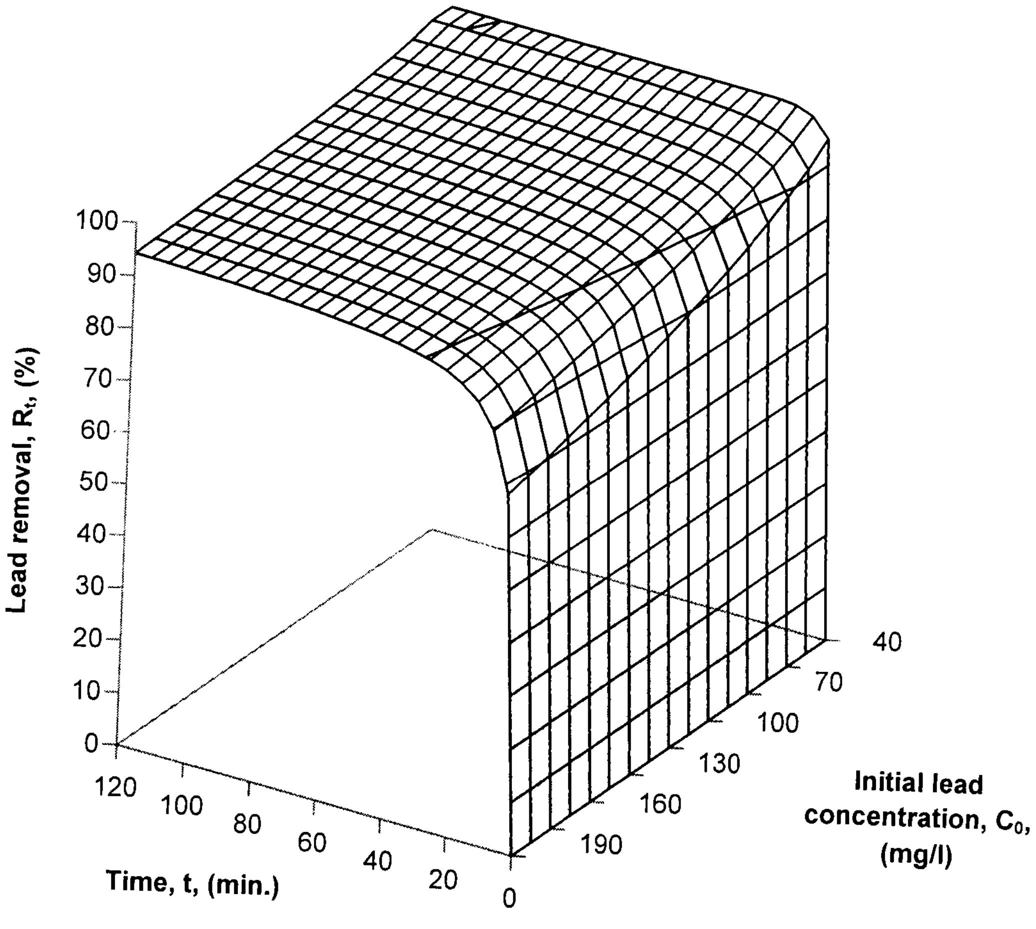


Figure 4.3.1-17: Effect of initial copper concentration (C_0) on copper removal (R_t) at various reaction times (t).

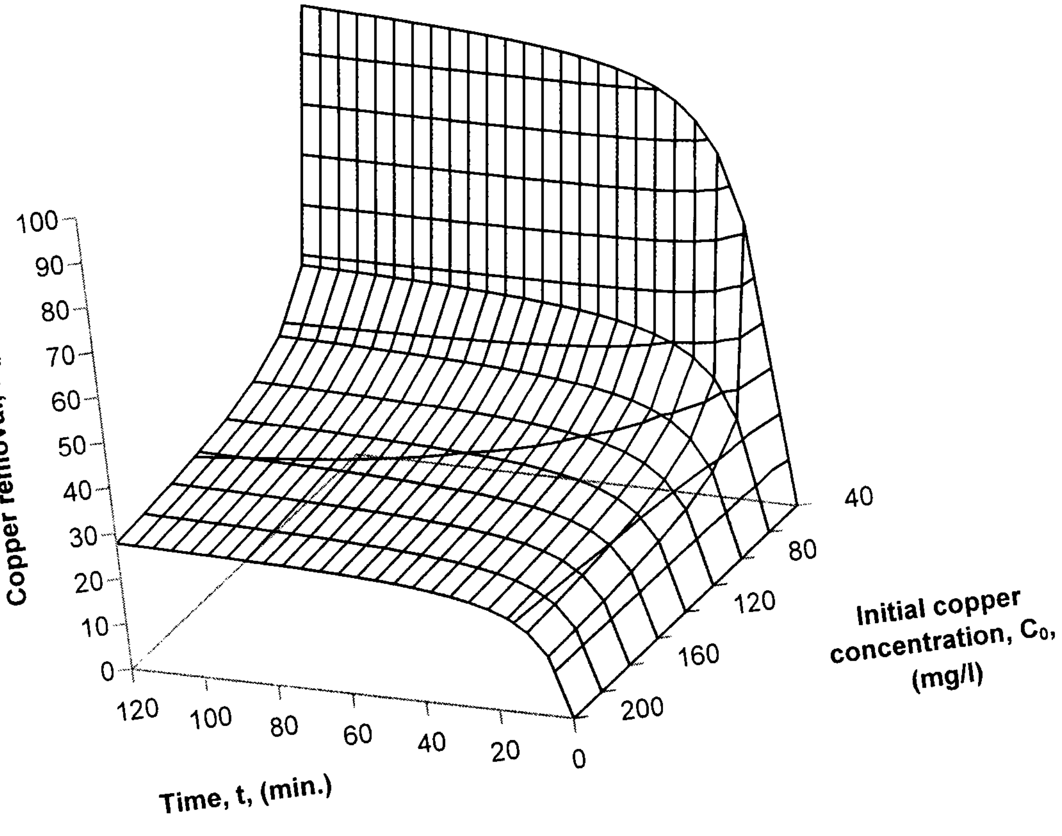


Figure 4.3.1-18: Effect of initial nickel concentration (C_0) on nickel removal (R_t) at various reaction time (t).

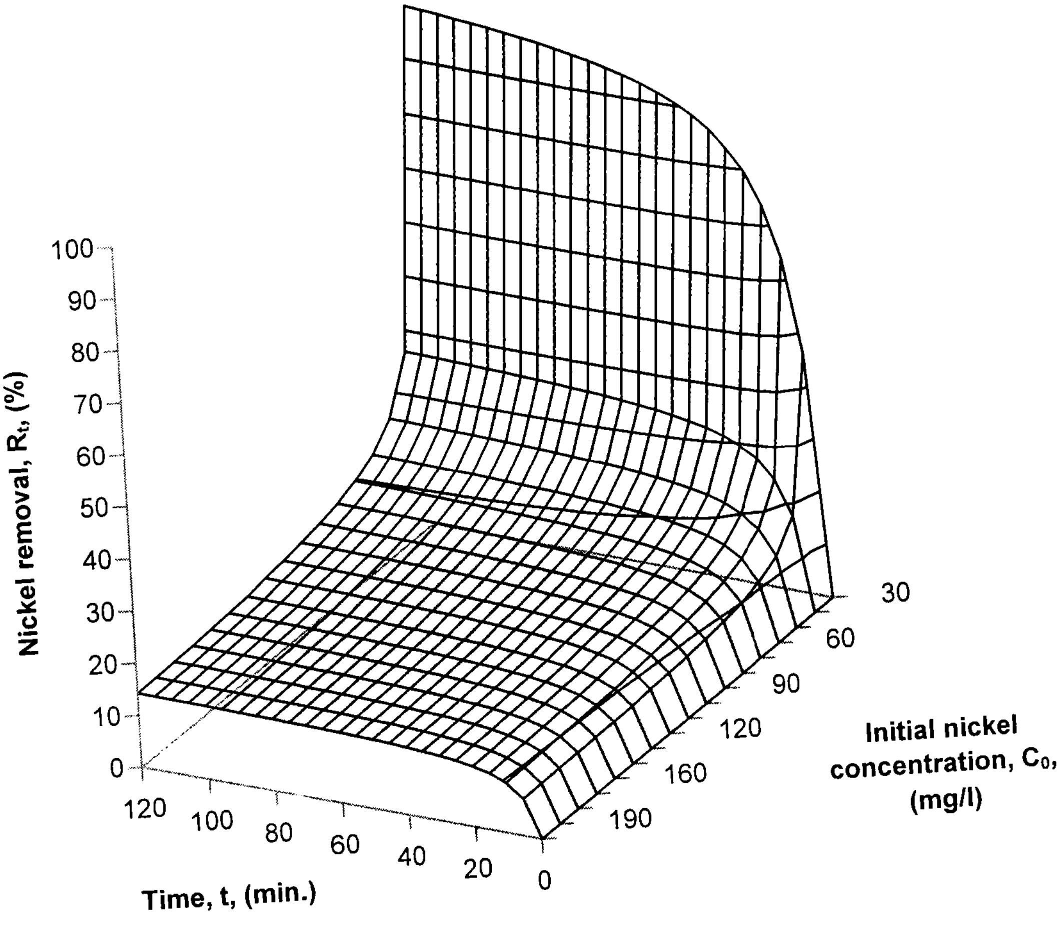


Figure 4.3.2-1: Effect of temperature on the adsorption kinetics of lead onto peat at an initial lead concentration of 100 mg/l, pH = 5.0 and peat dose = 4 g/l: plot of adsorbed amount (q_t) versus time (t).

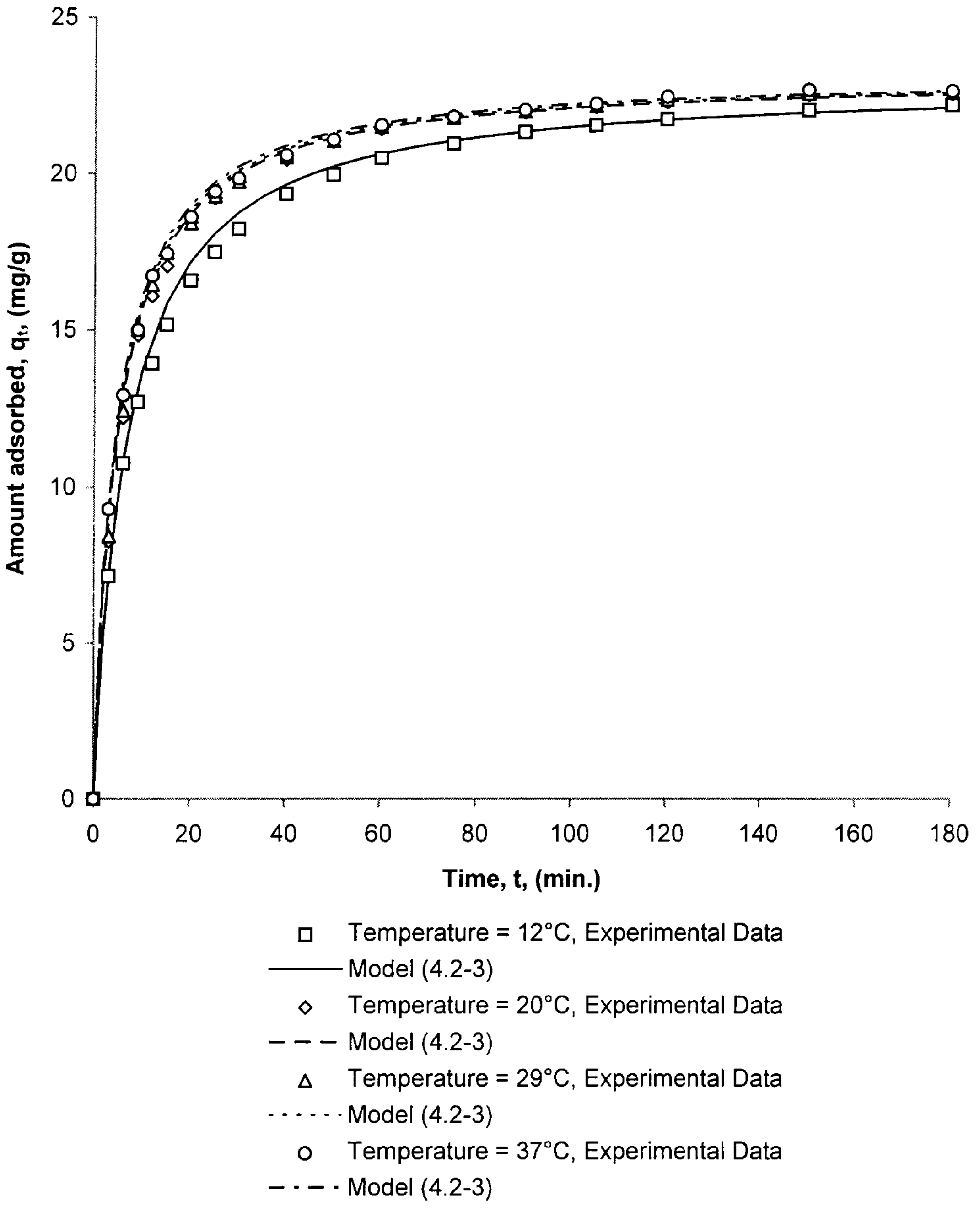
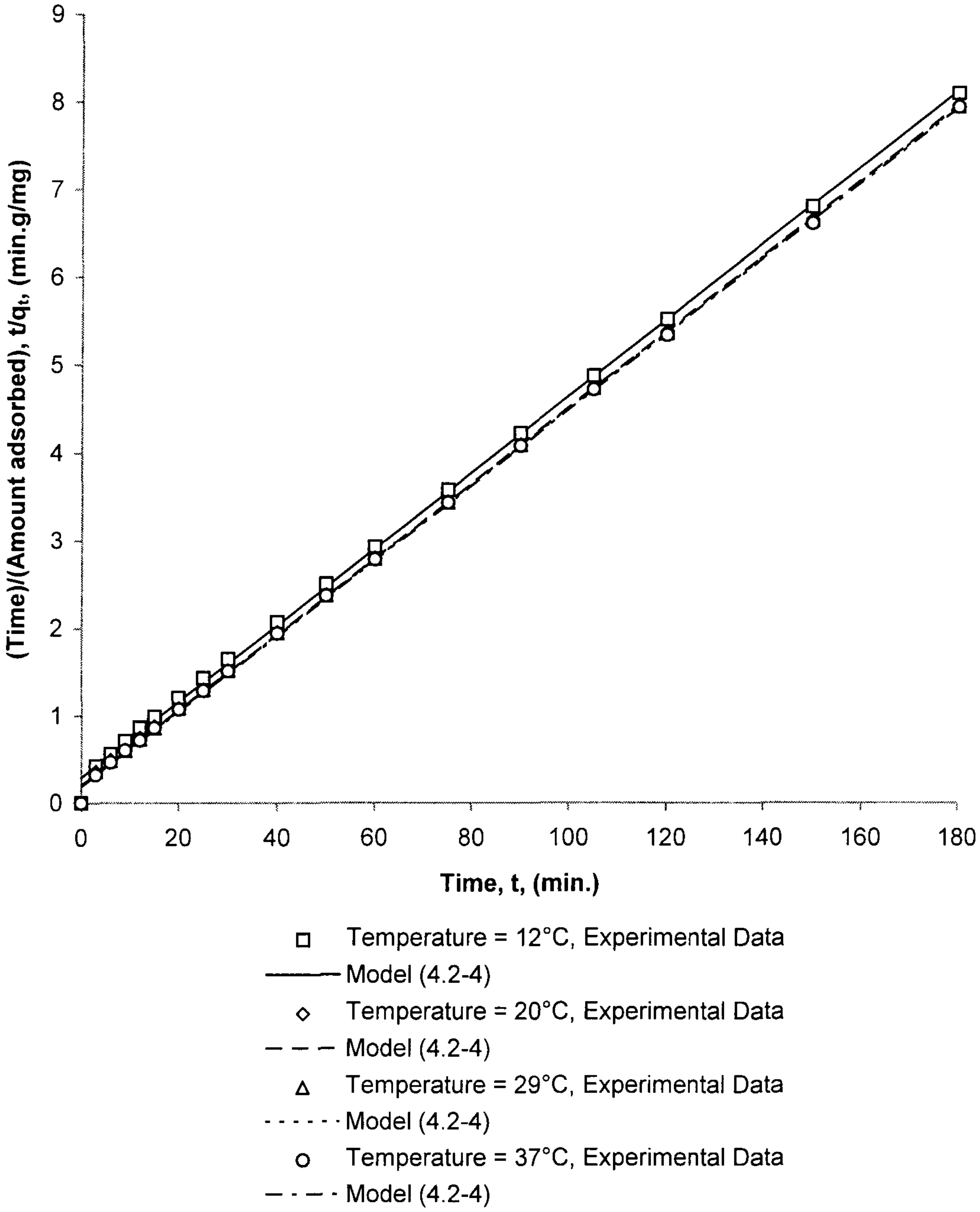


Figure 4.3.2-2: Plot of (time)/(adsorbed amount), (t/q_t), versus time (t) for adsorption of lead ion onto peat for an initial lead concentration of 100 mg/l, pH = 5.0 and peat dose = 8 g/l.



Data from a series of kinetics experiments at four different temperatures between 12 and 37°C are shown in **Table 4.3.2-1**. The values of K slightly increased from 0.00324 to 0.00489 g/mgmin. with the increase in reaction temperature. The increase in rates of reaction with increasing temperatures is described by the equation:

$$K = \frac{T}{1.60 \times 10^{2} T + 1.53 \times 10^{3}}, \tag{4.3.2-1}$$

where

T is temperature, (°C).

A linear relation occurs between (T/K) and (T) with correlation coefficient of 0.976 (**Figure 4.3.2-3**).

The initial adsorption rate increases from 3.41 to 5.26 mg/gmin. with increasing temperature from 12 to 37°C (**Table 4.3.2-1**). There is a linear relation between (T/h) and (T) with a correlation coefficient of 0.973 (**Figure 4.3.2-4**):

$$h = \frac{T}{1.46 \times 10^{-1} T + 1.52}. \tag{4.3.2-2}$$

The increase in the equilibrium adsorption of lead with temperature shown in these tests indicates that high temperatures favour lead removal by adsorption on peat. Obviously, the exothermic nature of the present process can be explained by this behaviour of the system (Sen and De, 1987; Aksu *et al.*, 1992). This effect may be that at higher temperatures; an increase in free volume occurs due to increased movement of the solute (Aminabhavi and Munnolli, 1993). Also, this may be due to the dissolution of the adsorbing species, changes in the size of the pores, and enhanced rate of intraparticle diffusion of adsorbent (Knocke and Hemphill, 1981). This effect could be explained by assuming that at higher values of temperature the total energy of the adsorbate molecules is increased, hence their escaping tendency is also increased and consequently the

Figure 4.3.2-3: Effect of temperature on the adsorption of lead onto peat: plot of (temperature)/(rate constant), (T/K), versus temperature (T).

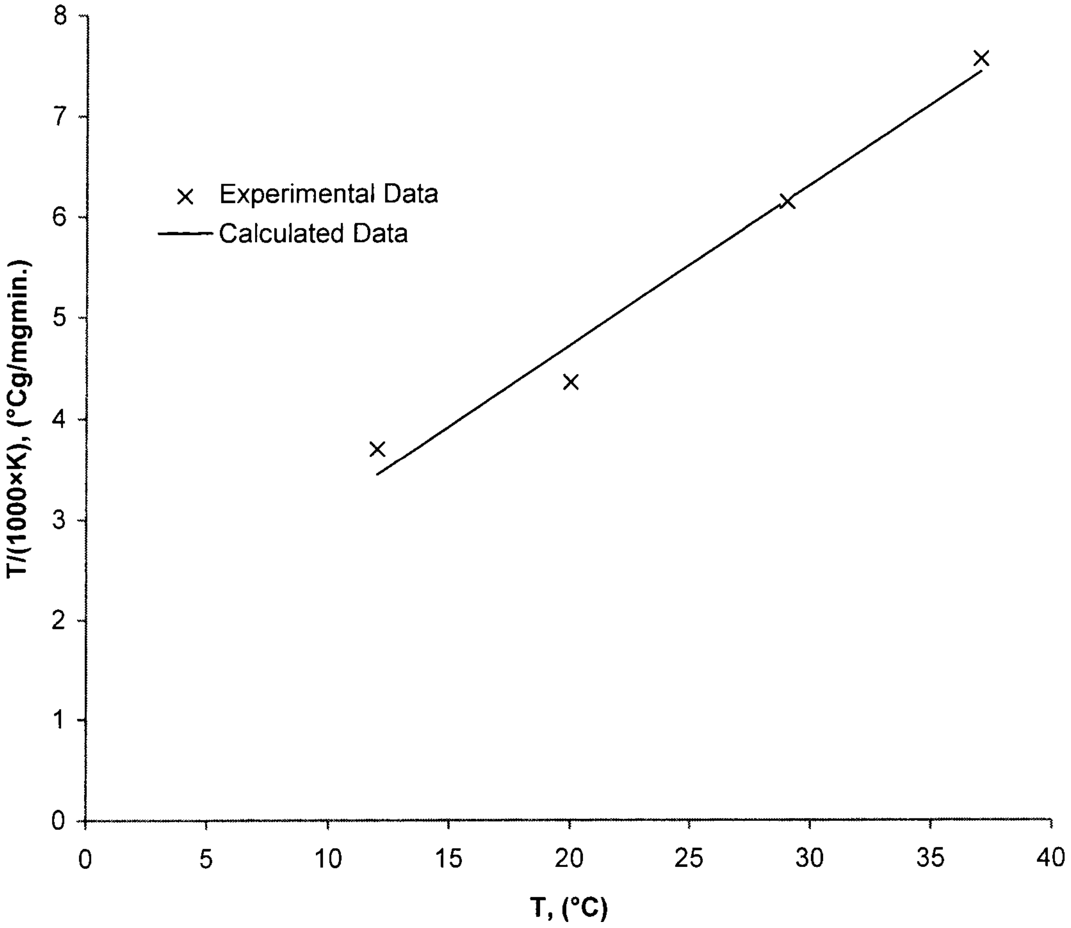
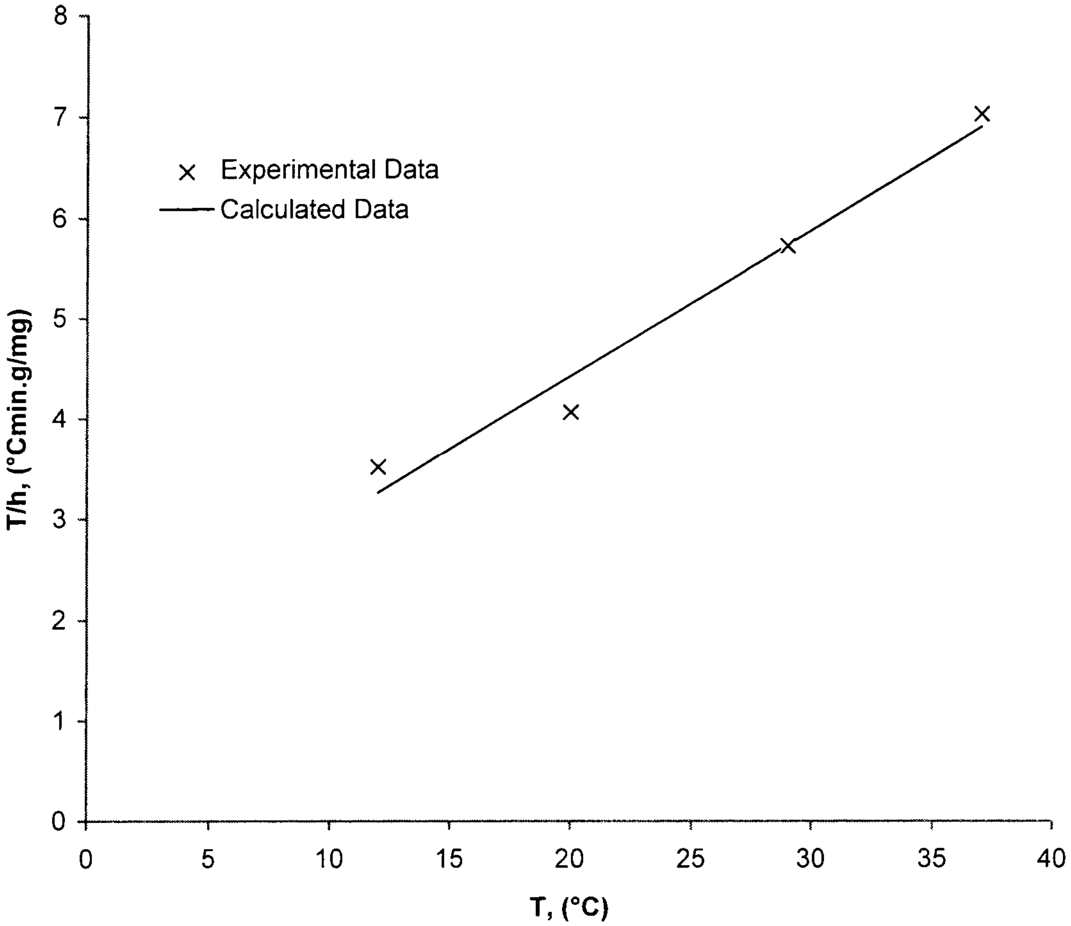


Figure 4.3.2-4: Effect of temperature on the adsorption of lead onto peat: plot of (temperature)/(initial adsorption rate), (T/h), versus temperature (T).



adsorption of lead species is lowered (Sharma *et al.*, 1991). Thus, on increasing the temperature of the reaction from 12 to 37°C, the equilibrium adsorption of the lead ion increased from 22.9 to 23.2 mg/g on peat. In other words, adsorption equilibrium is only slightly temperature dependent. Similarly, in other work by Brady *et al.* (1994), lead accumulation has been found to vary little with temperature, decreasing only 5% from 40°C to 0°C for biosorption of lead ion by non-viable yeast biomass.

It is further considered that q_e can be expressed as a function of T.

$$q_e = \frac{T}{4.29\times10^{-2}T+6.01\times10^{-3}}. \qquad (4.3.2\text{-}3)$$

A linear relation occurs between (T/q_e) and (T) with correlation coefficient of 0.999 **(Figure 4.3.2-5)**.

Substituting the values of q_e and K from equations **(4.3.2-3)** and **(4.3.2-1)** in equations **(4.2-2)** and **(4.2-6)**, the rate law for a second-order reaction and the relationship of q_t, T and t can be represented as:

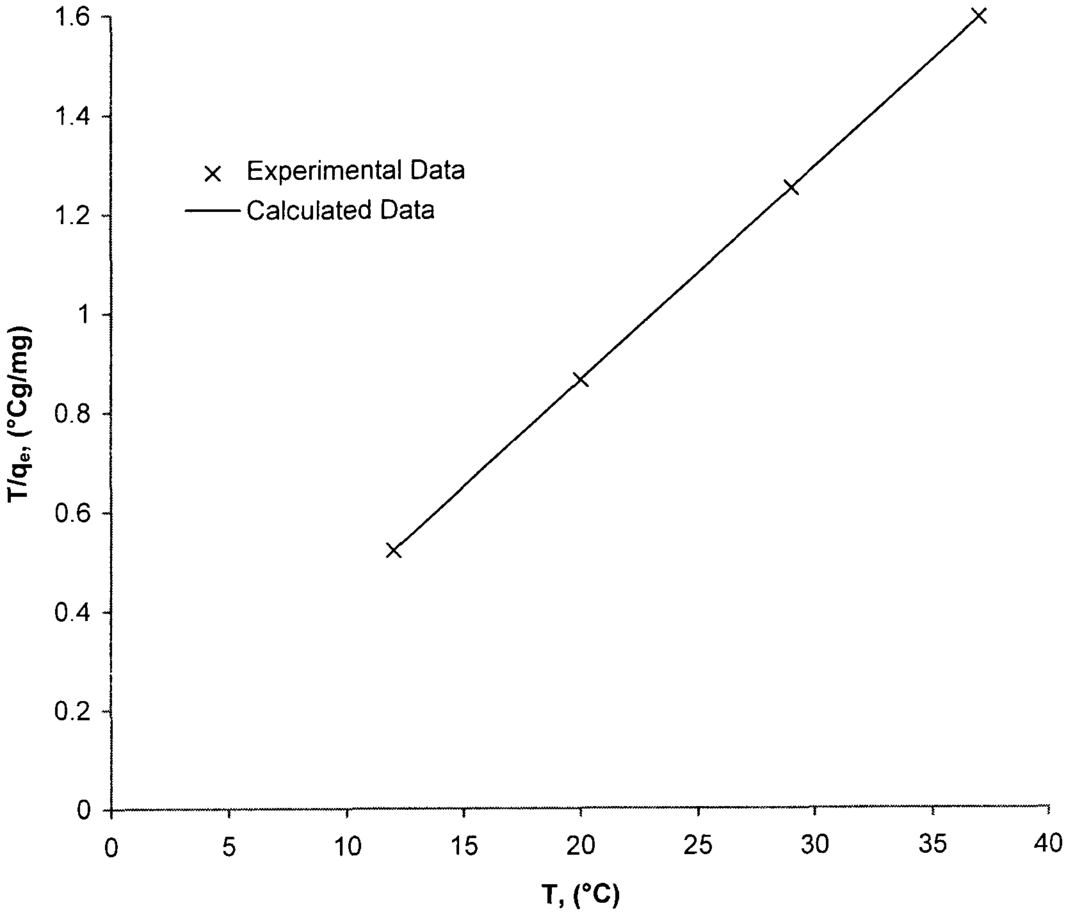
$$\frac{1}{\dfrac{T}{4.29\times10^{-2}T+7.71\times10^{-3}}-q_t} = \frac{1}{\dfrac{T}{4.29\times10^{-2}T+7.71\times10^{-3}}} + \frac{2T}{1.60\times10^{2}T+1.53\times10^{3}}\cdot t,$$

$$\frac{t}{q_t} = \frac{1.46\times10^{-1}T+1.52}{T} + \frac{\left(4.29\times10^{-2}T+7.71\times10^{-3}\right)}{T}\cdot t. \qquad (4.3.2\text{-}4)$$

Equation **(4.3.2-4)** represents a generalised predictive model for the lead ion adsorbed at any contact time, t, and involved temperature of reaction. It indicates that the lead ion adsorbed at any contact time is higher for greater temperature of reaction.

Similarly, a predictive model for the removal of lead ion, R_t, at any contact time, t, and involved temperature, T, can be presented as follows:

Figure 4.3.2-5: Effect of temperature on the adsorption of lead onto peat: plot of (temperature)/(amount adsorbed at equilibrium), (T/q_e), versus temperature (T).



$$R_t = \frac{t}{\frac{3.64\times10^{-2}T-3.79\times10^{-1}}{T}+\frac{\left(1.07\times10^{-2}T+1.93\times10^{-3}\right)}{T}\cdot t}.$$

This equation can then be used to derive the percent lead removal at any given temperature and the reaction time. The three dimension plot of the equation is shown in **Figure 4.3.2-6**.

4.3.3. Effect of Peat Dose

The results of effect of peat dose in tests carried out in the same initial ion concentration 100 mg/l, temperature of 25°C and pH of 5.0 are shown in **Figure 4.3.3-1**. Data from a series of kinetic experiments at five different peat doses between 4.0 to 32 g/l are shown in **Table 4.3.3-1**. These plots show that at all peat doses, the lead ion adsorbed increases rapidly with time in the beginning and very slowly towards the end of the reaction. Furthermore, a large fraction of the total amount of metal was removed within a short time. The plots also indicate that the adsorption was higher for lower peat doses at any time. There is an effect on the contact time required to reach saturation due to a variation in peat dose. With sphagnum moss peat as an adsorbent, using a peat dose from 4.0 to 32 g/l, equilibrium adsorption decreased from 24.2 to 3.08 mg/g. Equilibrium adsorption of lead ion is therefore a function of peat dose. The rate constant, the equilibrium adsorption and the initial adsorption rate at various peat doses were calculated from the intercept and slope of the straight line plots of (t/q_t) versus (t) in equation **(4.2-4)** **(Figure 4.3.3-2)**. The initial adsorption rate, h, increased with an increase in the peat dose. For example, when peat dose, m_s, was varied from 4.0 to 32 g/l, h varied from 5.55 to 13.4 mg/gmin. Finally, the values of the rate constant were found to increase from 0.00474 to 0.708 g/mgmin., with an increase in the peat dose from 4.0 to 32 g/l, so clearly changes in peat concentration have a fundamental effect on the course of the reaction.

Figure 4.3.2-6: Effect of temperature (T) on lead removal (R_t) at various reaction times (t).

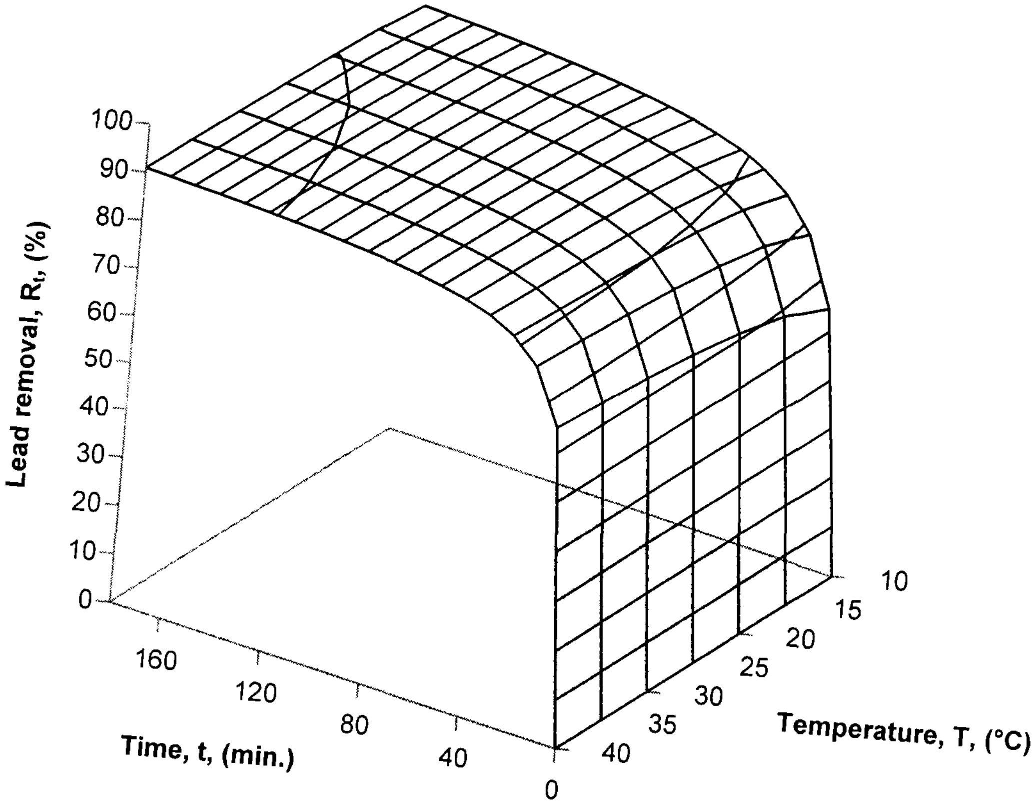


Figure 4.3.3-1: Effect of peat dose on the adsorption kinetics of lead onto peat at an initial lead concentration of 100 mg/l, pH = 5.0 and temperature of 25°C: plot of adsorbed amount (q_t) versus time (t).

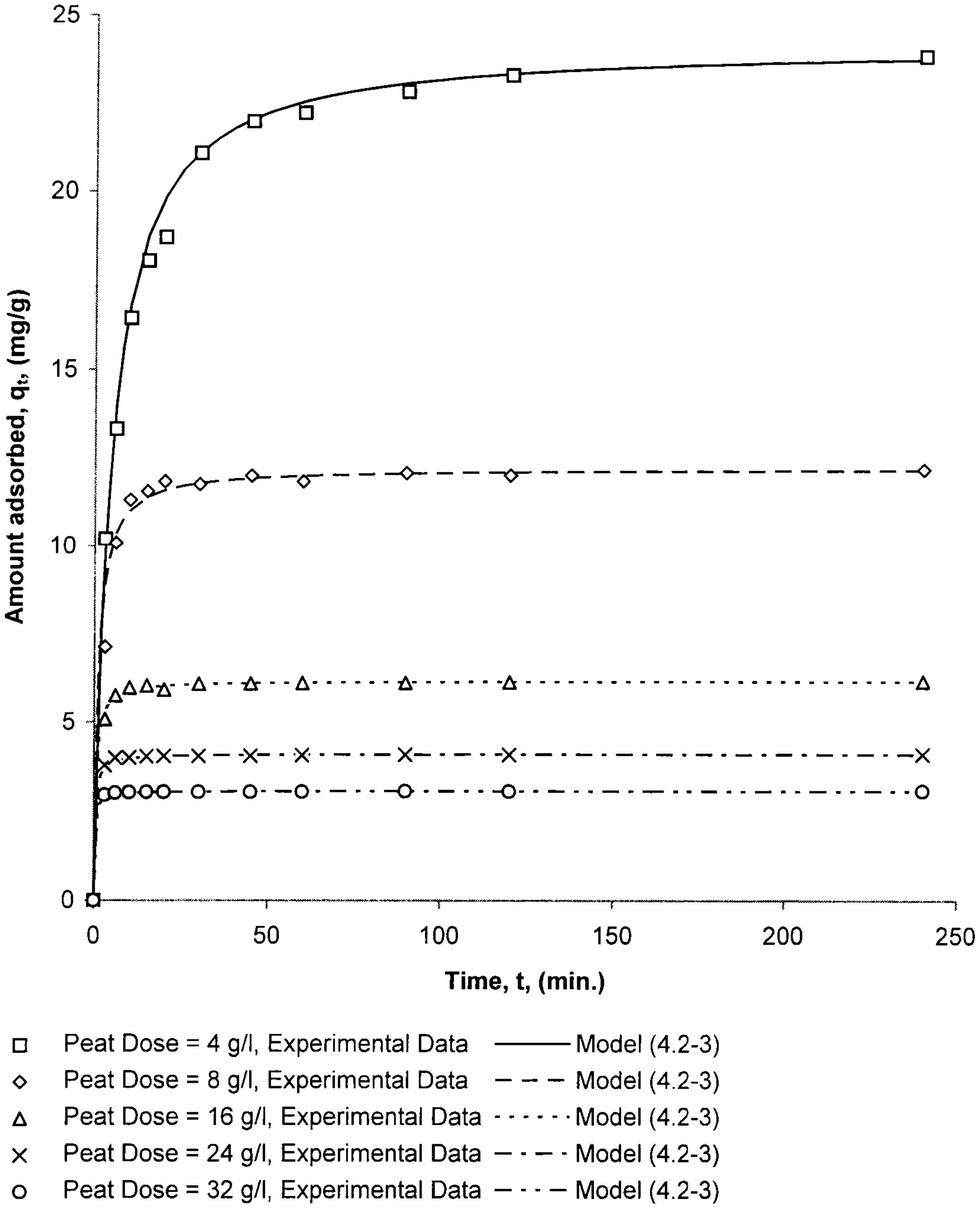


Figure 4.3.3-2: Plot of (time)/(adsorbed amount), (t/q_t), versus time (t) for adsorption of lead onto peat for an initial lead concentration of 100 mg/l, pH = 5.0 and temperature of 25°C.

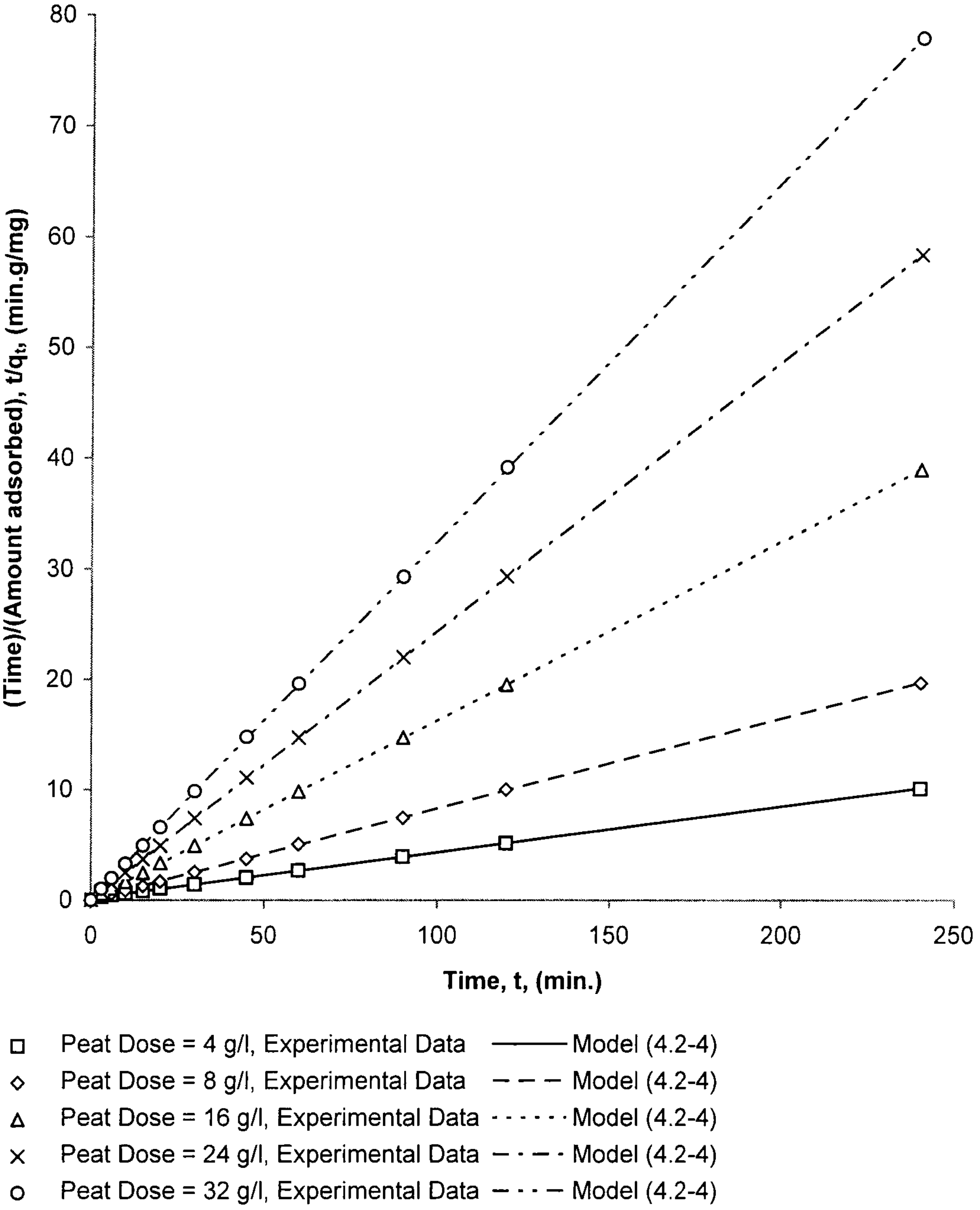


TABLE 4.3.3-1: Lead Ion Adsorption Data. Peat Dose, m_s; Lead Ion Removal Capacity at Equilibrium, q_e; Metal Ion Removed at Equilibrium, R_e; Initial Adsorption Rate, h; and Rate Constant, K; for Sphagnum Moss Peat in Respect of Various Peat Doses at pH = 5, Initial Lead Ion Concentration of 100 mg/l and Temperature of 25°C.

m_s (g/l)	q_e (mg/g)	R_e (%)	h (mg/gmin.)	K (g/mgmin.)
4	24.2	96.7	5.55	0.00474
8	12.2	97.8	11.3	0.0378
16	6.17	98.7	13.0	0.170
24	4.11	98.6	13.1	0.387
32	3.08	98.5	13.4	0.708

The corresponding linear plots of the values of q_e, h and K against m_s are displayed in **Figures 4.3.3-3** to **4.3.3-5** respectively, and were regressed to obtain expressions for these values in terms of the m_s parameters with correlation coefficients of 0.999, 0.978 and 0.993 respectively as follows:

$$q_e = \frac{1}{1.01 \times 10^{-2} m_s + 7.14 \times 10^{-4}}, \tag{4.3.3-1}$$

$$h = \frac{m_s}{6.28 \times 10^{-2} m_s + 3.21 \times 10^{-1}}, \tag{4.3.3-2}$$

$$K = 2.14 \times 10^{-4} m_s^{2.37}. \tag{4.3.3-3}$$

Substituting the values of q_e and K from equations **(4.3.3-1)** and **(4.3.3-3)** in equations **(4.2-2)** and **(4.2-6)**, the relationship between q_t, m_s and t follows the rate law for a second-order reaction and can be represented as:

Figure 4.3.3-3: Effect of peat dose on the adsorption of lead onto peat: plot of 1/(amount adsorbed at equilibrium), ($1/q_e$), versus peat dose (m_s).

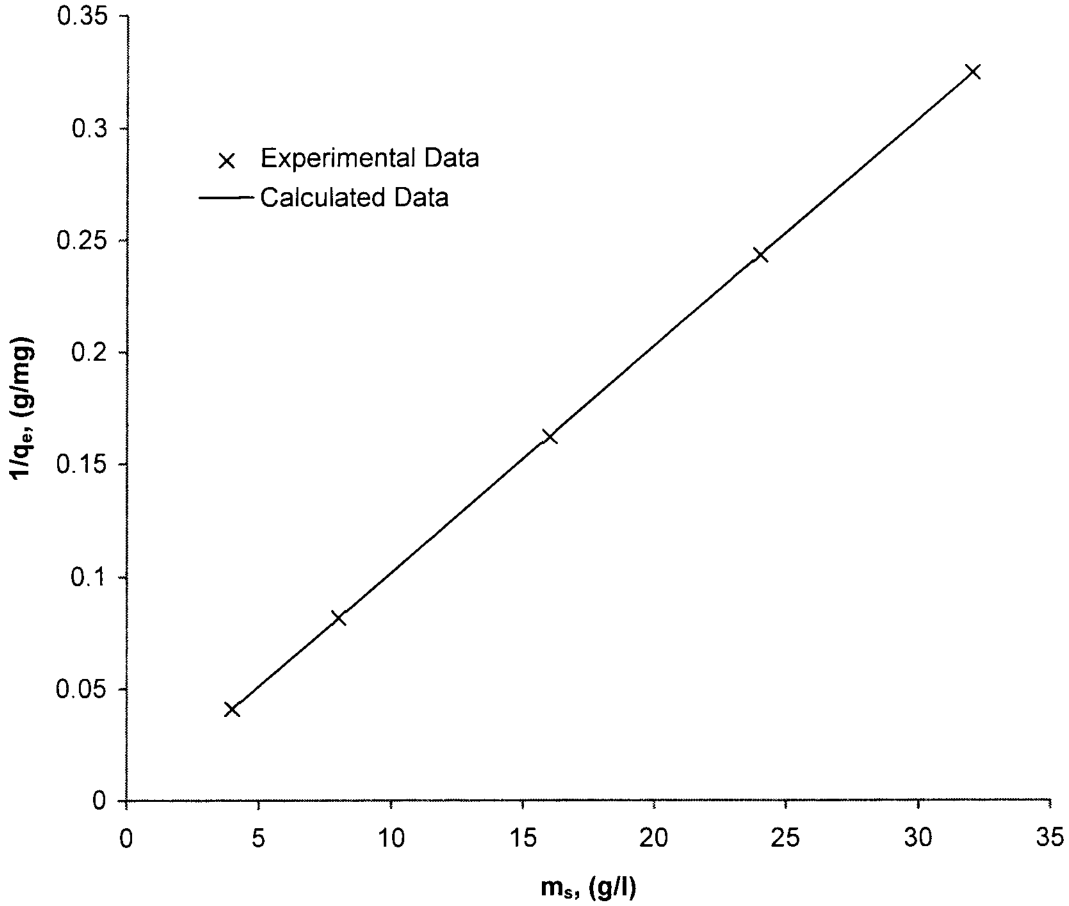


Figure 4.3.3-4: Effect of peat dose on the adsorption of lead onto peat: plot of (peat dose)/(initial adsorption rate), (m_s/h), versus peat dose (m_s).

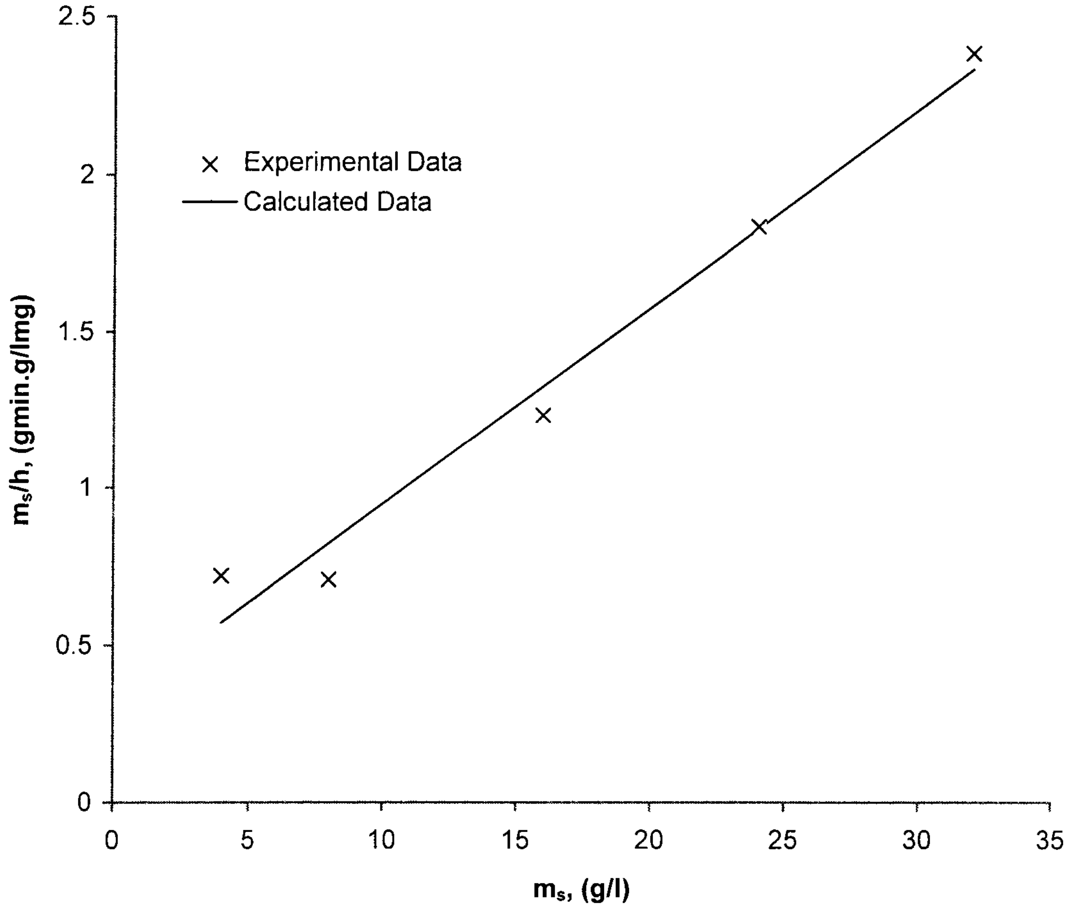
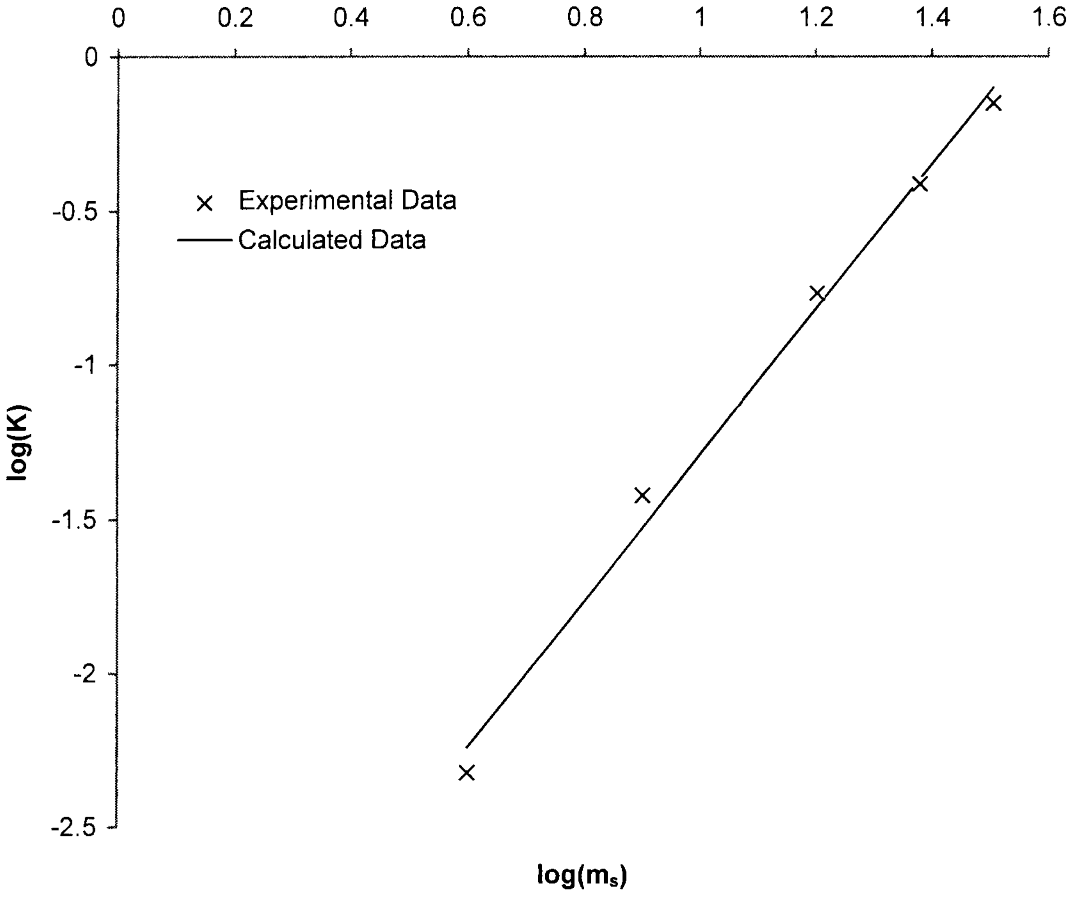


Figure 4.3.3-5: Effect of peat dose (m_s) on the adsorption of lead onto peat: plot of log(rate constant), log(K), versus log(peat dose), log(m_s).



$$\frac{1}{\dfrac{1}{1.01\times10^{-2}m_s+7.14\times10^{-4}}-q_t}=\frac{1}{\dfrac{1}{1.01\times10^{-2}m_s+7.14\times10^{-4}}}+4.28\times10^{-4}m_s^{\;2.37}\cdot t,$$

$$\frac{t}{q_t}=\frac{6.28\times10^{-2}m_s+3.21\times10^{-1}}{m_s}+\left(1.01\times10^{-2}m_s+7.14\times10^{-4}\right)\cdot t. \qquad (4.3.3\text{-}4)$$

Equation (**4.3.3-4**) represents a generalised predictive model for the metal ion adsorbed at any contact time and particular peat dose. It indicates that at any contact time, the lead adsorbed per unit weight of peat is higher the lower the peat dose. This is because the increasing peat dose increases the surface area for adsorption and hence, at constant initial lead ion concentrations, the rate of lead adsorption is increased, as clearly indicated in equation (**4.3.3-4**).

Similarly, a predictive model for the removal of lead ion, R_t, at any contact time, t, and involved peat dose, m_s, can be presented as follows:

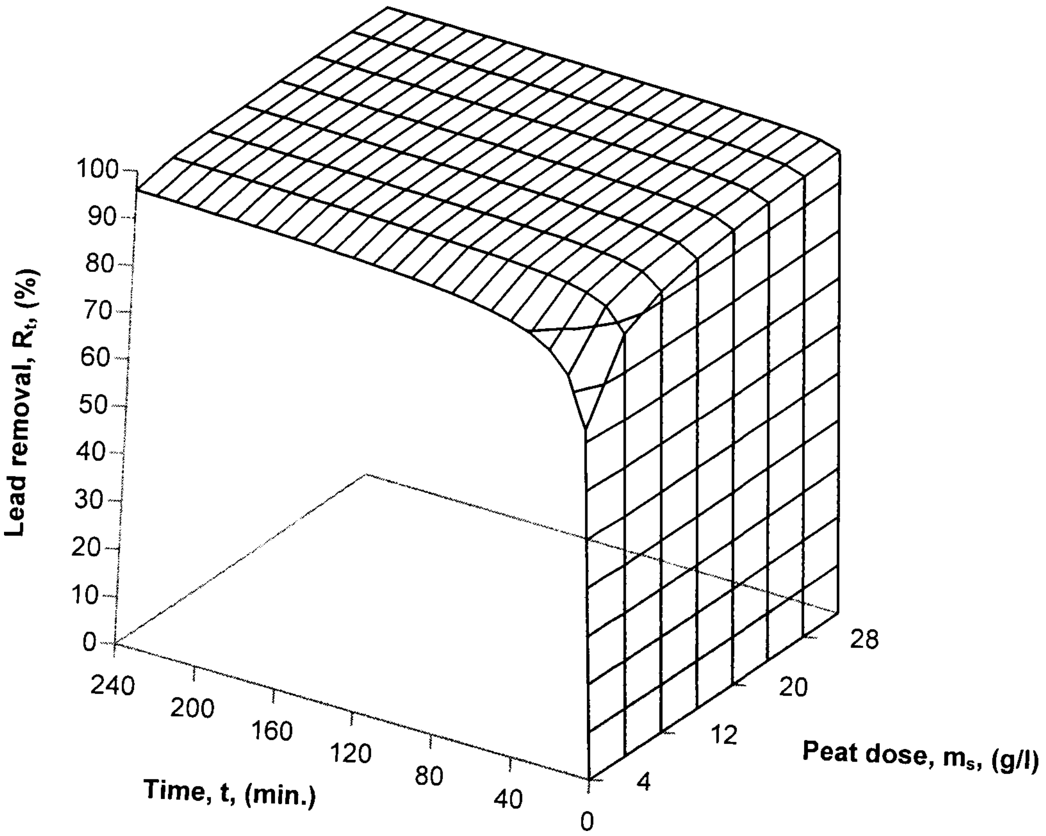
$$R_t=\frac{t}{\dfrac{1}{1.44\times10m_s-2.89\times10}+\dfrac{\left(1.01\times10^{-2}m_s+7.14\times10^{-4}\right)}{m_s}\cdot t}. \qquad (4.3.3\text{-}5)$$

This equation can then be used to derive the percent lead removal at any given peat dose and the reaction time. A three dimensional plot of the equation is shown in **Figure 4.3.3-6**.

A kinetic model has been developed and fitted for the adsorption of divalent metal ions onto sphagnum moss peat. The parameter which has most influence on the kinetics of the adsorption reaction is adsorption equilibrium. This is a function, principally, of temperature, initial metal ion concentration, peat dose and nature of solute.

The adsorption of metal ions onto peat at various initial concentrations of metal ions, temperatures, peat doses and solute types shows that the amount of metal adsorbed

Figure 4.3.3-6: Effect of peat dose (m_s) on lead removal (R_t) at various reaction times (t).



initially increases rapidly with time, but only increases very slowly towards the end of the reaction. Indeed, a large fraction of the total amount of metal was removed within a short time. Hence, the sorption process could have been complex and might have involved more than one mechanism. According to Taylor (1931) chemisorption is usually associated with an appreciable activation energy and therefore may be a relatively scow process. By contrast, physisorption requires no activation energy and therefore occurs more rapidly than chemisorption. It was also observed that the initial lead ion concentration and peat dose were more effective parameters than temperature in estimating the sorption rate, and overall, this suggests that the bulk of the initial adsorption of lead by sphagnum moss peat arises through a physisorption process.

The results clearly establish that a pseudo second order model provides a more appropriate description of the binding of copper, nickel, and lead to peat than a first order equation. When the second order reaction equation was used to describe kinetic behaviour of metal adsorption onto sphagnum moss peat, the adsorption capacity was predicted well. The data also confirm that chemical bonding is more important than pore diffusion in determining the adsorption rates and that their relative significance depends on the temperature, initial metal ion concentration, pH, peat dose and nature of solute.

Finally, it is important to note that our second order model has already found an interesting application. Thus Fernandez *et al.* (1995) have published a paper which uses the model described in section (Chapter 5.3.1) which we have already developed and published (Ho *et al.*, 1995). Moreover, they applied it to results which they obtained from a system which is significantly of lauryl benzyl sulphonate from aqueous solution by algal pulp. In spite of the obvious differences, the model fitted their results well. This confirms our findings that it is suitable for predicting what will go and in a wide variety of adsorption situations, and gives us confidence that it can be used as a tool for process design.

It is clear that this more accurate description permits improved modelling of these processes, and will, overall, lead to improved process design in the future.

4.4. INTERAPARTICLE DIFFUSION

In the batch adsorption system, there is high speed shaking and since the peat particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk liquid to the particle's external surface. One might then postulate that the limiting step is intra-particle diffusion, and if this is the case a rate constant can be found from a plot of the amount of ion adsorbed against $t^{0.5}$. If the postulated mechanism is correct, then a linear plot passing though the origin is obtained for each adsorption condition. Furthermore, the value of the rate constant for diffusion can be obtained from the slope of the line.

Removal of adsorbate at various conditions takes place in two phases. The first phase of solute uptake; the "immediate solute removal", is achieved within a short time. This is followed by the "subsequent removal of solute" and this continues for much longer. The logarithmic plot of R_t and t for the result is linear and can be expressed as: (Srivastava *et al.*, 1987)

$$R = K_t \cdot t^{m_1},$$

where

R_t is the percentage of metal ion removal at equilibrium, (%);

t is the contact time, (min.);

m_1 is the slope of linear plot;

K_t is a constant coefficient;

m_1K_t is the percentage of metal ion removal at first minute, (%).

Slope m depicts the adsorption mechanism (Srivastava *et al.*, 1987) and the term K_t may be taken as the rate factor (i.e. percent solute removal per min.). Higher values of K_t indicate an enhancement in the rate of removal, whereas larger m values indicate a better sorption mechanism, which may be due to improved bonding between solute ions and adsorbent particles.

According to Weber and Morris (1963), a value of $m_1 = 0.5$ reflects intraparticle diffusion as the rate determining step. The results of this study (**Table 4.4-1**) show that the values of m_1 are much less than 0.5, which suggests that both the processes are involved to an almost equal extent. The adsorption reaction is not a pore diffusion limiting step.

TABLE 4.4-1: Variations of log(Time) Versus log(Percent Metal Ion Removal) Constants From Plot for Various Conditions.

Effects		K_1	m_1	m_1K_1	r^2
Peat dose on lead	4 g/l	40.0	0.186	7.45	0.864
	8 g/l	66.3	0.0882	5.85	0.561
	16 g/l	85.4	0.0322	2.75	0.603
	24 g/l	92.5	0.0135	1.25	0.692
	32 g/l	95.1	0.00696	0.662	0.802
Temperature on lead	12°C	28.7	0.245	7.04	0.890
	20°C	35.6	0.206	7.32	0.836
	29°C	36.6	0.200	7.31	0.830
	37°C	38.7	0.087	3.24	0.855
Initial lead ion concentration	35 mg/l	88.0	0.0303	2.66	0.427
	50 mg/l	81.5	0.0456	3.72	0.680
	100 mg/l	64.9	0.102	6.61	0.648
	160 mg/l	56.6	0.132	7.47	0.781
	210 mg/l	49.1	0.154	7.56	0.749
Initial nickel ion concentration	10 mg/l	54.3	0.0990	5.38	0.915
	25 mg/l	25.5	0.189	4.82	0.961
	50 mg/l	21.7	0.171	3.73	0.976
	100 mg/l	10.5	0.219	2.29	0.982
	200 mg/l	6.08	0.168	1.03	0.967
Initial copper ion concentration	25 mg/l	60.5	0.0958	5.79	0.785
	50 mg/l	27.4	0.201	5.52	0.933
	100 mg/l	17.3	0.226	3.91	0.882
	200 mg/l	10.2	0.215	2.19	0.925
	1000 mg/l	5.57	0.300	1.67	0.870

In these investigations the values of m were found to range from 0.03 to a value 0.23 which indicates that pore diffusion is not the only rate determining step in peat-metal adsorption. Rather, transport of adsorbate from solution to the particle solution interface and the binding reaction are equally responsible. It is observed that an increase in the peat dose and temperature again results in a decrease in m values with a corresponding increase in the factor K_t. However, a decrease in the initial lead ion concentration results in an increase in m values with a corresponding decrease in the factor K_t. The adsorption data as shown in **Table 4.4-1** indicate that an increase in initial temperature causes an insignificant decrease in slope m and an increase in constant K_t. The larger values of m, indicating stronger bonding between adsorbate and adsorbent, also justify subsequent removal of solute by diffusion through peat particles, when temperature is lower at the solid-liquid interface. Smaller values of K_t for comparatively higher temperatures, result in smaller values of lead removal in the first phase (immediate solute removal) and this may be due to comparatively fewer active sites available on peat for high level lead adsorption.

A comparison (**Table 4.4-2**) between adsorption of small and large metal ions by peat indicates that a smaller particle results in a smaller m_1, whereas a larger molecule results in a larger m_1. The constant, m_1, increased with increasing metal concentration for all of metals in this study but decreased with increasing temperature and increase in peat dose (**Table 4.4-1**). The effect also seems to apply to adsorption of larger organic molecules (Srivastava *et al.*, 1987). The pore diffusion step also seems more significant as a rate limiting step for larger molecules, higher concentration, lower adsorbent dose, and lower temperature. Indeed, in such conditions the rate of pore diffusion of a particle would be at lower.

The influential factors are influence of the adsorption surface and metal ion concentration. For a smaller peat dose, intraparticle diffusion will be the main mechanism for a greater portion of adsorption reaction than with larger peat doses. Indeed, the smaller peat dose could not offer enough bare surface for adsorption of ions. Thus, diffusion of ions to micropores will in such cases be the predominant mechanism.

Furthermore, for the larger initial metal ion concentrations, intraparticle diffusion will be the main mechanism for a greater portion of adsorption reaction than with smaller initial metal ion concentration. The metal ions will occupy the bare sites an any surface where ionic diffusion to micropores is the predominant mechanism in adsorption systems involving larger initial metal ion concentrations. Temperature seemed to have little effect on these overall conclusions, for the influence of temperature was very slight over the whole range 12 to 37°C.

TABLE 4.4-2: Comparison of m_1 for a Range of Adsorbates.

	Radii (Å)	m_1	Reference
Ni^{2+}	0.78	0.099-0.22	This study
Cu^{2+}	0.72	0.096-0.23	This study
Pb^{2+}	1.32	0.030-0.15	This study
$HCrO_4^-$	2.42	0.34-0.37	Shama, 1994

CHAPTER FIVE

RESULTS AND DISCUSSION OF ADSORPTION IN MULTI-METAL SYSTEMS

5.1. ADSORPTION EQUILIBRIA

The work reported in this volume shows that peat is effective at binding metals. However, to employ sphagnum moss peat in a treatment system, more information is needed on the binding capacities of various metals and on reaction rates. In particular, it is important to find out what happens to solution of mixed cations. Hence, in this section, uptake of heavy metals from bimetallic solutions of copper and nickel, copper and lead, as well as lead and nickel have been evaluated in our test sphagnum moss peat biosorption system under controlled conditions of pH and reaction time.

Peat has been recognised as a good adsorbent for the purification of industrial wastewaters and the adsorption of heavy metal ions onto sphagnum moss peat from aqueous solution has been studied for single solute systems (Sharma and Forster, 1993; and Ho *et al.*, 1994). However, in most cases, industrial wastewaters contain complex mixtures of components. Trujillo *et al.* (1991) have investigated competitive adsorption of six metal ions from wastewater both in batch systems and in semicontinuous packed-bed experiments. The results show that mathematical models can provide effective multi-component equilibrium constants, adsorptive capacities and reduced overall mass-transfer coefficients. Gould and Genetelli (1984) have also examined the competition between heavy metal ions for binding sites using zinc, nickel, cadmium and copper as test metals. The results show that their adsorbent had the highest binding capacity for copper; that this was independent of the others and that copper also exerted the largest competing effect. Jain and Snoeyink (1973) found that not only was there adsorption with equal competition for adsorption sites but also that adsorption without competition for different types of site occurred in a binary organic system. In addition, it has been found that the effects of competitive adsorption become more marked with the increase in the number of solutes in solution (Martin and Al-Bahrani, 1977).

5.1.1. Adsorption of Similar Size Metal Bi-Solute System

The purpose of this study was to investigate competitive adsorption onto sphagnum moss peat from an aqueous bi-solute mixture of selected metal ions which are of a similar size; namely the divalent metal ions, copper(II) and nickel(II).

Many studies have been reported concerning removal of organics from bi-solute organic solution systems (Jain and Snoeyink, 1973; Martin and Al-Bahrani, 1977; Yaacoubi *et al.*, 1991; and Srivastava and Tyagi, 1995), but few have dealt with competitive adsorption of metal ions. The most common model for describing adsorption equilibrium in multi-adsorbate systems is the Langmuir model for competitive adsorption. According to Jain and Snoeyink (1973) adsorption without competition has been used as a basis to modify the Langmuir theory for binary adsorbate systems. Therefore, a Jain and Snoeyink model can be proposed for this system as:

$$q_{e,Ni} = \frac{X_{m,Ni} \cdot B_{Ni} \cdot C_{e,Ni}}{1 + B_{Cu} \cdot C_{e,Cu} + B_{Ni} \cdot C_{e,Ni}},$$

$$q_{e,Cu} = \frac{\left(X_{m,Cu} - X_{m,Ni}\right) \cdot B_{Cu} \cdot C_{e,Cu}}{1 + B_{Cu} \cdot C_{e,Cu}} + \frac{X_{m,Ni} \cdot B_{Cu} \cdot C_{e,Cu}}{1 + B_{Cu} \cdot C_{e,Cu} + B_{Ni} \cdot C_{e,Ni}}.$$

However, this model proved not good enough for our purposes. We therefore modified the equation, using a coefficient, based on the ratio of solute in the solution; the Ho coefficient. On this basis, the following mathematical models are proposed:

$$q_{e,Ni} = Y_l \cdot \frac{X_{m,Ni} \cdot k_{Ni} \cdot C_{e,Ni}}{1 + k_{Cu} \cdot C_{e,Cu} + k_{Ni} \cdot C_{e,Ni}}, \qquad (5.1.1\text{-}1)$$

$$q_{e,Cu} = Y_h \cdot \frac{\left(X_{m,Cu} - X_{m,Ni}\right) \cdot k_{Cu} \cdot C_{e,Cu}}{1 + k_{Cu} \cdot C_{e,Cu}} + \frac{X_{m,Ni} \cdot k_{Cu} \cdot C_{e,Cu}}{1 + k_{Cu} \cdot C_{e,Cu} + k_{Ni} \cdot C_{e,Ni}}. \qquad (5.1.1\text{-}2)$$

The addition term of equation **(5.1.1-2)** is the Langmuir expression for the number of copper ions that adsorb without competition on the surface area proportional to ($X_{m,Cu}$ - $X_{m,Ni}$) and Y_h is the coefficient of the ratio of the concentrations for the higher competitive solute. The second term on the right side of equation **(5.1.1-2)**, represents the number of copper ions adsorbed on the surface area proportional to $X_{m,Ni}$ under competition with nickel(II), and is based on the Langmuir model for competitive adsorption. The number of nickel ions adsorbed on surface area proportional to $X_{m,Ni}$ under competition with copper(II) can be calculated from the corresponding Equation **(5.1.1-1)** and Y_l is the coefficient of ratio of concentration for the lower competitive solute. The value of the Langmuir constant $X_{m,Cu}$ (0.196 mM/g) is higher than $X_{m,Ni}$ (0.148 mM/g) in the single-solute system. It may be that there are different sorts of sites on the surface, some of which are specific for only one of the ions. There is no evidence of size and charge of metal ions which might otherwise account for the difference between $X_{m,Cu}$ and $X_{m,Ni}$. However, it has been suggested that positively charged ions compete for binding with the negatively charged adsorbent surfaces and that the uptake mechanism might depend on the charge, including electrostatic attraction (Kuyucak and Volesky, 1989), and could be correlated with ionic or hydrated ionic radii of the ions

(Tobin *et al.*, 1984). From the high correlation coefficient, it seems that competitive adsorption not only depends on the adsorption capacity in a single-solute system but also the ratio of the two solute ions in the solution.

Competitive adsorption was studied with the bi-solute system of copper(II) and nickel(II). A pH of 5.0 was used to determine the adsorption isotherms for initial concentrations in the mole ratio of 1:1.3 (Cu:Ni), 1.7:1 (Cu:Ni), and 1:2.6 (Cu:Ni) of 5 to 100 mg/l of copper(II) and nickel(II), respectively. Adsorption isotherms for each individual metal ion in the single-solute, and bi-solute systems are shown in **Figures 5.1.1-1** to **5.1.1-4** respectively. These relationships can be expressed with high correlation coefficients as:

for the mole ratio of 1:1.3 (Cu:Ni)

$$q_{e,Ni} = 0.49 \times \frac{2.28 \cdot C_{e,Ni}}{1 + 1.67 \times 10 \cdot C_{e,Cu} + 1.54 \times 10 \cdot C_{e,Ni}},$$

$$q_{e,Cu} = 2.3 \times \frac{8.12 \times 10^{-1} \cdot C_{e,Cu}}{1 + 1.67 \times 10 \cdot C_{e,Cu}} + \frac{2.47 \cdot C_{e,Cu}}{1 + 1.67 \times 10 \cdot C_{e,Cu} + 1.54 \times 10 \cdot C_{e,Ni}};$$

for the mole ratio of 1.7:1 (Cu:Ni)

$$q_{e,Ni} = 0.37 \times \frac{2.28 \cdot C_{e,Ni}}{1 + 1.67 \times 10 \cdot C_{e,Cu} + 1.54 \times 10 \cdot C_{e,Ni}},$$

$$q_{e,Cu} = 2.6 \times \frac{8.12 \times 10^{-1} \cdot C_{e,Cu}}{1 + 1.67 \times 10 \cdot C_{e,Cu}} + \frac{2.47 \cdot C_{e,Cu}}{1 + 1.67 \times 10 \cdot C_{e,Cu} + 1.54 \times 10 \cdot C_{e,Ni}};$$

for the mole ratio of 1:2.6 (Cu:Ni)

$$q_{e,Ni} = 0.55 \times \frac{2.28 \cdot C_{e,Ni}}{1 + 1.67 \times 10 \cdot C_{e,Cu} + 1.54 \times 10 \cdot C_{e,Ni}},$$

Figure 5.1.1-1: Adsorption isotherms for single-solute system.

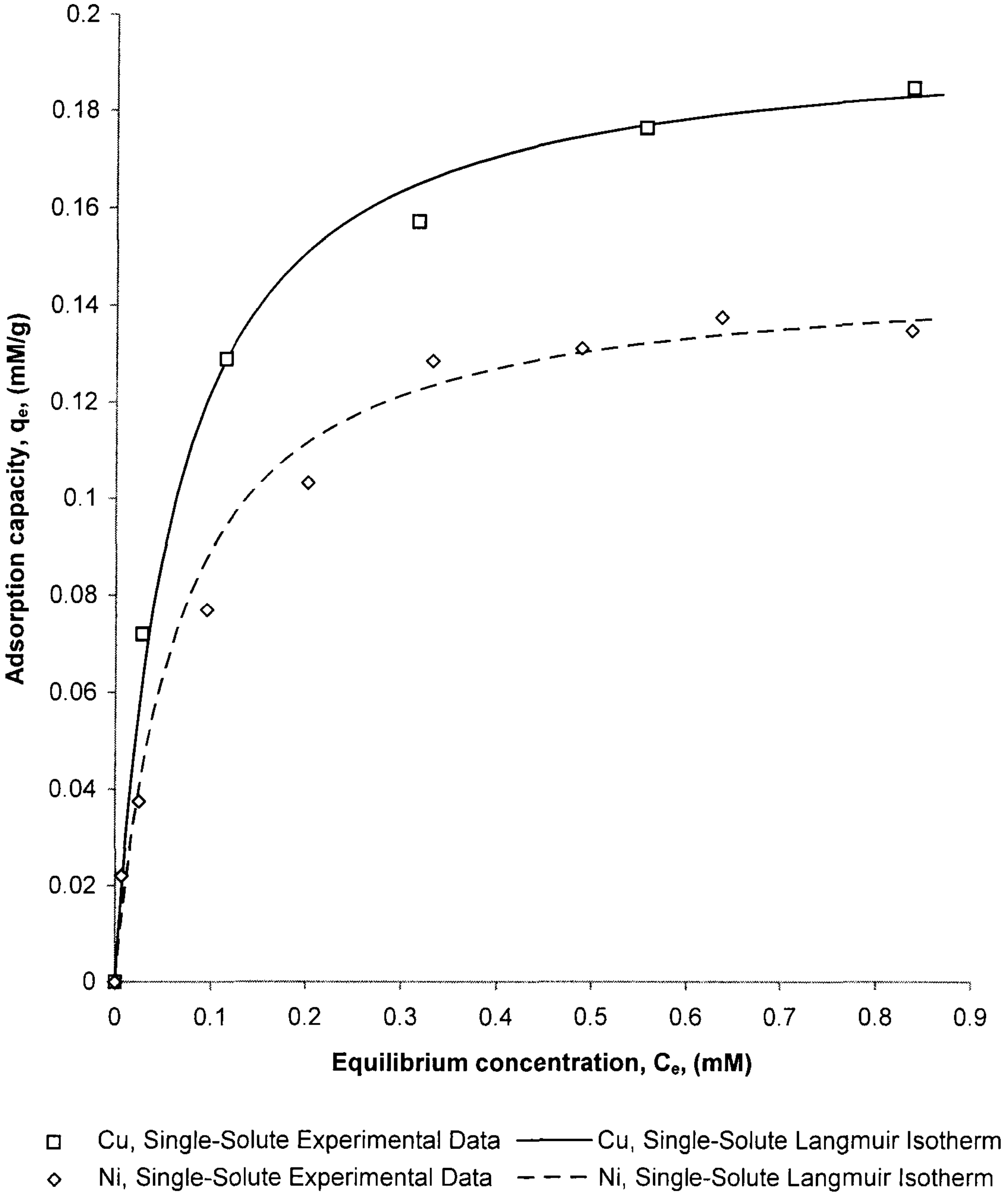


Figure 5.1.1-2: Adsorption isotherms for bi-solute system (Cu:Ni = 1:1.3).

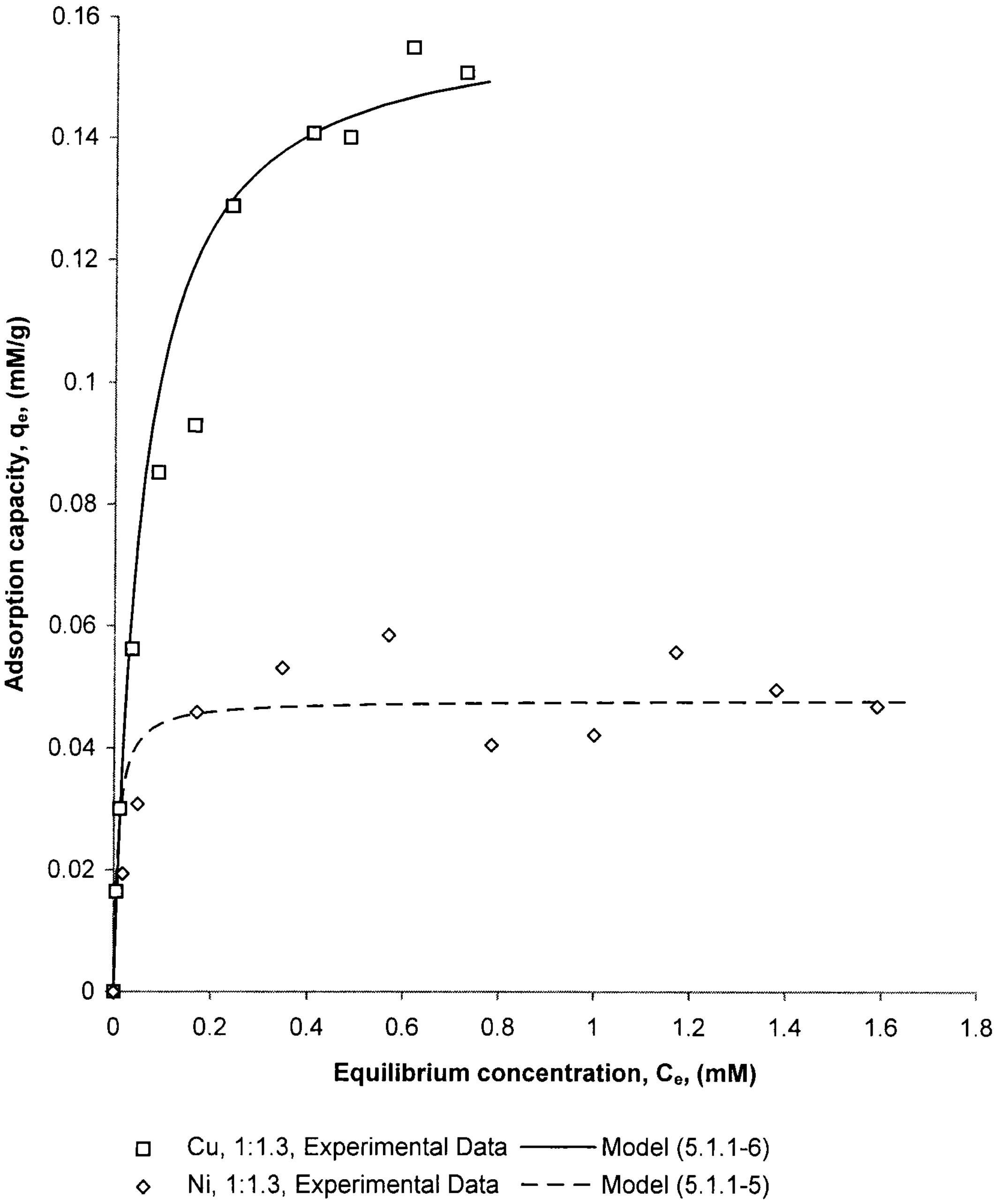


Figure 5.1.1-3: Adsorption isotherms for bi-solute system (Cu:Ni = 1.7:1).

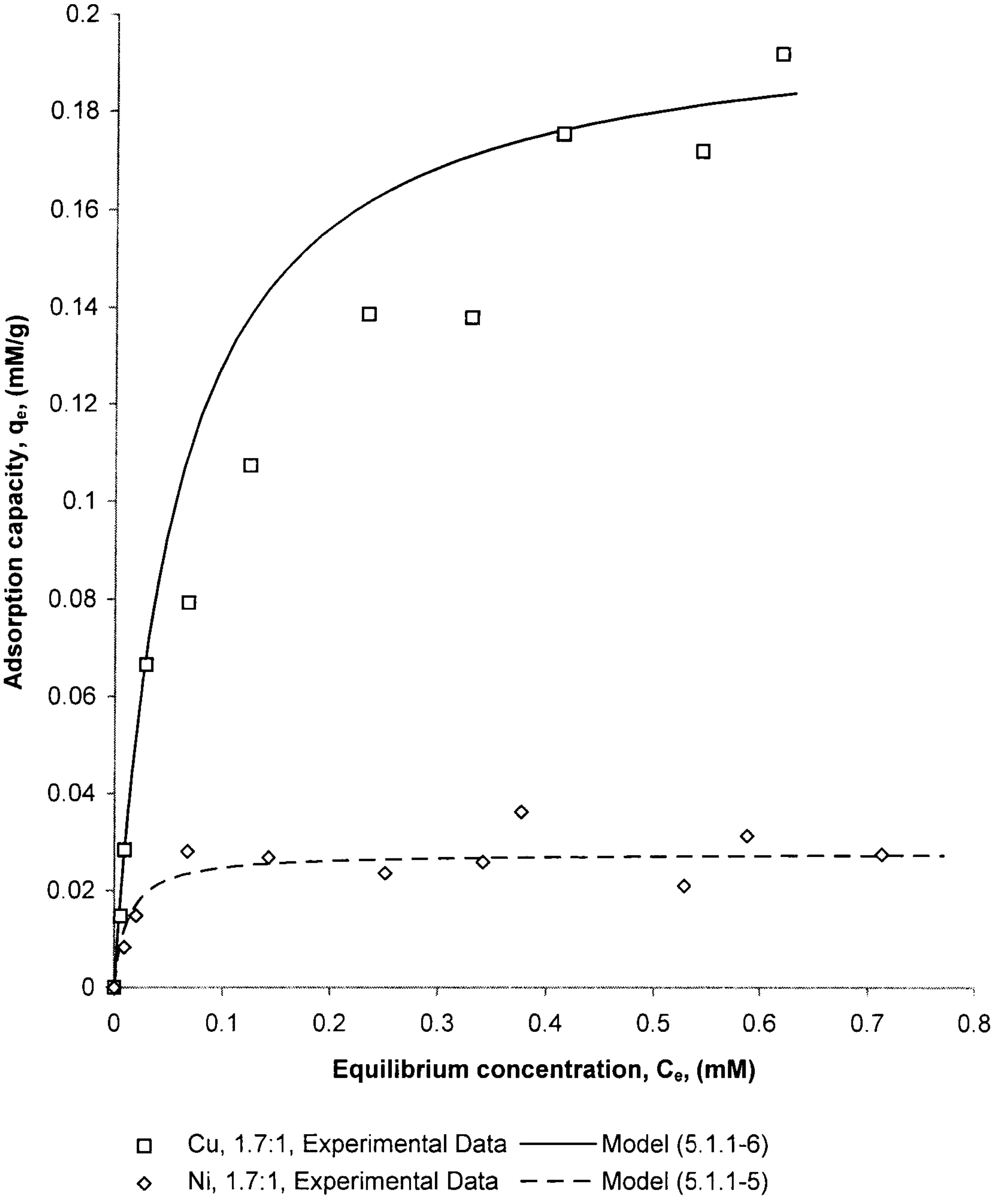
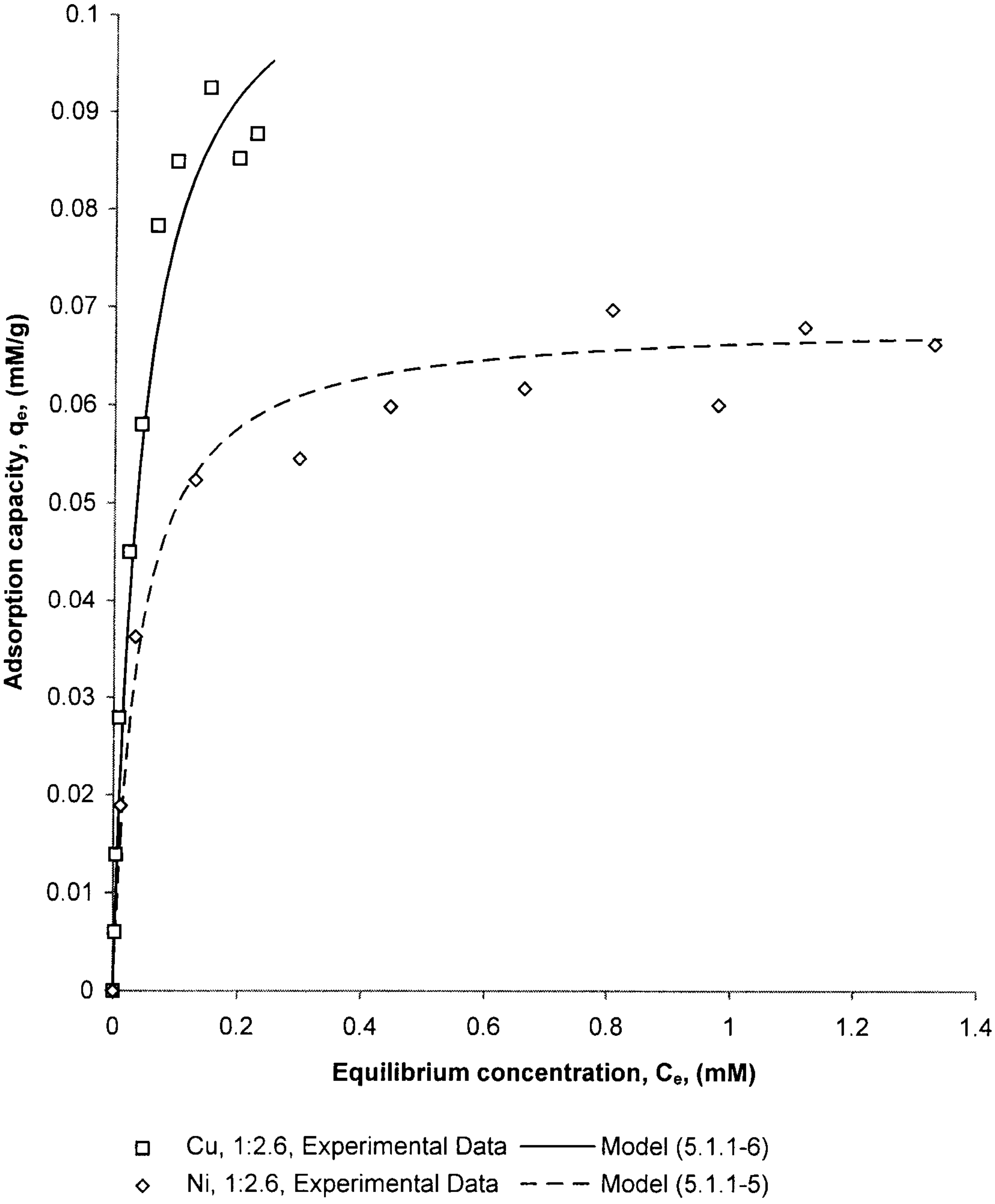


Figure 5.1.1-4: Adsorption isotherms for bi-solute system (Cu:Ni = 1:2.6).



$$q_{e,Cu} = 1.9 \times \frac{8.12 \times 10^{-1} \cdot C_{e,Cu}}{1 + 1.67 \times 10 \cdot C_{e,Cu}} + \frac{2.47 \cdot C_{e,Cu}}{1 + 1.67 \times 10 \cdot C_{e,Cu} + 1.54 \times 10 \cdot C_{e,Ni}}.$$

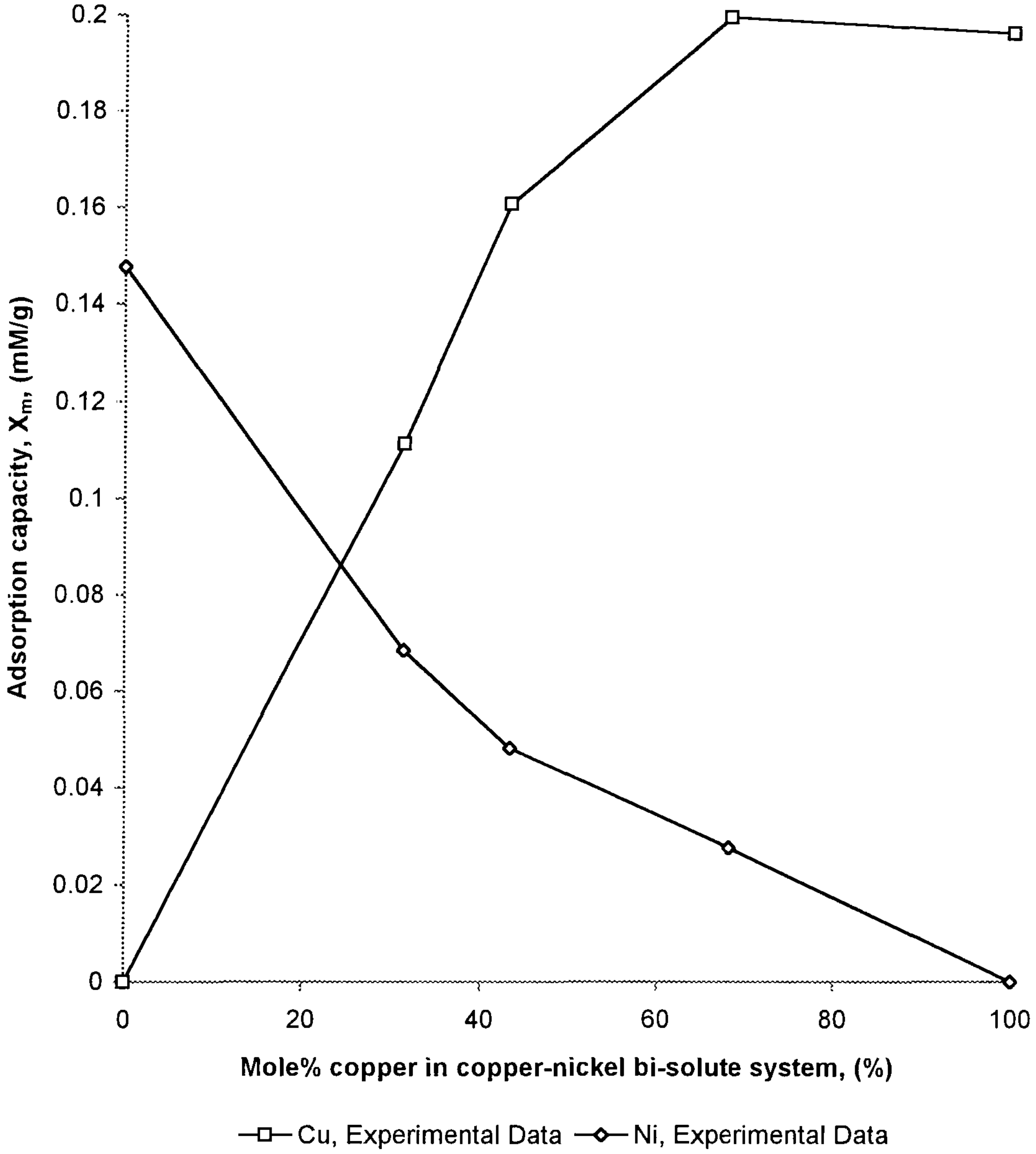
For the binary solute systems, the adsorption capacities of the primary metals were lower than in their respective single-solute systems (0.196 mM/g for copper and 0.148 mM/g for nickel) as shown in **Table 5.1.1-1**. It is clear that copper appears to have a higher competitive effect than nickel. In the three concentration mole ratios, the adsorption capacities for copper were much higher than nickel. **Table 5.1.1-1** also shows values for the mathematical model constants and coefficients in the bi-solute systems. It seems that the coefficient, Y_h, is higher for the metal which has most competitive effect; namely copper. The coefficient increased with increasing adsorption capacity, but the constant k decreased. In the case of the less competitive metal ion, which is nickel in this case, the coefficient Y_l also increased with increasing adsorption capacity.

TABLE 5.1.1-1: Adsorption Capacities, X_m; Langmuir Constants, k; and Ho Coefficients, Y; for Bi-Solute System.

Concentration	Copper			Nickel		
Cu:Ni	X_m, (mM/g)	k, (1/mM)	Y_h	X_m, (mM/g)	k, (1/mM)	Y_l
1:1.3	0.161	18.0	2.3	0.0482	117	0.49
1.7:1	0.199	18.1	2.6	0.0276	82.3	0.37
1:2.6	0.111	23.2	1.9	0.0684	26.2	0.55

The mathematical model constants are shown in **Table 5.1.1-1** and it can be seen that the maximum adsorption capacity of copper, X_m, is increased when ratio of concentration of copper to that of nickel increases. The maximum adsorption capacity of nickel increases when the mole ratio of concentration of nickel increases but decreases when the ratio of the concentration of copper increases (**Figure 5.1.1-5**).

Figure 5.1.1-5: Metal ion adsorption capacity (X_m) of peat as a function of concentration ratio in a bi-solute system.



To examine the correlation between the coefficient Y and the concentration mole ratio X, these evaluated coefficients, Y, were plotted against X in **Figure 5.1.1-6**. The data plots in **Figure 5.1.1-6** were regressed to express the coefficients Y as function of X in the experimental conditions to obtain equations

for copper:

$$Y_h = 1.97 \cdot \log(X_{Cu}) + 3.00, \tag{5.1.1-3}$$

for nickel:

$$Y_l = 0.624 \cdot \log(X_{Ni}) + 0.641, \tag{5.1.1-4}$$

where

Y_h is the coefficient for higher competitive metal ion;

X_{Cu} is mole ratio of concentration of copper;

Y_l is the coefficient for lower competitive metal ion;

X_{Ni} is mole ratio of concentration of nickel.

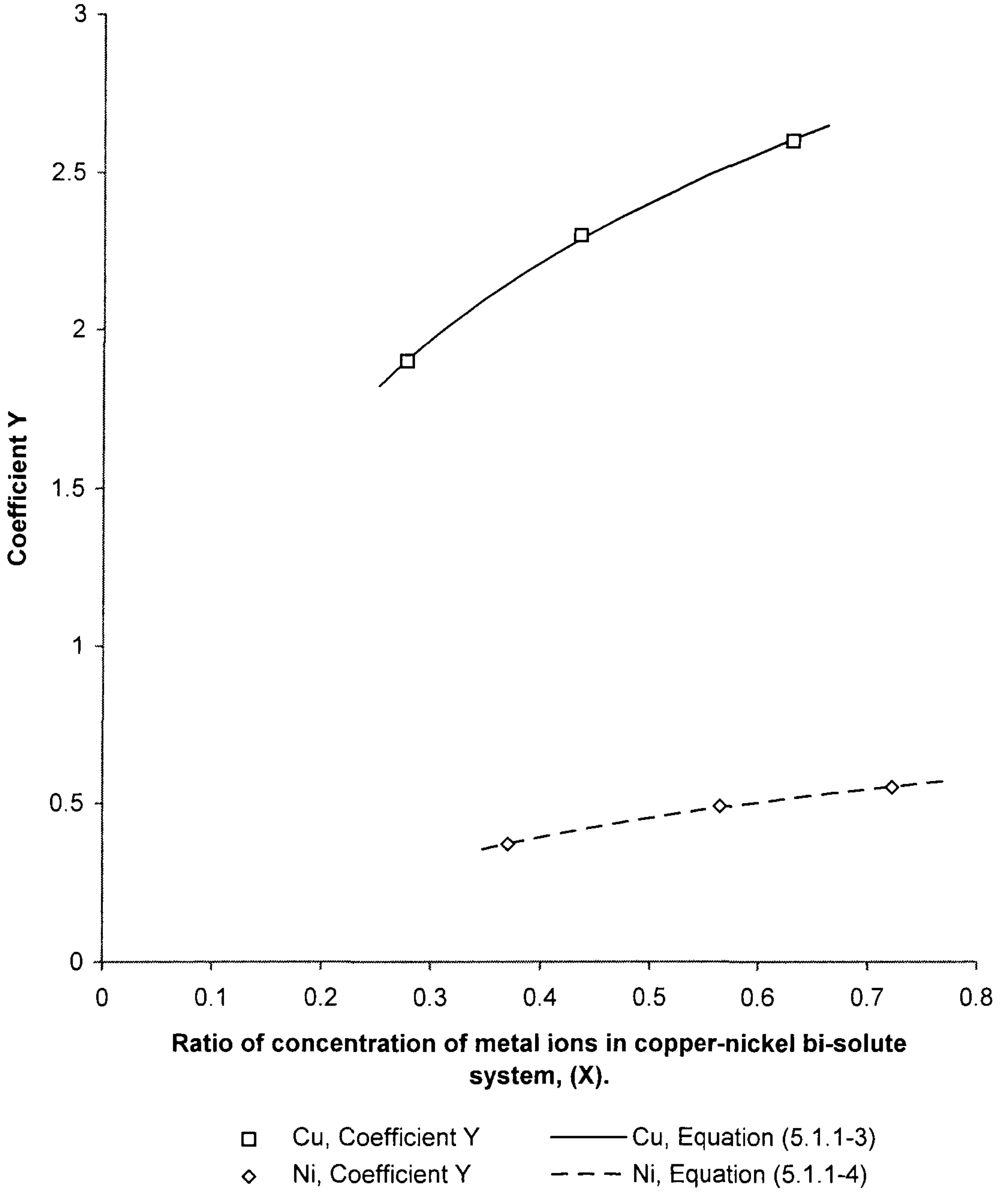
Substituting for Y_h and Y_l, q_e can be represented as the mathematical model:

$$q_{e,Ni} = \left[6.24 \times 10^{-1} \cdot \log(X_{Ni}) + 6.41 \times 10^{-1}\right] \times \frac{2.28 \cdot C_{e,Ni}}{1 + 1.67 \times 10 \cdot C_{e,Cu} + 1.54 \times 10 \cdot C_{e,Ni}}, \tag{5.1.1-5}$$

$$q_{e,Cu} = \left[1.97 \cdot \log(X_{Cu}) + 3.00\right] \times \frac{8.12 \times 10^{-1} \cdot C_{e,Cu}}{1 + 1.67 \times 10 \cdot C_{e,Cu}} + \frac{2.47 \cdot C_{e,Cu}}{1 + 1.67 \times 10 \cdot C_{e,Cu} + 1.54 \times 10 \cdot C_{e,Ni}}. \tag{5.1.1-6}$$

The effectiveneses of these mathematical models is examined graphically in **Figures 5.1.1-2** to **5.1.1-4**.

Figure 5.1.1-6: The relation between coefficient (Y) and ratio of concentration of metal ions (X).



Results of tests on the mixed solutes in the mole ratio of 1:1.3 (Cu:Ni), used in our adsorption system, appear to show that copper(II) adsorbs maximally at pH 5.0, with an initial concentration range of approximately 84.8% of the copper(II) in a single solute system, plus nickel. Nickel itself furnishes a value approximately 32.9% of its single solute system calculated from the Langmuir equation. These results indicated not only that competition occurred for the ions but also that there was a specific adsorption for copper(II) and nickel(II), respectively, when included in the bi-solute adsorption systems. There is a weak competition in adsorptive capacity of nickel(II) in the presence of copper(II), whereas the capacity of adsorption of copper(II) is reduced by the presence of nickel(II).

A further adsorption test on mixed solutes at the higher ratio of 1:2.6 (Cu:Ni) appears to show that copper(II) has maximum adsorption at this pH and that there is an initial concentration range of approximately 50.9% of the copper(II) in a single solute system. Calculations from the Langmuir equation show that nickel adsorption is approximately 46.1% of that of its single solute system. These results show that the copper competitive effect decreased by decreasing the concentration ratio of copper whereas the nickel competitive effect increased by increasing the concentration ratio of nickel. However, when we turn to an examination of the lower ratio tested, namely 1.7:1 (Cu:Ni), we find that while copper(II) again adsorbs maximally at this pH (5.0); the initial concentration range is approximately 1.04 times of the copper(II) in single solute system while nickel is approximately 18.7% of its single solute system value, as calculated from the Langmuir equation.

For bi-solute systems, the capacity of copper(II) increased with increasing equilibrium concentration but nickel(II) increased only at lower equilibrium values. There are only a few specific sites on the surface which are for nickel(II) and the competition for copper(II) is much stronger than for the nickel(II). For a mole ratio of 1:2.6 (Cu:Ni) the cumulative adsorption capacity for two ions was less than the adsorption capacity for copper(II) from its single-solute system. This observation is explained on the basis that the total surface area of moss peat available for the adsorption of the two ions was not more than that available for the adsorption of copper(II) from its single-solute system. Since this area was shared with the other less effectively adsorbed ion, less efficient use of the available area resulted (Martin and Al-Bahrani, 1977).

5.1.2. Adsorption of Different Size Metal Bi-Solute System

The purpose of this study was to investigate competitive adsorption onto sphagnum moss peat from an aqueous bi-solute mixture of selected metal ions which are of different size but are divalent metal ions. We therefore used lead(II) and copper(II) as well as lead(II) and nickel(II) systems.

Competitive adsorption was studied with the bi-solute of lead and copper as well as using the lead and nickel system. A pH of 5.0 was used to determine adsorption isotherms for initial concentrations in the ratio of 1:3.2 (Pb:Cu) of 5 to 70 mg/l of lead and of 5 to 80 mg/l of copper ions, respectively as well as the ratio of 1:3.8 (Pb:Ni) of 5 to 80 mg/l of lead and of 5 to 100 mg/l of nickel ions, respectively.

Tables 5.1.1-1 and **5.1.1-2** show that some of the metals are adsorbed on the same sites. Lead adsorption was hindered by the presence of the other metals. Copper had a greater effect (37.0%) on lead adsorption than did nickel (18.7%). Nickel removal was reduced by 25.3% when lead was also in solution. The amount of lead adsorbed when other metals were present was less than when only lead was in solution. However, the amount of copper adsorbed when lead was present was only slightly less than when copper alone was in solution. The reduction caused by the lead which was present was 6.4%. Similar results have been reported (Netzer and Hughes, 1984) for adsorption of copper, lead and cobalt by activated carbon. Gould and Genetelli (1984) have also reported that nickel shows some site specificity in tests of binding by anaerobically digested sludges. When nickel was used for salting out other metals, the amount of bound nickel was almost constant. Nickel may not be able to compete with metals for sites that are not specific for nickel and likewise the other metals may not compete effectively with nickel for sites that are specific for nickel. In addition, these results indicated that although the metals did compete for the binding sites of peat, there was a decrease in the number of active sites when both metals were present. In both the bi-solute systems, the two metal ions shared most of active sites and there are only a few specific sites on the surface which are for copper and nickel, with more specific sites for copper than for nickel.

Holan and Volesky (1994) have examined biomass of marine algae to remove lead and nickel from solution. They found three types of brown marine algae biomass were excellent sorption materials for binding lead well in excess of 20% of the material dry weight. However, nickel sorption by the same biomass types was almost an order of magnitude lower.

TABLE 5.1.2-1: Some Characteristics and Adsorption Constants of Lead and Copper Ions.

	Molecular Weight	Radii Å	Single-Solute System		Bi-Solute System		
			X_m, (mg/g)	k, (l/g)	X_m, (mg/g)	k, (l/g)	Δ, (%)
Cu	63.5	0.72	12.5	0.264	11.7	0.318	6.40
Pb	207	1.3	23.0	4.01	14.5	0.931	37.0

TABLE 5.1.2-2: Some Characteristics and Adsorption Constants of Lead and Nickel Ions.

	Molecular Weight	Radii Å	Single-Solute System		Bi-Solute System		
			X_m, (mg/g)	k, (l/g)	X_m, (mg/g)	k, (l/g)	Δ, (%)
Ni	58.7	0.78	8.66	0.263	6.47	0.184	25.3
Pb	207	1.3	23.0	4.01	18.7	2.16	18.7

5.1.3. Adsorption of Copper, Nickel and Lead Triple-Solute System

Adsorption isotherms for all the metal ions listed in **Table 5.1.3-1** are shown in **Figure 5.1.3-1**. The equilibrium results for adsorption for the metal ions correlated well with the Langmuir equation. The monolayer capacity, X_m, and the Langmuir equation constant, k, for the equilibrium concentration range 5 to 90 mg/l and pH 5.0 for each individual metal ion in the mixture, and for their cumulative adsorption are shown in **Figures 5.1.3-2** and **5.1.3-3**. It is clear from the results that the equilibrium capacity for each solute on the peat was affected adversely by the presence of the other solutes. The competitive effect appears to have affected the three ions in the order nickel > lead > copper with nickel affected most; the adsorption capacities for each solute from the mixed solution was 15.9, 57.4, and 71.5% of that of a single-solute system for copper, lead and nickel, respectively. The cumulative adsorption capacity for copper and nickel ions from the triple-solute system was, however, less than the adsorption capacity for lead ions from a single-solute system. This can be explained on the basis that the total surface area of peat available for the adsorption of the three ions was not more than that available for the adsorption of lead from single-solute system (Martin and Al-Bahrani, 1977). When this active surface was shared with the two other less effectively adsorbed ions, less efficient use of the available area resulted.

TABLE 5.1.3-1: Some Characteristics of Metal Ions.

			Langmuir Constants			
			Single-Solute System		Triple-Solute System	
	Molecular Weight	Radii Å	X_m, (mg/g)	k, (l/g)	X_m, (mg/g)	k, (l/g)
Cu	63.5	0.72	9.93	0.319	8.35	0.230
Ni	58.7	0.78	8.66	0.263	2.47	0.430
Pb	207	1.3	23.0	4.01	9.80	0.518

Figure 5.1.3-1: Adsorption isotherms for single-solute system (Cu, Ni and Pb).

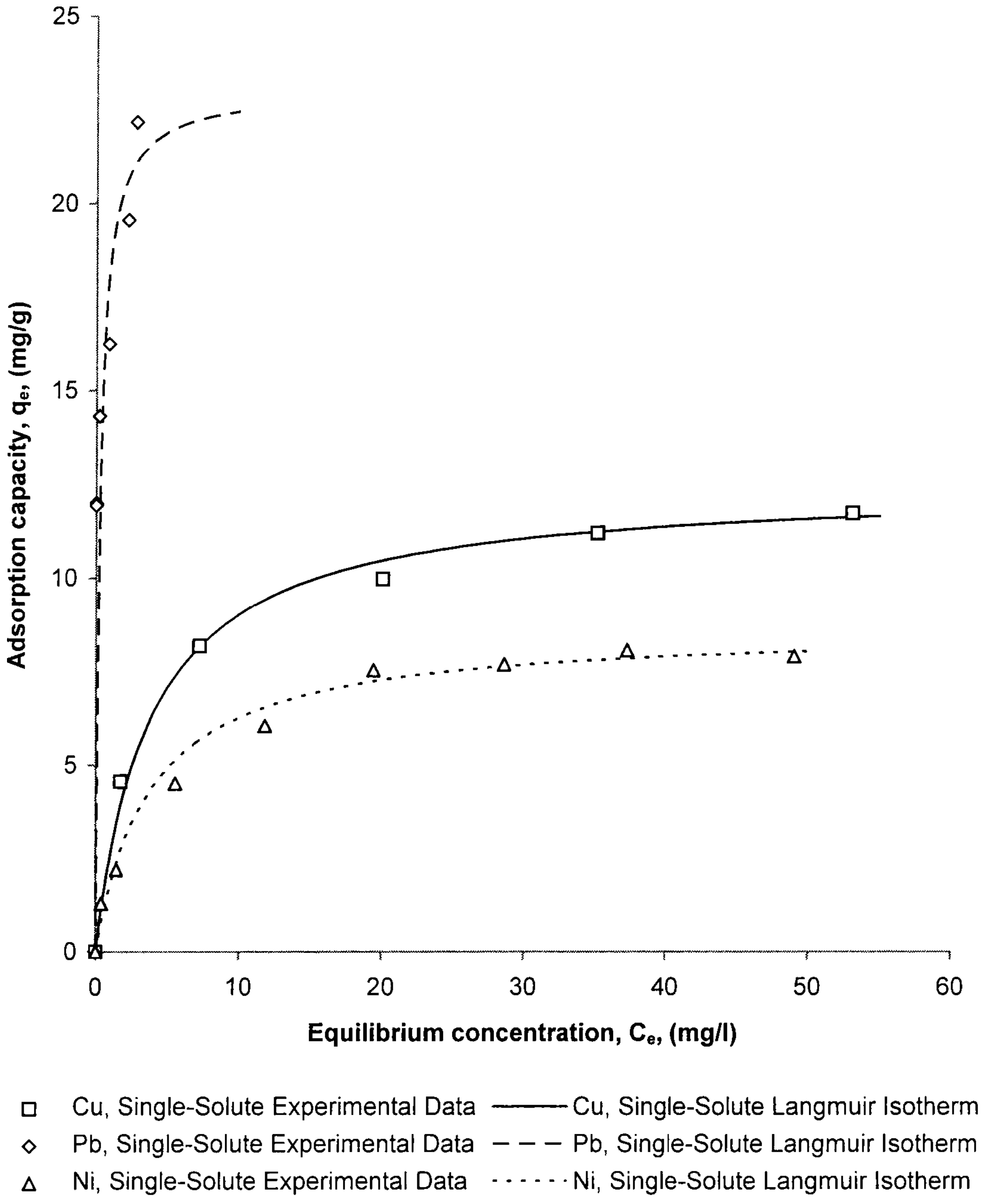


Figure 5.1.3-2: Adsorption isotherms of individual ions in triple-solute system.

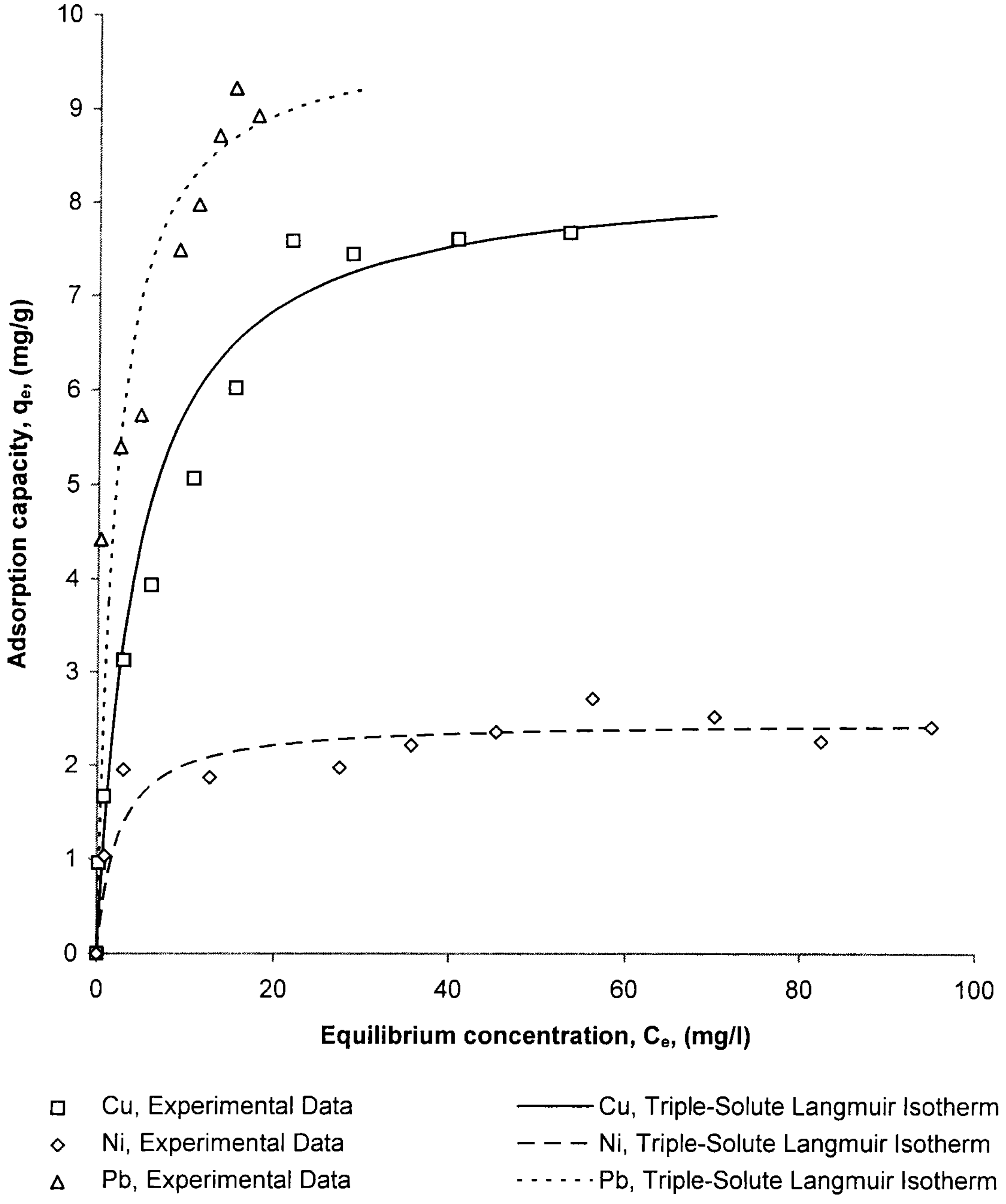
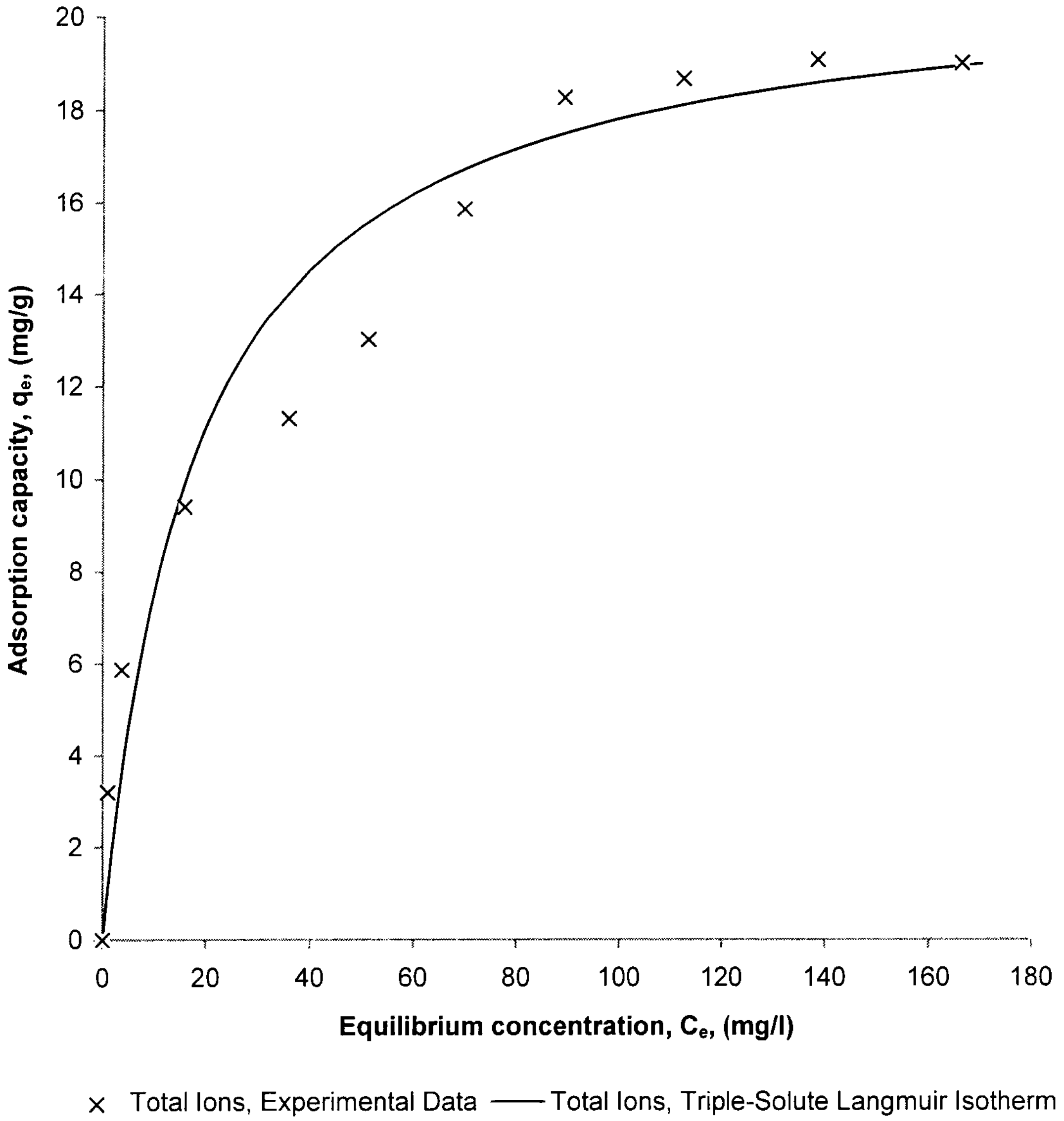


Figure 5.1.3-3: Adsorption isotherm for the three solutes in triple-solute system.



The equilibrium results for total adsorption of the three ions calculated agreed well with the Langmuir equation. Langmuir plots of the adsorption results are shown in **Figures 5.1.3-4** and **5.1.3-5**.

In order to explain that the cumulative adsorption data for the three solutes fitted the Langmuir equation, Martin and Al-Bahrani (1977) assumed that the maximum amount of any the three solutes adsorbed formed a complete monolayer on the peat surface. However, it cannot at the same time be assumed that the maximum amount of *each* solute adsorbed has formed a complete monolayer on the peat surface. Therefore the fact that the equilibrium adsorption data for each solute from the mixture fitted the Langmuir equation does not imply that the basic assumption, that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, has been met.

5.1.4. Comparison With Other Adsorbents

Irish sphagnum moss peat is a suitable adsorbent for removing copper(II), nickel(II) and lead(II) from aqueous solution. The strongest adsorption is shown by lead and the order of adsorption is as follows: $Pb^{2+} > Cu^{2+} > Ni^{2+}$ for single-solute systems. Sorption of metal cations is pH dependent. The data therefore obtained might be helpful to environmental engineering for designing and establishing a continuous water pollution control for copper(II), nickel(II), and lead(II). A comparison of metal removal for different adsorbents has been presented (**Table 5.1.4-1**). Chistova *et al.* (1990) have reported an order for the cation chelation capacity with peat as $Fe^{3+} > Pb^{2+} > Ba^{2+} > Cu^{2+} > Ni^{2+}$. Brady *et al.* (1994) have reported biosorption of metal cations by granular biosorbent from mixed metal cation solutions that results show as $Pb^{2+} > Cu^{2+} > Ni^{2+}$. A similar order of removal, $Pb^{2+} > Cu^{2+} > Ni^{2+}$, has also been reported by Low *et al.* (1993) using dye-treated and natural oil-palm fibres for the sorption of various metals from electroplating waste, and also, Kumar and Dara (1982) using treated bagasse and acacia, laurel and techtona bark for decontamination of wastewaters. In addition,

Figure 5.1.3-4: Langmuir plots of adsorption isotherms of individual ions in triple-solute system.

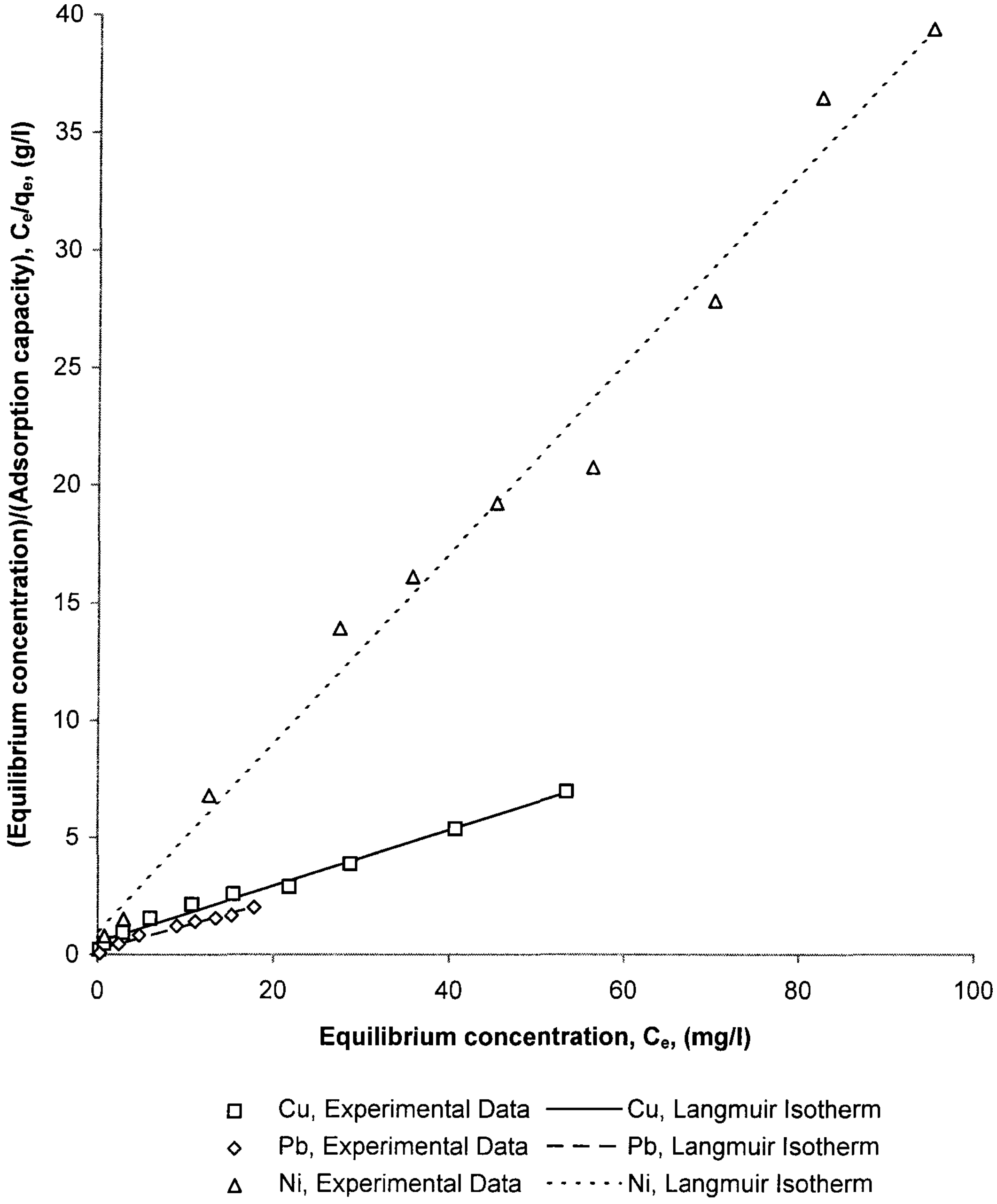
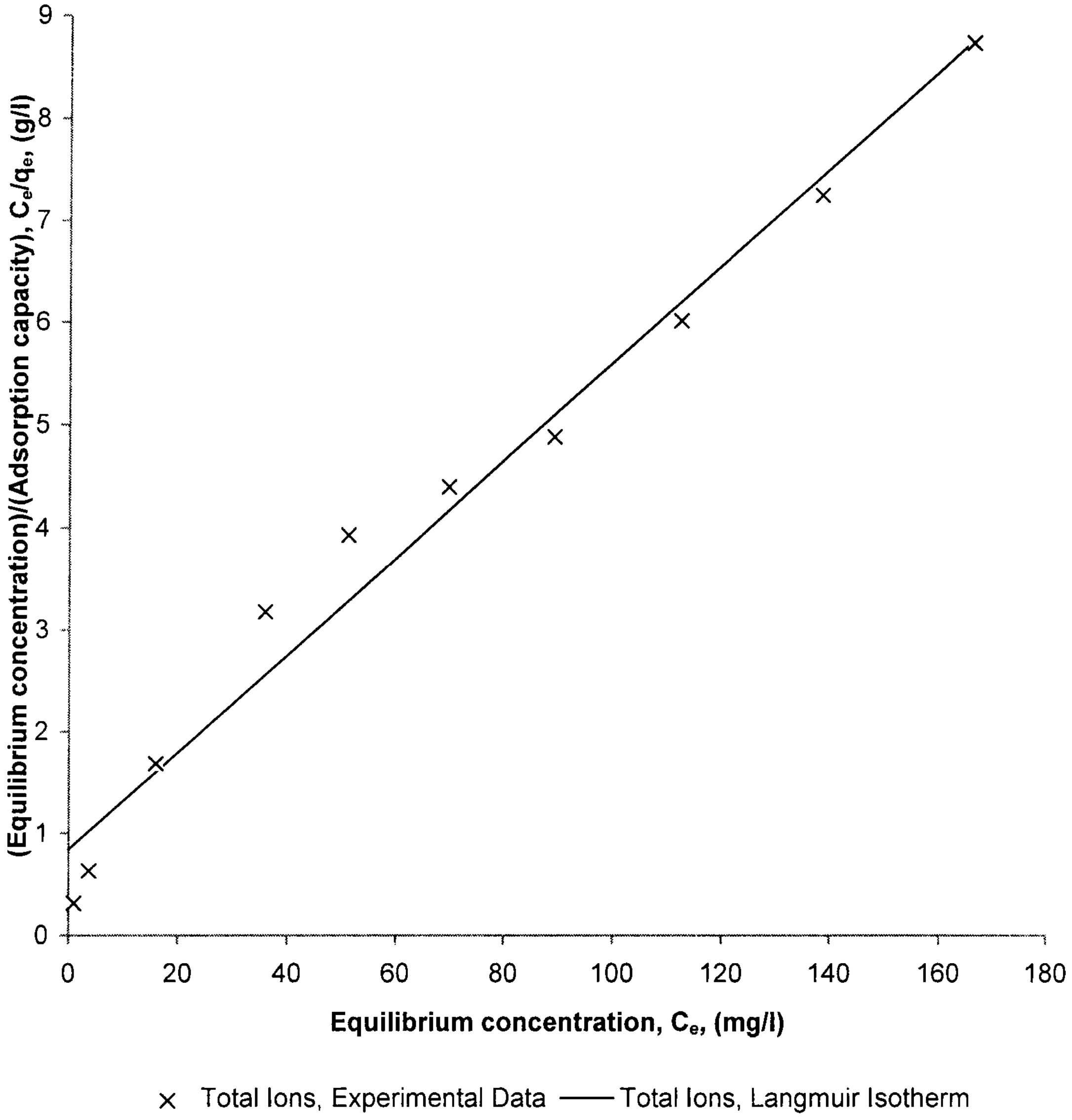


Figure 5.1.3-5: Langmuir plots of total ion adsorption isotherms for the three ions in the triple-solute system.



Suemitsu *et al.* (1986) have also used dyestuff-treated (red) rice hulls and dyestuff-treated (yellow) rice hulls to remove heavy metal ions from solution obtained an order of cation capacity as Pb^{2+} > Cu^{2+} > Ni^{2+} but Pb^{2+} > Ni^{2+} > Cu^{2+} for rice hulls. It therefore seems that these metals are not necessarily adsorbed by similar mechanisms for all bioadsorbents, and that each needs to be tested to determine its characteristics. Adsorption of lead by most of materials is greater than copper and adsorption of nickel is usually weaker than others.

TABLE 5.1.4-1: A Comparison of Adsorption Capacities of Various Adsorbents.

Capacity, (mg/g)			Material	Reference
Cu	Ni	Pb		
5.10	2.40	20.0	Peat (Rastunsuo)	Tummavuori and Aho, (1980)
4.44	7.45	10.2	Treated Bagasse	Kumar and Dara, (1982)
3.46	3.4	10.4	Treated Acacia Bark	
3.08	4.2	10.9	Treated Laurel Bark	
3.69	3.5	10.8	Treated Techtona Bark	
3.58	5.58	8.90	Rice Hulls	Suemitsu *et al.*,
7.88	6.16	12.0	Dyestuff-Treated (Red) Rice Hulls	(1986)
7.0	6.08	12.0	Dyestuff-Treated (Yellow) Rice Hulls	
23.0	-	40.0	Sphagnum Moss Peat	McLellan and Rock, (1988)
14.0	6.75	-	Iron Hydroxide	Mustafa and Haq, (1988)
27.3	-	79.7	Tea Leaves	Tan and Abd. Rahman, (1988)
13.8	5.22	19.0	*Aspergillus oryzae*	Huang *et al.*, (1991)
31.8	12.4	114	Treated *Aspergillus oryzae*	
35.7	40.8	90.9	Sludge Solid	Tien and Huang, (1991)
18.5	0.672	-	Sphagnum Peat	Viraraghavan and Dronamraju, (1993)
1.89	0.50	0.08	Oil-Palm Fibres	Low *et al.*, (1993)
22.2	6.46	41.4	Yeast Biomass	Brady *et al.*, (1994)
13.0	9.26	30.2	Sphagnum Moss Peat	This Study

5.2. EFFECT OF PEAT DOSE ON BI-SOLUTE ADSORPTION SYSTEM

The percentage of copper and nickel ion removal at equilibrium with various peat doses at 25°C in the bi-solute system, is presented in **Table 5.2-1**.

TABLE 5.2-1: Effect of Peat Dose, m_s (g/l) on Adsorption Data. Initial Metal Ion Concentration, C_e (mg/l); Percent Metal Ion Removal at Equilibrium, R_e (%); and Metal Ion Removal Capacity at Equilibrium, q_e (mg/g); With Various Peat Doses at a Temperature of 25°C.

	Copper			Nickel			
m_s	C_e	q_e	R_e	C_e	q_e	R_e	pH_{fin}
4	152	12.0	24.0	200	0	0	3.10
8	117	10.4	41.4	192	1.02	4.08	2.89
16	80.0	7.50	60.0	178	1.38	11.0	2.90
24	54.0	6.08	73.0	158	1.75	21.0	2.89
32	41.5	4.95	79.2	139	1.90	30.5	2.89
40	33.6	4.16	83.2	123	1.92	38.5	2.90

The effect of varying the peat dose, m_s, using an initial concentration of 200 mg/l for copper and nickel, respectively, is summarised in **Figures 5.2-1** and **5.2-2**. It can be seen that the removal increases with increasing peat doses for the given initial concentration. It is also seen that by increasing the peat doses from 4.0 to 40 g/l, the removal efficiency was increased from 24.0% to 83.2% and 0% to 38.5% for copper and nickel, respectively. Copper appears to have a greater effect as the "contaminant" than nickel. When the peat dose is 4.0 g/l the removal efficiency for nickel is reduced to zero. The data in **Table 5.2-1** can be used to derive a mathematical relationship.

The relationship for a single-solute system has already been discussed (Chapter 3), and was expressed as:

Figure 5.2-1: Copper removal (R_e) and adsorption capacity (q_e) of peat as a function of peat does (m_s) in a bi-solute system.

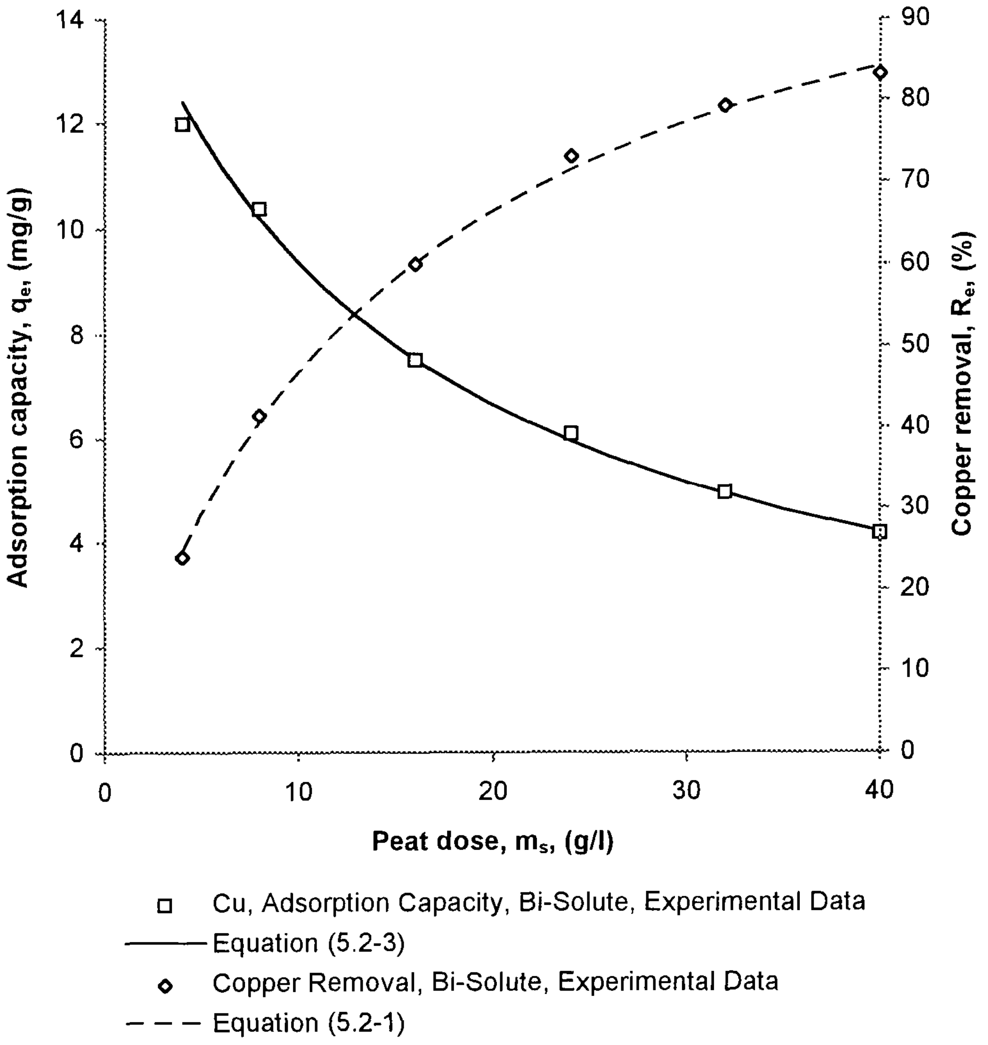
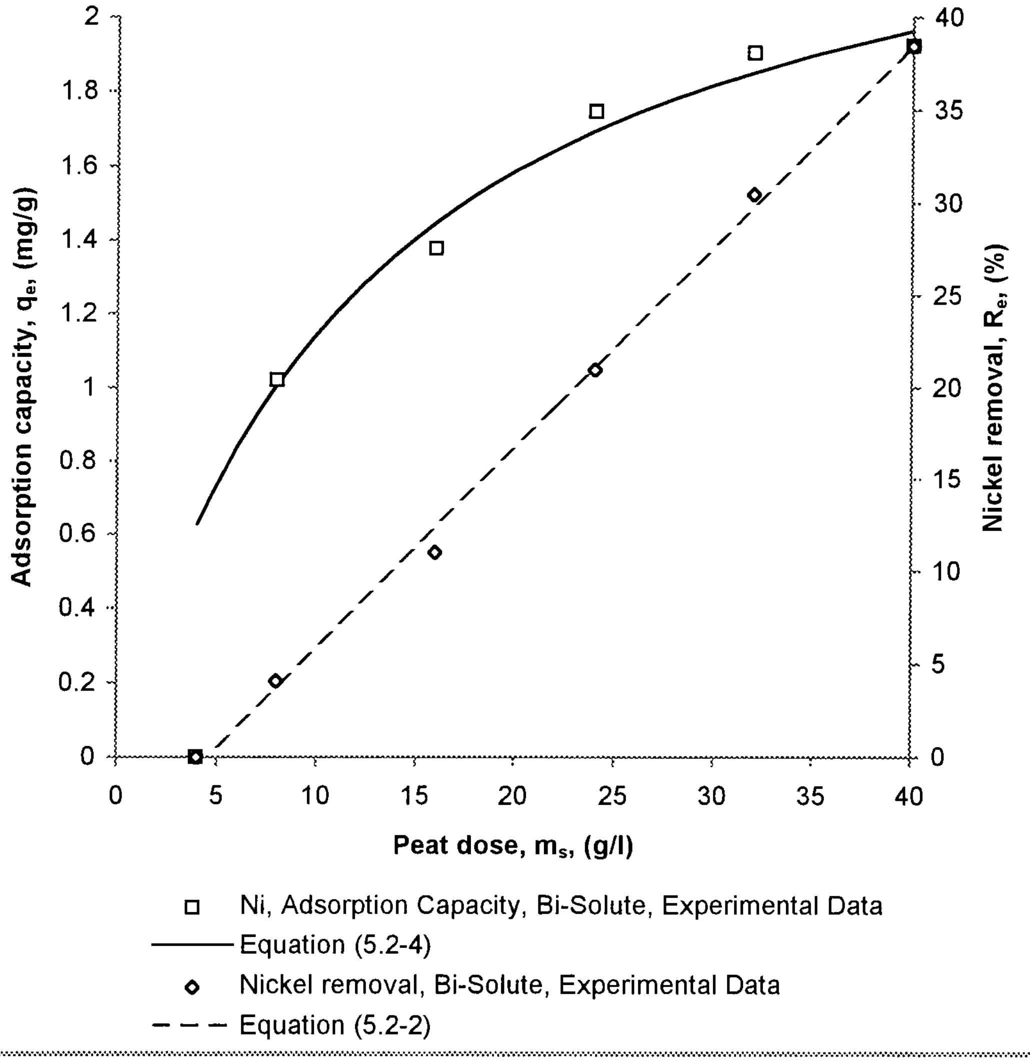


Figure 5.2-2: Nickel removal (R_e) and adsorption capacity (q_e) of peat as a function of peat does (m_s) in a bi-solute system.



$$R_e = \frac{m_s}{S_1 + \frac{m_s}{R_0}}, \qquad (4.1.5\text{-}1)$$

where

R_e is the percentage of metal ion removal at equilibrium, (%);

m_s is the peat dose, (g/l);

R_0 is the maximum percentage of metal ion removal at equilibrium, (%); when peat dose is infinity;

$1/S_1$ is the tangent to the curve when $m_s = 0$, (%l/g).

Substituting for copper in a bi-solute mixture gives a predictive model for the percent copper ion removal for any peat dose at pH 5.0 and initial copper concentration 200 mg/l with a correlation coefficient of 0.998 as follows:

$$R_e = \frac{m_s}{1.26 \times 10^{-1} + 8.73 \times 10^{-3} m_s}. \qquad (5.2\text{-}1)$$

However, when it comes to nickel, there is quite a different relationship, as the percent nickel adsorption fits a model with correlation coefficient 0.997 as follows:

$$R_e = 1.08 m_s - 4.92, \qquad (5.2\text{-}2)$$

calculated directly from the results. This difference can be explained on the basis that copper is the strongly adsorbed anion, and is adsorbed in preference to the weakly competitive nickel. At a peat dose of 4.56 g/l, nickel removal can be calculated as zero when copper removal is still 27.5% using the model.

The adsorption capacity curve on **Figure 5.2-1** indicates that the adsorption capacity of copper decreased from 12.0 mg/g to 4.16 mg/g of peat when the peat doses were increased from 4.0 to 40 g/l. In contrast, the adsorption capacity of nickel increased from 0 mg/g to 1.92 mg/g of peat when the peat doses were increased from 4.0 to 40 g/l. The relationship between adsorption capacity and peat dose follows equation **(4.1.5-3)** for copper and nickel, respectively as previously discussed. The resulting models are:

for copper

$$q_e = \frac{1}{6.32 \times 10^{-2} + 4.36 \times 10^{-3} m_s}, \qquad (5.2\text{-}3)$$

for nickel

$$q_e = \frac{1}{4.83 + 3.89 \times 10^{-1} m_s}, \qquad (5.2\text{-}4)$$

Previous work (Ho *et al.*, 1994 and 1995) for single-solute systems is shown in **Figures 5.2-3** and **5.2-4** together with these bi-solute system results. With both systems, the adsorption capacity of peat for the primary metal was lower in a binary solute system than in their respective single solute systems, and it can be seen that copper appears to have a greater effect as the "contaminant" than nickel. **Figure 5.2-5** shows that the effect of nickel increased with increasing peat dose. In contrast, the increase in copper adsorption with increasing peat dose is much less than that of nickel. Thus, while the ratio of adsorption capacity of bisolute/single solute systems is almost constant at around 0.8, for copper, that for nickel increases from zero as peat dose is increased. This is because as more peat surface is made avaiable (i.e. the dose is increased), the number of sites specific for nickel also increases.

Figure 5.2-3: Copper and nickel adsorption capacity (q_e) of peat as a function of peat dose (m_s) in single- and bi-solute systems.

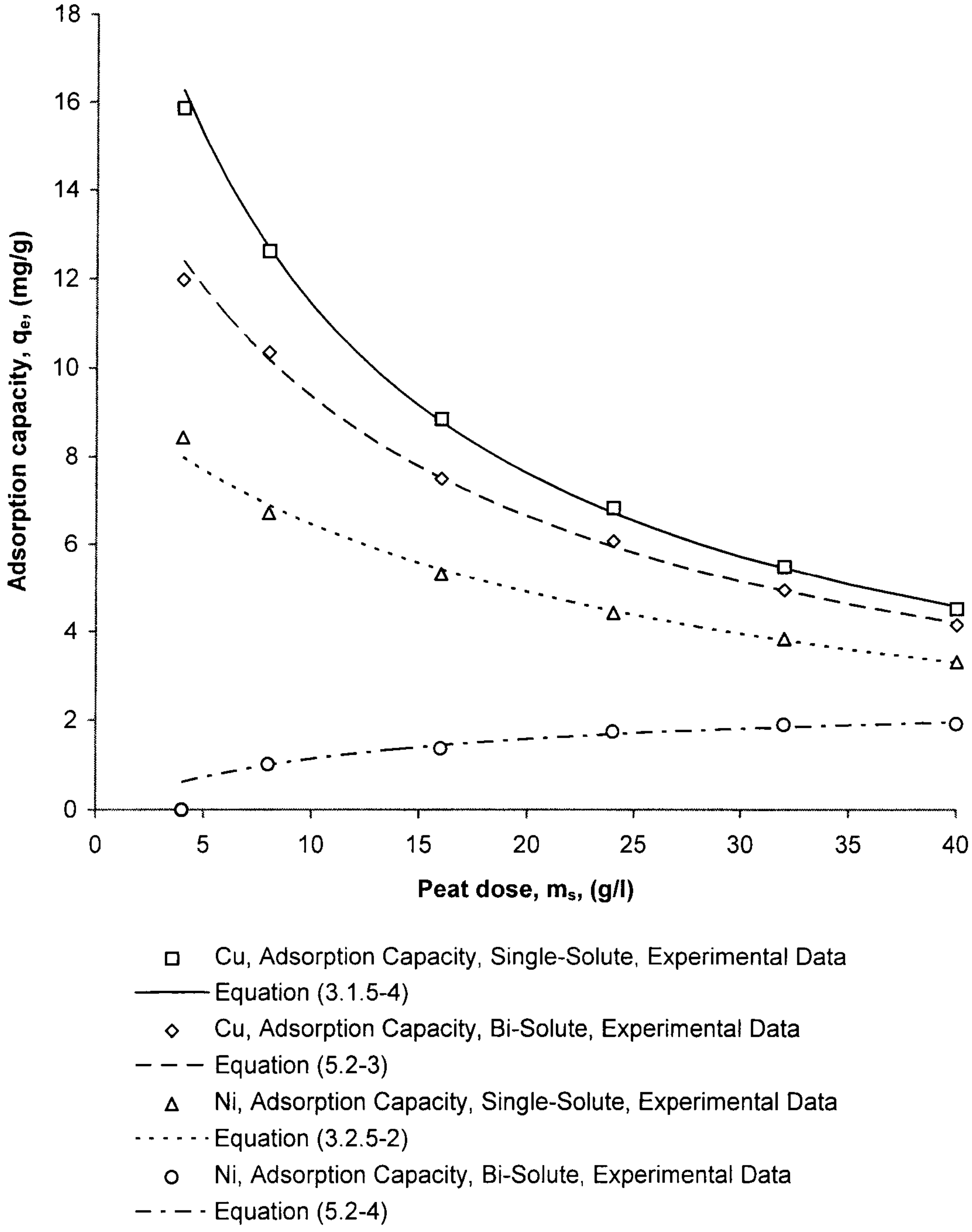


Figure 5.2-4: Copper and nickel removal (R_e) of peat as a function of peat dose (m_s) in single- and bi-solute systems.

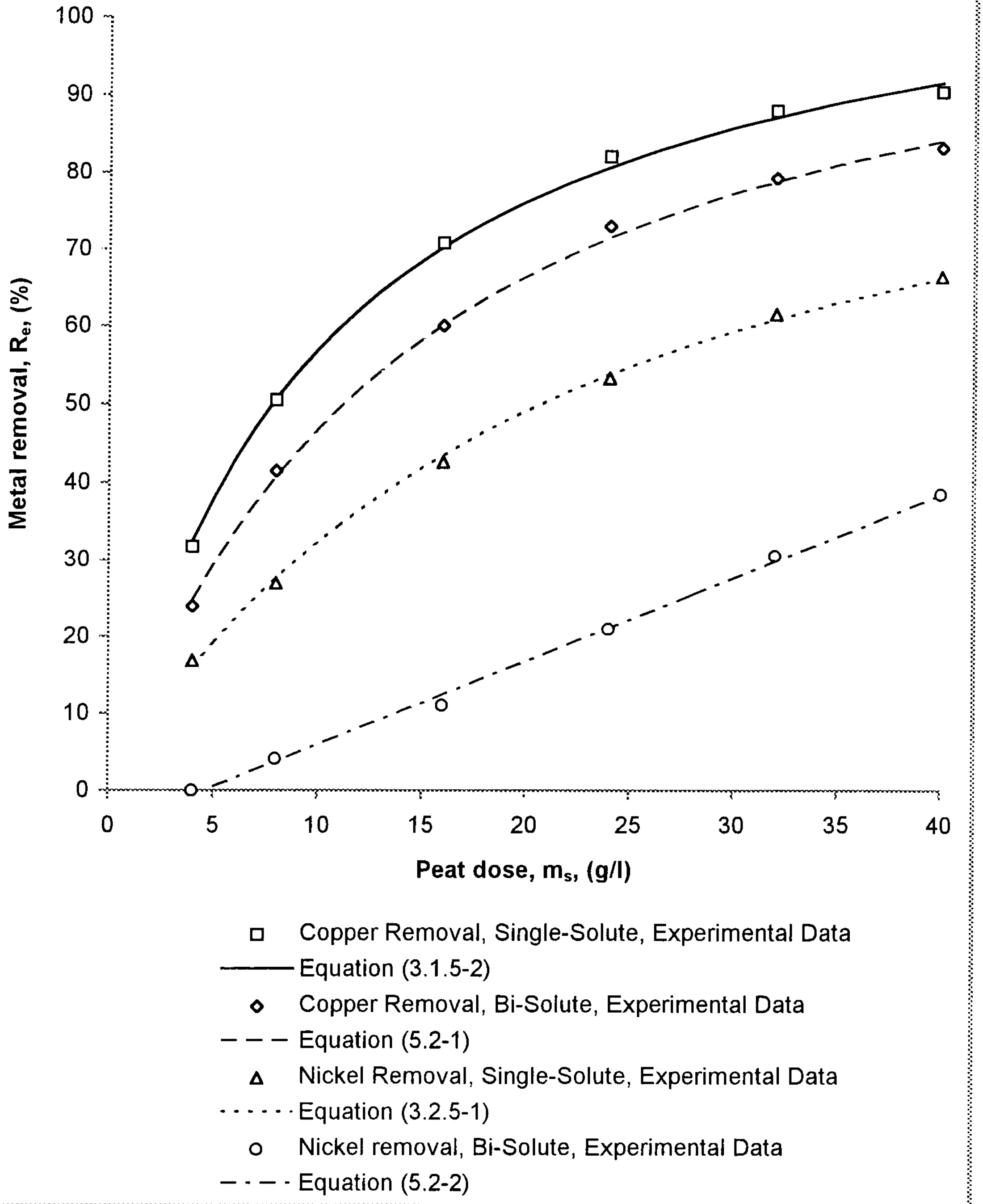
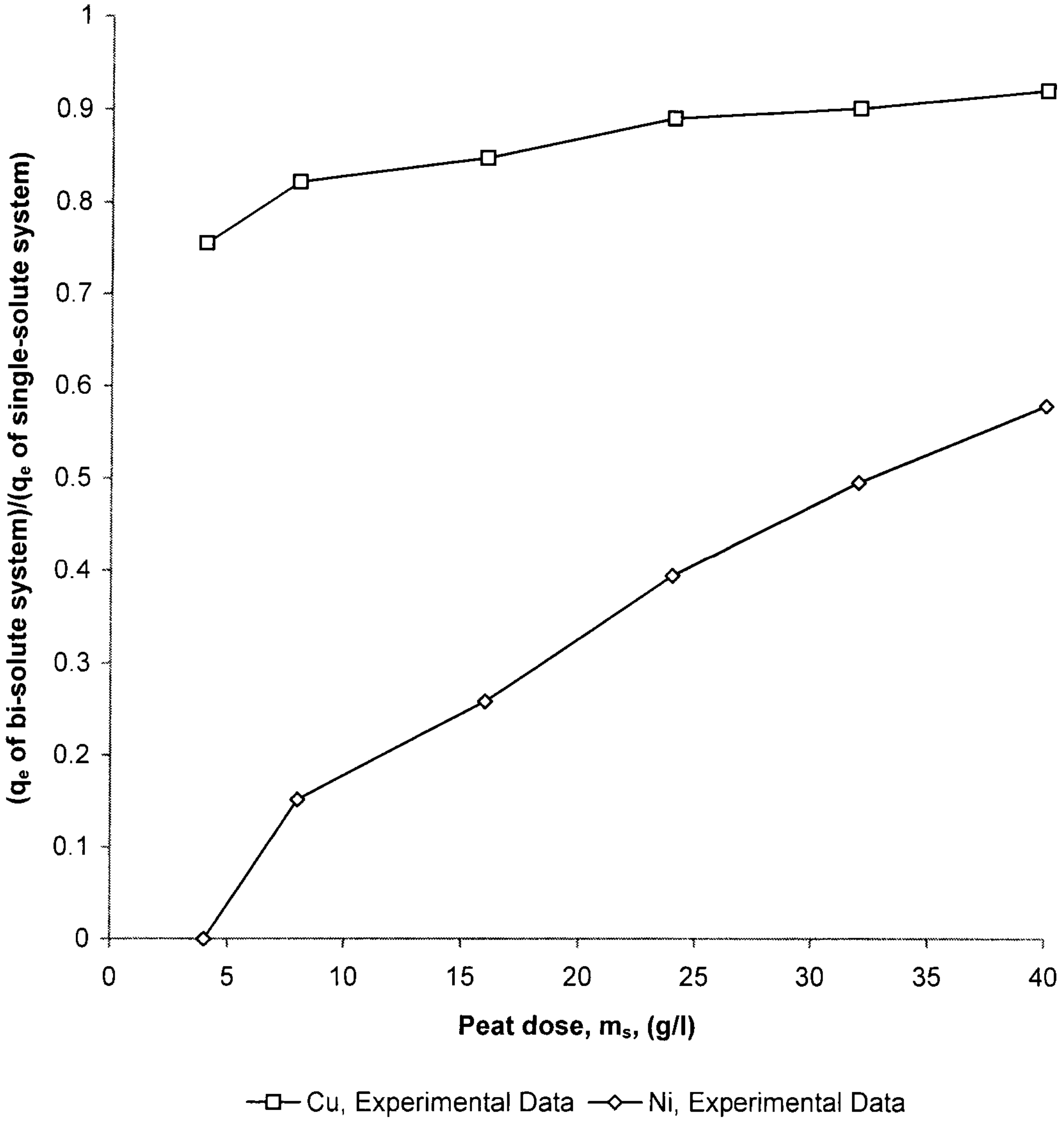


Figure 5.2-5: The effect of competitive adsorption at various peat doses (m_s).



5.3. ADSORPTION KINETICS

Much of the work on the adsorption of metals by low-cost, natural biosorbents has focused on the uptake of single metals. In practice, wastewaters are polluted with multiple metals. In addition, the kinetics of adsorption, which are important in the design of treatment systems, have largely been neglected.

In recent years there has been an increased awareness of the potential impact of pollutants such as heavy metals. Moreover, the traditional methods for treating aqueous streams containing metal contaminants are expensive and can have inadequate efficiencies (D'Avila *et al.*, 1992). This is particularly true in developing countries. This has led to the examination of alternative technologies. The use of biological materials to remove metals is one such technology which has received considerable attention and many materials have been examined. For example, wood-rotting fungi have been used for the removal of rare earths (Muraleedharan *et al.*, 1994), the sorption of uranyl ions by chitosan has been studied by Saucedo *et al.*, (1992), tea leaves have been used for the removal of lead, cadmium and zinc (Tan and Abd. Rahman, 1988) and the uptake of lead and zinc by lignin has been examined by Srivastava *et al.* (1994). Peat has also been used as a biosorbent (Allen *et al.*, 1994; Viraraghavan and Dronamraju, 1993; and Sharma and Forster, 1993). Many of the studies into the effectiveness of biosorbents have concentrated on the sorption of single metals whereas, in practice, wastewater streams will contain several metal ions. This means that the possibility of competition for adsorption sites will occur.

Multicomponent adsorption systems are likely to form an important unit process in wastewater treatment. It is, therefore, desirable to develop a model to describe the kinetics of multicomponent adsorption. There have been only a few studies reported in the literature in the area of multicomponent adsorption rate modelling (Gariepy and Zwiebel, 1971; Zwiebel *et al.*, 1972; Collins and Chao, 1973; Zwiebel *et al.*, 1974; Mathews and Weber, 1980; Talbot *et al.*, 1989; and Talbot *et al.*, 1994).

5.3.1. Kinetics of Bi-Solute System

Copper and Nickel Bi-Solute System

This section describes the results of an examination into the adsorption by peat of copper and nickel from both single- and bi-solute systems. These showed that, in general, pore diffusion appeared to be the rate-controlling step, and that the presence of "contaminant" copper ions reduced the binding of nickel. In fact, the best interpretation which could be placed on the data was that the behaviour of nickel was unusual. The results also showed that the kinetics of adsorption were best described by a second order expression rather than a first order model.

Figure 5.3.1-1 shows how the presence of the secondary metal affects the adsorption of both copper and nickel, and although this Figure contains only data for initial concentrations of 50 mg/l, the pattern of behaviour is typical of the other concentrations. It is clear from this that the presence of the second solute has a distinct impact on the sorption of the primary metal. With both bi-solute systems, the equilibrium concentrations of the primary metal in the liquid phase were lower than in their respective single-solute systems and it can be seen that copper appears to have a greater effect as the "contaminant" than nickel. This can be quantified by an examination of the specific adsorption values (q_t, mg metal/g of peat) calculated at 180 minutes. **Table 5.3.1-1** shows these values, together with values for the reduction in the specific adsorption of the primary metal in the bi-solute systems.

Kinetic studies are important in determining the time needed to reach equilibrium and examinations into the rates of adsorption can be used to develop models and an understanding into the processes which influence the uptake of solutes. If diffusion through the bulk liquid is ignored, three such processes can be identified:

- Mass transfer (Boundary layer diffusion);
- Sorption of ions onto sites;
- Intraparticle diffusion.

Figure 5.3.1-1: Variations in the metal concentrations (C_t) with time (t) for both single- and bi-solute systems.

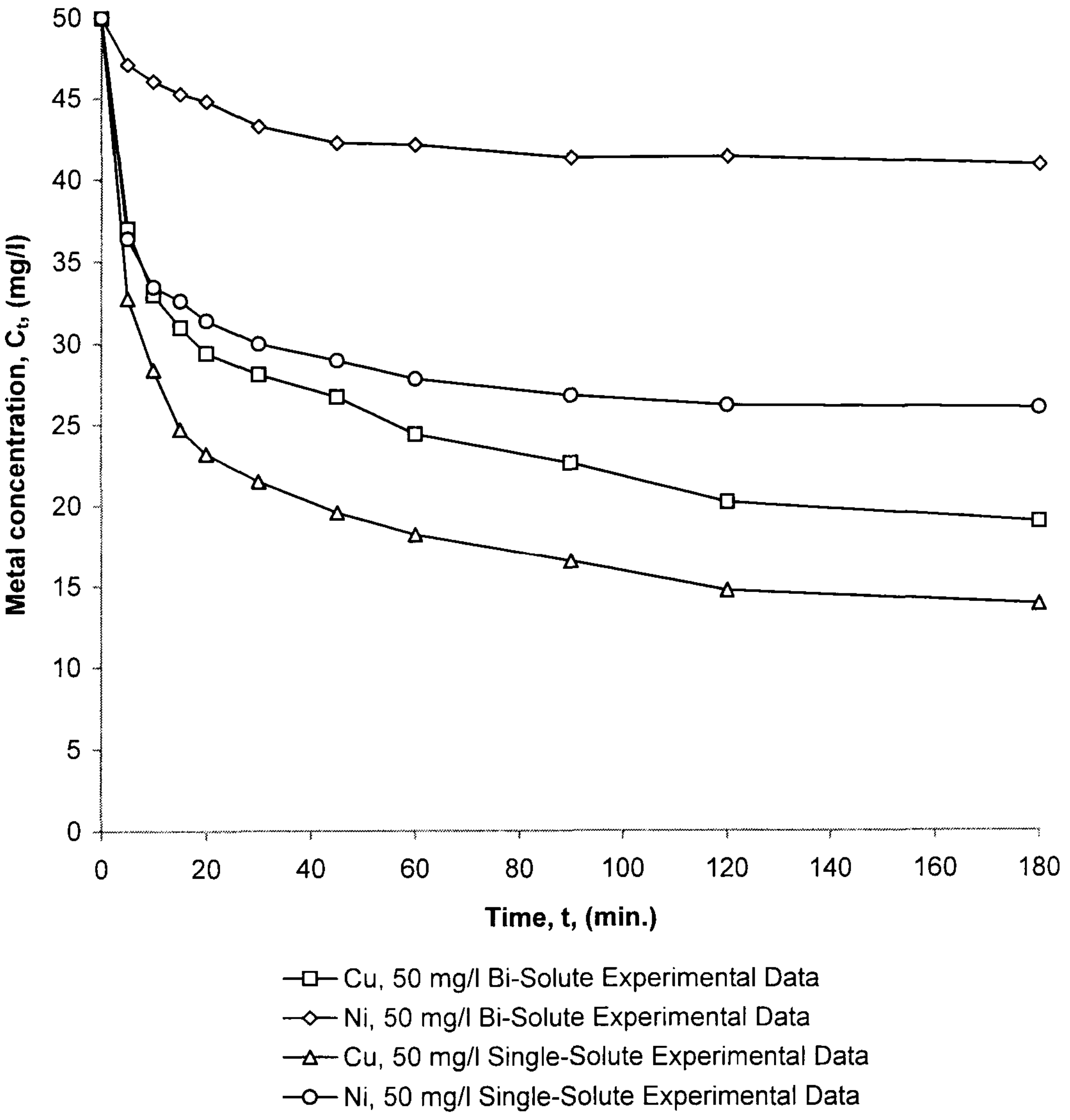


TABLE 5.3.1-1: Values for the Specific Adsorption (mg/g) After 180 Minutes Showing the Reductions Caused by the Addition of a Second Metal.

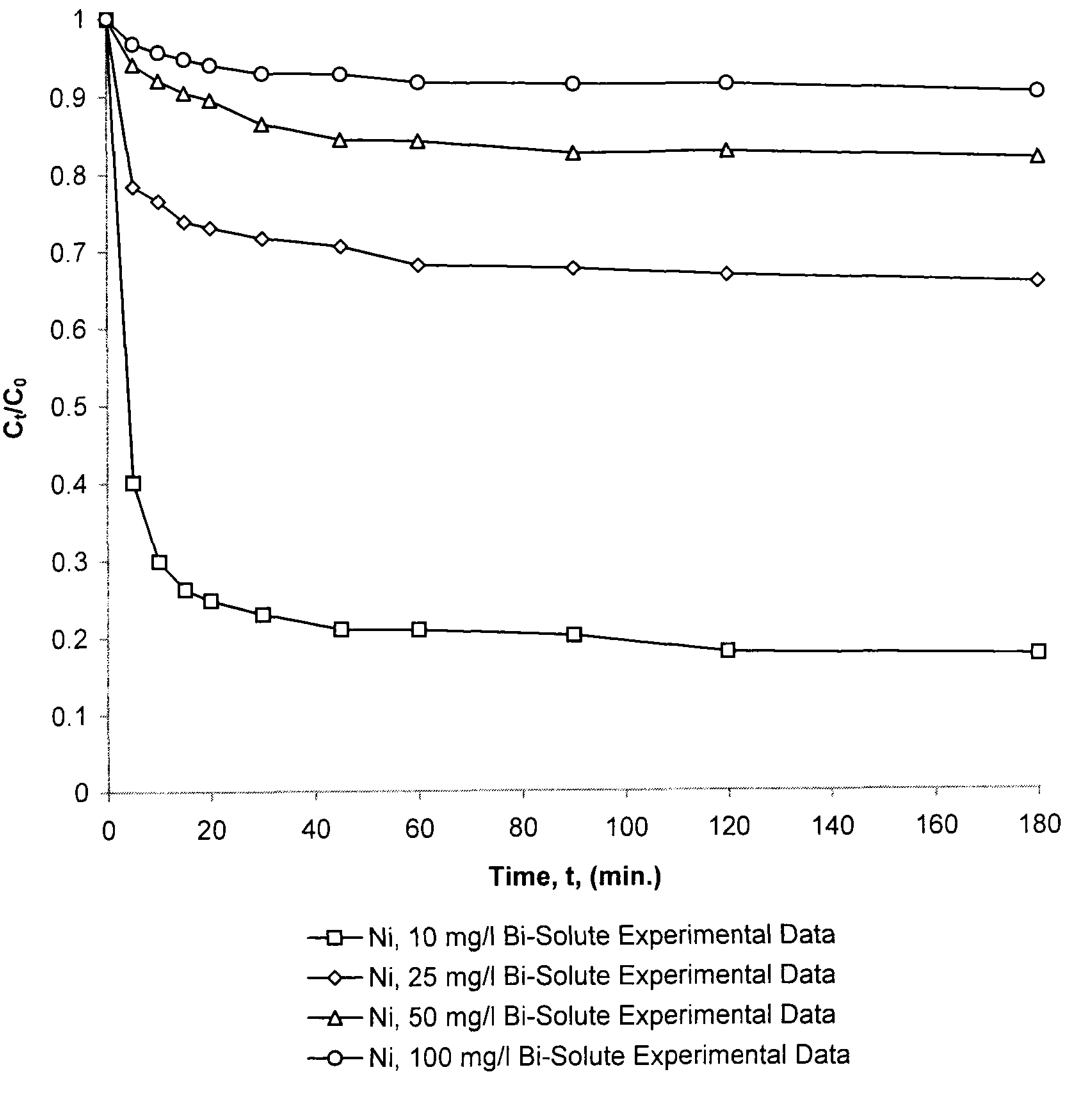
Initial Concentration	Copper			Nickel		
(mg/l)	Single-solute	Bi-solute	Δ (%)	Single-solute	Bi-solute	Δ (%)
10	2.37	2.16	8.89	2.16	2.08	3.54
25	5.74	5.12	10.8	3.90	2.20	43.6
50	9.36	8.13	13.2	6.20	2.46	60.3
100	12.7	9.88	22.1	7.49	2.57	65.8

External mass transfer is characterised by the initial rate of solute sorption (McKay and Poots, 1984). This can be calculated from the initial slope of the C_t/C_0 - time curves (**Figure 5.3.1-2**). These slopes can be derived either from a derivation of the polynomial approximation of C_t/C_0 at $t = 0$ (Saucedo *et al.*, 1992) or, more simply, by assuming that the relationship is linear over the first 5-10 minutes (Forster *et al.*, 1985). **Table 5.3.1-2** presents a comparison of the initial rates calculated on this latter basis. These results show that increasing the initial metal concentration resulted in a decrease in the initial rate. The data also show that the most marked effect occurred when the initial concentration increased from 10 to 25 mg/l and that further increases in the metal ion concentration had less of an effect.

TABLE 5.3.1-2: Initial (5 minute) Sorption Rates (min^{-1}) Based on $\left[\left(1-\frac{C_5}{C_0}\right)\Big/5\right]$.

Initial Concentration	Copper		Nickel	
(mg/l)	Single-Solute	Bi-Solute	Single-Solute	Bi-Solute
10	0.182	0.158	0.120	0.120
25	0.127	0.0824	0.0661	0.0431
50	0.0689	0.0520	0.0544	0.0117
100	0.0423	0.0334	0.0288	0.00641

Figure 5.3.1-2: The effect of initial nickel concentration on the changes in C_t/C_0 with time for the Ni/Cu bi-solute system.



Weber and Morris (1963) have concluded that, for processes which are controlled by site adsorption, the initial rate will be directly proportional to the solute concentration. The non-proportionality shown in **Table 5.3.1-2**, therefore, indicates that the sorption phase is not the rate controlling step (Weber and Morris 1963; and Saucedo *et al.*, 1992).

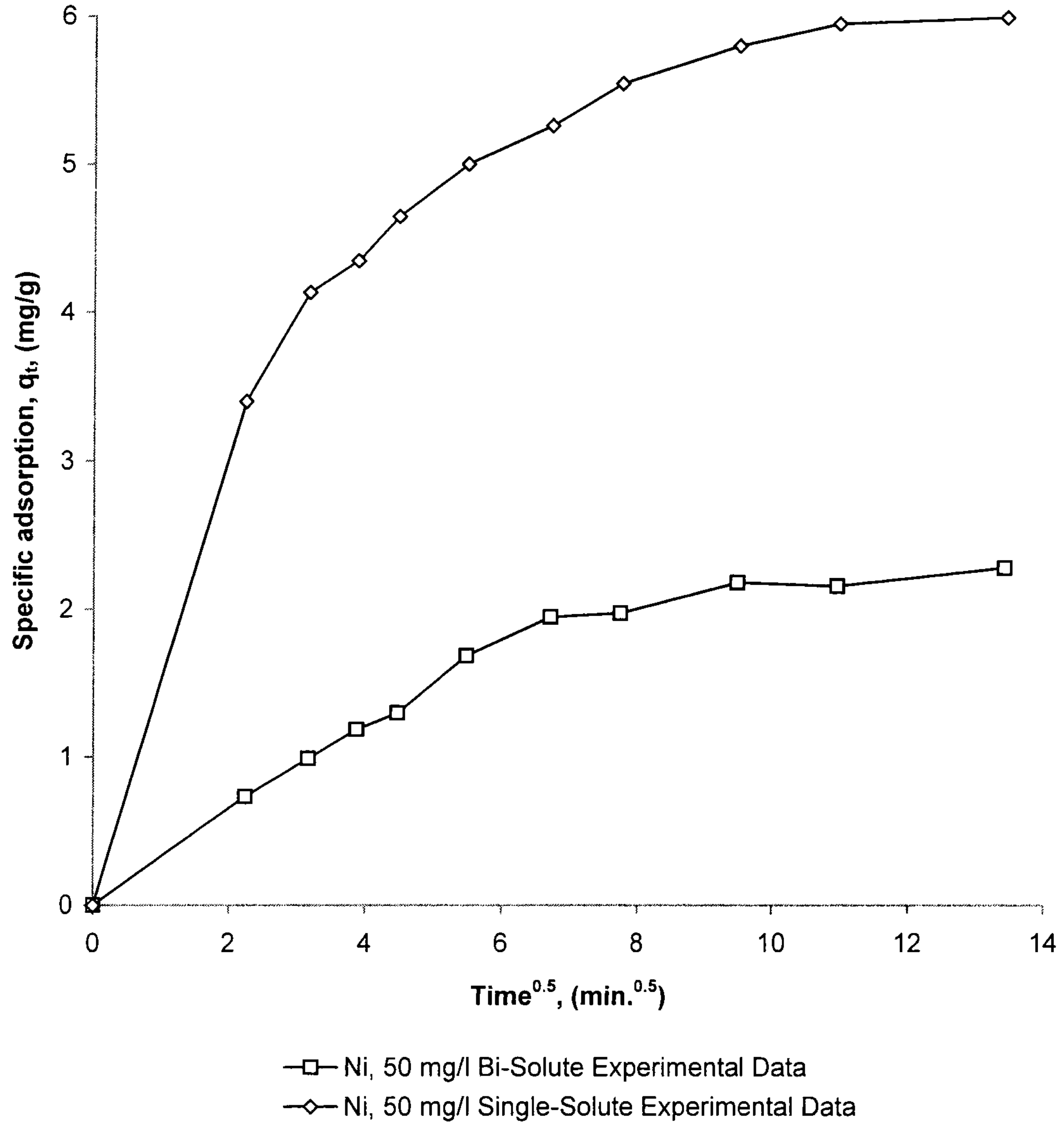
Intraparticle diffusion is characterised by a dependence between the specific adsorption (q_t) and the square root of time with the slope of the relationship being the intraparticle diffusion rate parameter. As can be seen from a typical set of data for the systems investigated (**Figure 5.3.1-3**), the relationships are not linear. This non-linearity has been reported previously (McKay *et al.*, 1980; Gupta *et al.*, 1990; and Gaid *et al.*, 1994) and has been explained in terms of both of the diffusion processes having an effect on the adsorption. The initial part of the curve is attributed to boundary layer effects and the final portion to intraparticulate diffusion. It is possible to derive an initial rate parameter (ϕ) by linear regression between $t = 0$ and t_{lim} where t_{lim} is the first breakpoint in the q_t - $t^{0.5}$ relationship. Values for these parameters are given in **Table 5.3.1-3**. These are rate parameters with units of $mg/gmin^{-0.5}$, and as such, are not a direct quantification of the rates. Nevertheless, they can be interpreted in relative terms. Examined in this way, the data show that, except for the nickel bi-solute system, the rate of diffusion increases with the initial metal concentration. According to the theoretical equations for diffusion, when intraparticulate diffusion is the only rate determining step, the rate parameter is directly related to the square root of the initial concentration (Weber and Morris, 1963).

$$\phi = (C_0)^n,$$

where

$n = 0.5$.

Figure 5.3.1-3: The effect of copper on the pore diffusion model for nickel (50 mg/l).



Regression analysis showed that there was little difference between the value obtained for "n" and that the values ranged from 0.21 to 0.30. This confirms that intraparticulate diffusion is not the only operative mechanism. The results in **Table 5.3.1-3** also show that increasing concentrations of copper ions had a significant effect on the uptake of nickel in the bi-solute system causing a decrease in the diffusion rate. Although this is obviously a competitive effect, the mechanism by which it occurs is, at the moment, unclear. However, it is known that the binding of nickel to certain types of biological material is different from other metals (Forster, 1985). This anomalous behaviour has been attributed to there being binding sites which are available to other metals but not to nickel (Gould and Genetelli, 1978).

TABLE 5.3.1-3: Initial Rate Parameters (mg/gmin$^{-0.5}$).

Initial Concentration (mg/l)	Copper		Nickel	
	Single-Solute	Bi-Solute	Single-Solute	Bi-Solute
10	1.02	0.882	0.673	0.576
25	1.58	0.978	0.796	0.380
50	1.53	1.17	1.35	0.300
100	2.15	1.43	1.17	0.321

The kinetics of adsorption by biological materials have been described previously by the first order expression given by Langergren (Namasivayam and Yamuna, 1992):

$$\ln(q_e - q_t) = \ln(q_e) - Kt,$$

where

q_e is mass of metal adsorbed at equilibrium (mg/g);

q_t is mass of metal adsorbed at time, t, (mg/g);

K is rate constant.

It was found that, although this equation provided a very good description for some of the current data, it was not applicable to all the results. No further consideration of this model was, therefore, attempted.

It has been established recently in the previous chapter that a pseudo second order reaction can be used to describe a multi-component system:

$$\frac{t}{q_t} = \frac{1}{2Kq_e^2} + \frac{t}{q_e},$$

where

K is the rate constant for adsorption (g/mgmin);

q_e is the amount of metal adsorbed at equilibrium (mg/g);

q_t is the amount of metal adsorbed at any time, t (mg/g).

The initial adsorption rate, h, is given by;

$$h = 2Kq_e^2.$$

Values for these constants were derived from a regression analysis of (t/q_t):t and are given in **Tables 5.3.1-4** and **5.3.1-5** and comparisons between the data and the predictions made by the equation are shown in **Figures 5.3.1-4** and **5.3.1-5**. The data in these Figures show that the second order equation does provide a realistic description of the adsorption process. Applying the Weber and Morris philosophy to the variations in the initial rate, h, with C_0 shows that in none of the cases is there any consistent relationship:

- the rate is not directly proportional to C_0 which confirms the earlier analyses and indicates that the sorption process was not the rate limiting step,

Figure 5.3.1-4: Data (points) and predictions (curves) for the 2nd-order rate model applied to the single- and bi-solute systems for copper (50 mg/l).

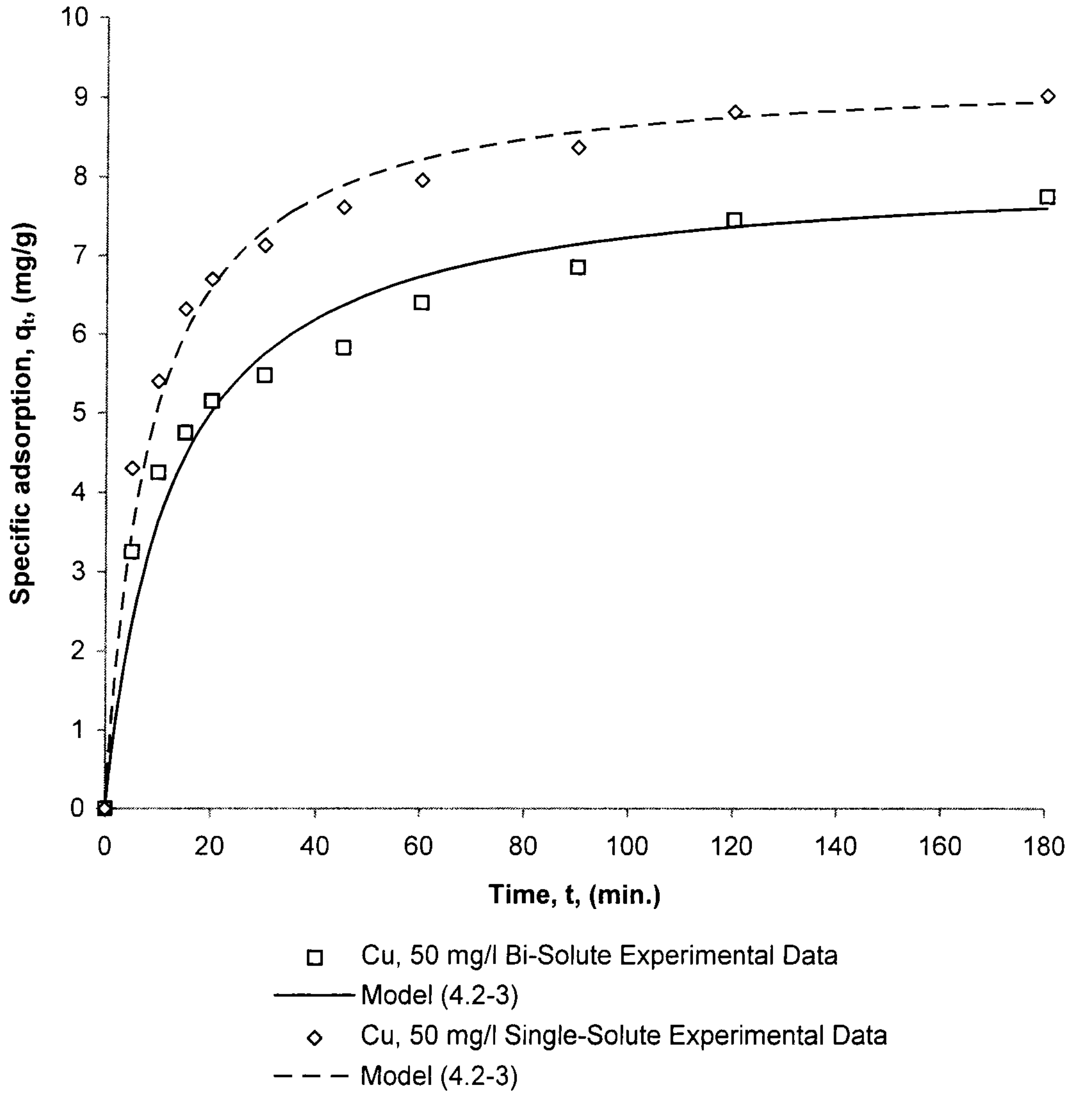
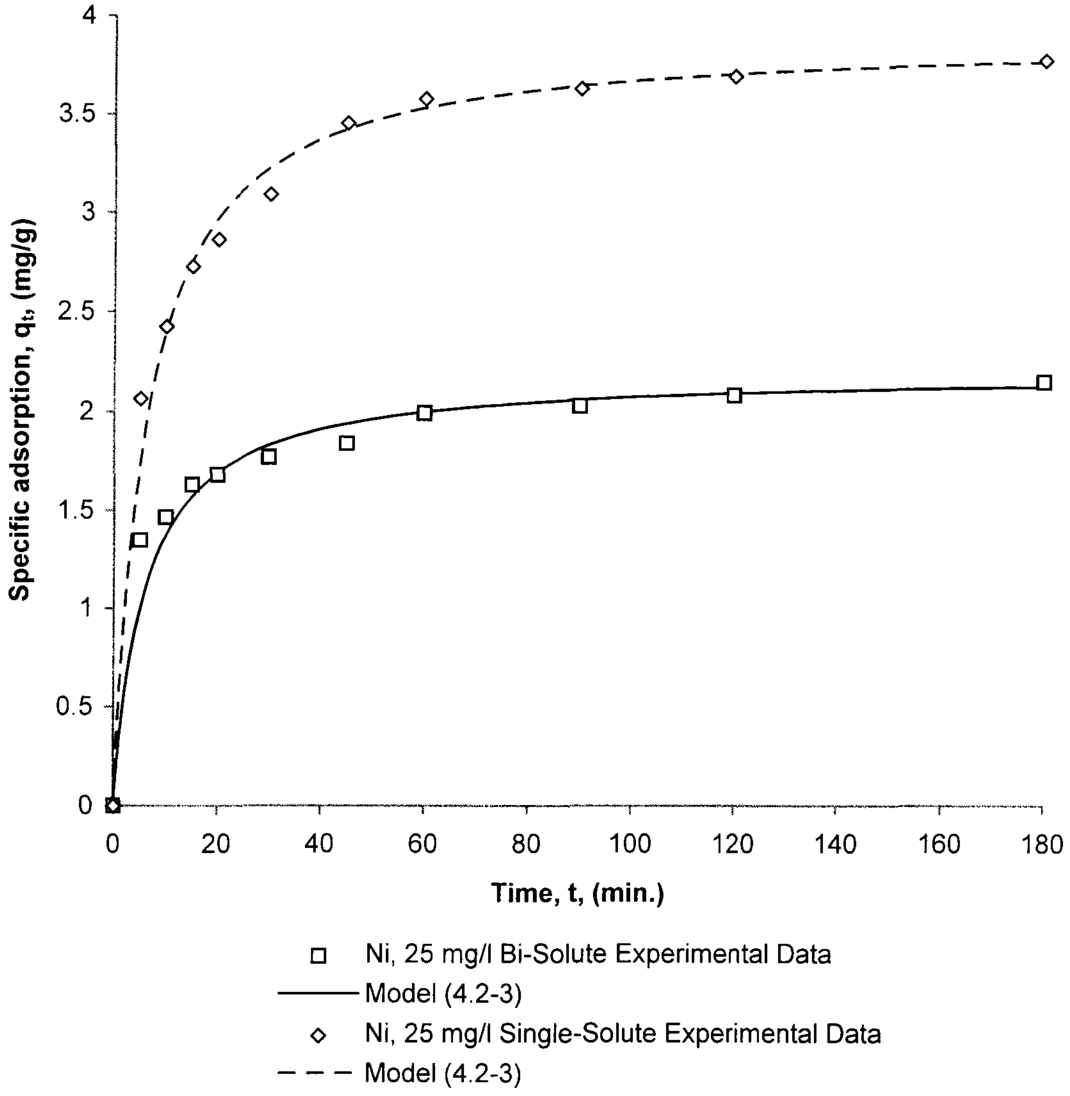


Figure 5.3.1-5: Data (points) and predictions (curves) for the 2nd-order rate model applied to the single- and bi-solute systems for nickel (25 mg/l).



- the rate is not directly related to the square root of C_0 which again implies that intraparticulate diffusion was not the only mechanism involved.

TABLE 5.3.1-4: Second Order Constants for Copper Adsorption.

(q_e = mg/g; K = g/mgmin; h = mg/gmin)

Initial Concentration (mg/l)	Single-Solute			Bi-Solute		
	q_e	K	h	q_e	k	K
10	2.37	0.260	2.94	2.16	0.201	1.88
25	5.74	0.0507	3.34	5.12	0.0213	1.11
50	9.36	0.00640	1.12	8.13	0.00497	0.657
100	12.7	0.00483	1.55	9.88	0.00481	0.941

TABLE 5.3.1-5: Second Order Constants for Nickel Adsorption.

(q_e = mg/g; K = g/mgmin; h = mg/gmin)

Initial Concentration (mg/l)	Single-Solute			Bi-Solute		
	q_e	K	h	q_e	K	h
10	2.16	0.0799	0.744	2.08	0.103	0.892
25	3.90	0.0206	0.627	2.20	0.0380	0.367
50	6.20	0.0131	1.01	2.46	0.0141	0.171
100	7.49	0.00828	0.929	2.57	0.0130	0.171

Copper and Lead Bi-Solute System

This section examines the use of peat for the removal of two metals, copper and lead, from bi-solute solutions. In particular, it reports the effect that a competing ion has on the rates of removal and examines the mechanisms which may affect the uptake of metals.

Figure 5.3.1-6 shows how the presence of the lead affects the adsorption of copper. It is clear from this that the presence of lead has very little effect on the sorption of copper. With bi-solute systems, the equilibrium concentrations of copper in the liquid phase were similar to those in its respective single-solute systems. This can be quantified by an examination of the specific adsorption values (q_t, mg metal/g of peat) calculated at 120 minutes. **Table 5.3.1-6** shows these values, together with values for the reduction in the specific adsorption of the primary metal in the both copper/nickel and copper and lead bi-solute systems. It can be seen from this table that the presence of nickel has a greater effect as the "contaminant" than lead on the sorption of copper.

External mass transfer is characterised by the initial rate of solute sorption (McKay and Poots, 1984). This can be calculated from the initial slope of the C_t/C_0 - time curves (**Figure 5.3.1-7**). These slopes can be derived by assuming that the relationship is linear over the first 5-10 minutes (Forster *et al.*, 1985). **Table 5.3.1-7** presents a comparison of the initial rates calculated for the both copper/nickel and copper/lead bi-solute systems. These results show that the effect of decreasing initial rate of copper adsorption by addition of nickel is higher than by addition of lead.

Intraparticle diffusion characteristics were compared by the intraparticle diffusion rate parameter (**Figure 5.3.1-8**). Values for these parameters in the both copper/nickel and copper and lead bi-solute systems are given in **Table 5.3.1-8**. Initial rate parameters for copper in copper and nickel bi-solute system were lower than for the single-solute system. However, they are higher in the copper/lead system.

TABLE 5.3.1-6: Values for the Specific Adsorption (mg/g) of Copper After 120 Minutes Showing the Reductions Caused by the Addition of Nickel or Lead.

	Copper/Lead System		Copper/Nickel System	
Mono-Solute	Bi-Solute	Δ (%)	Bi-Solute	Δ (%)
9.36	9.39	-0.321	8.13	13.2

Figure 5.3.1-6: Variations in the metal concentrations (C_t) with time (t) for Cu/Pb bi-solute systems.

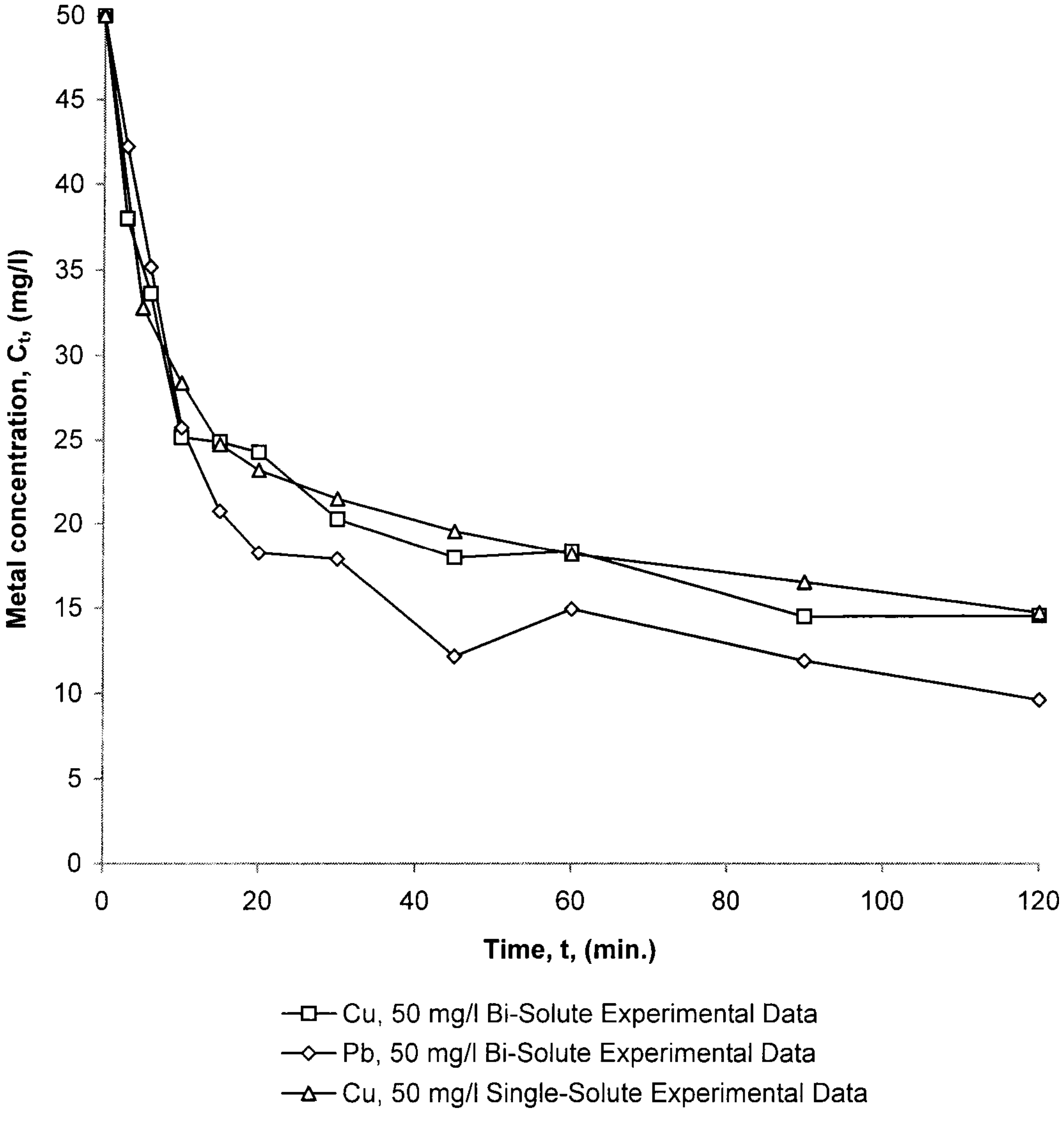


Figure 5.3.1-7: The effect of initial nickel concentration on the changes in C_t/C_0 with time for the Cu/Pb bi-solute system.

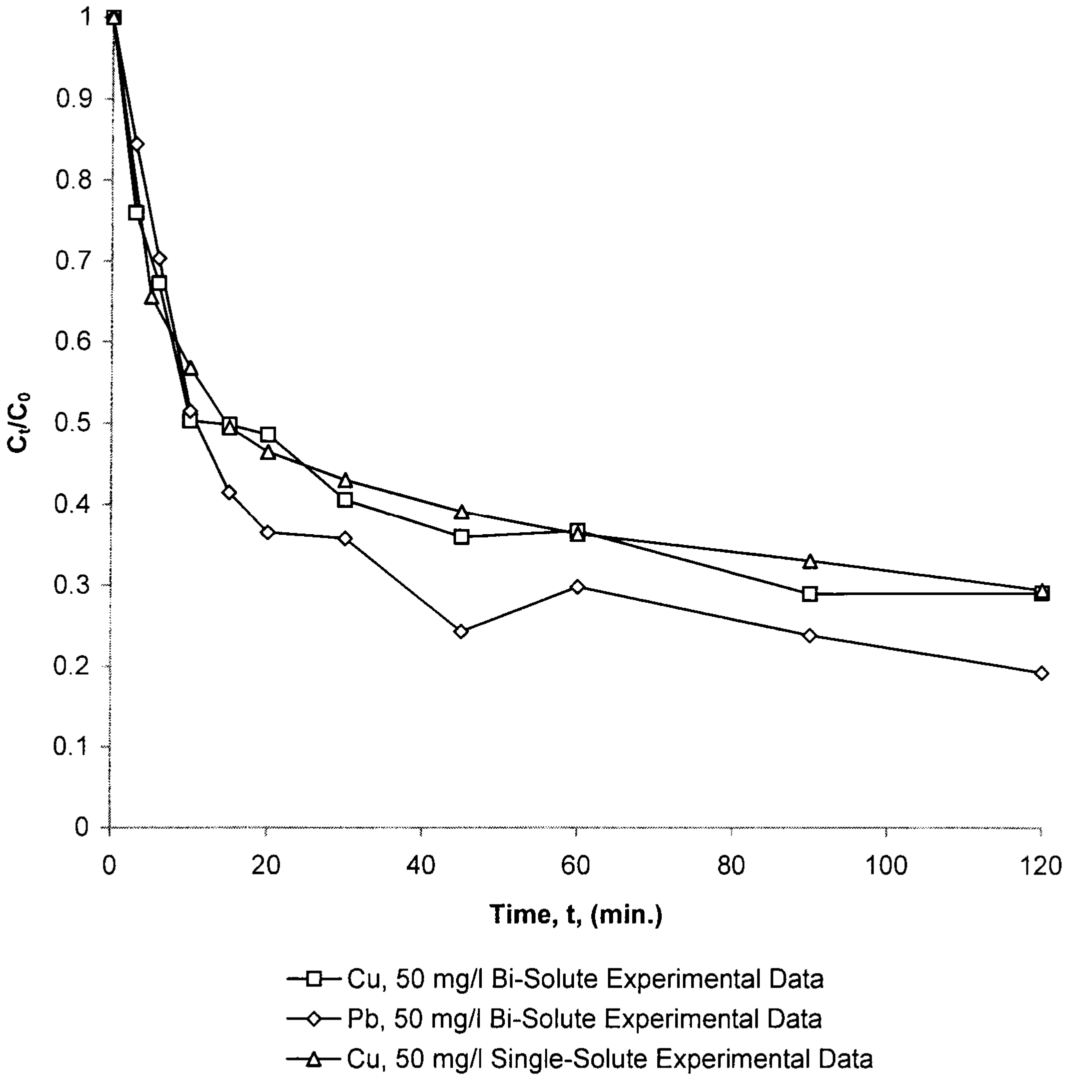
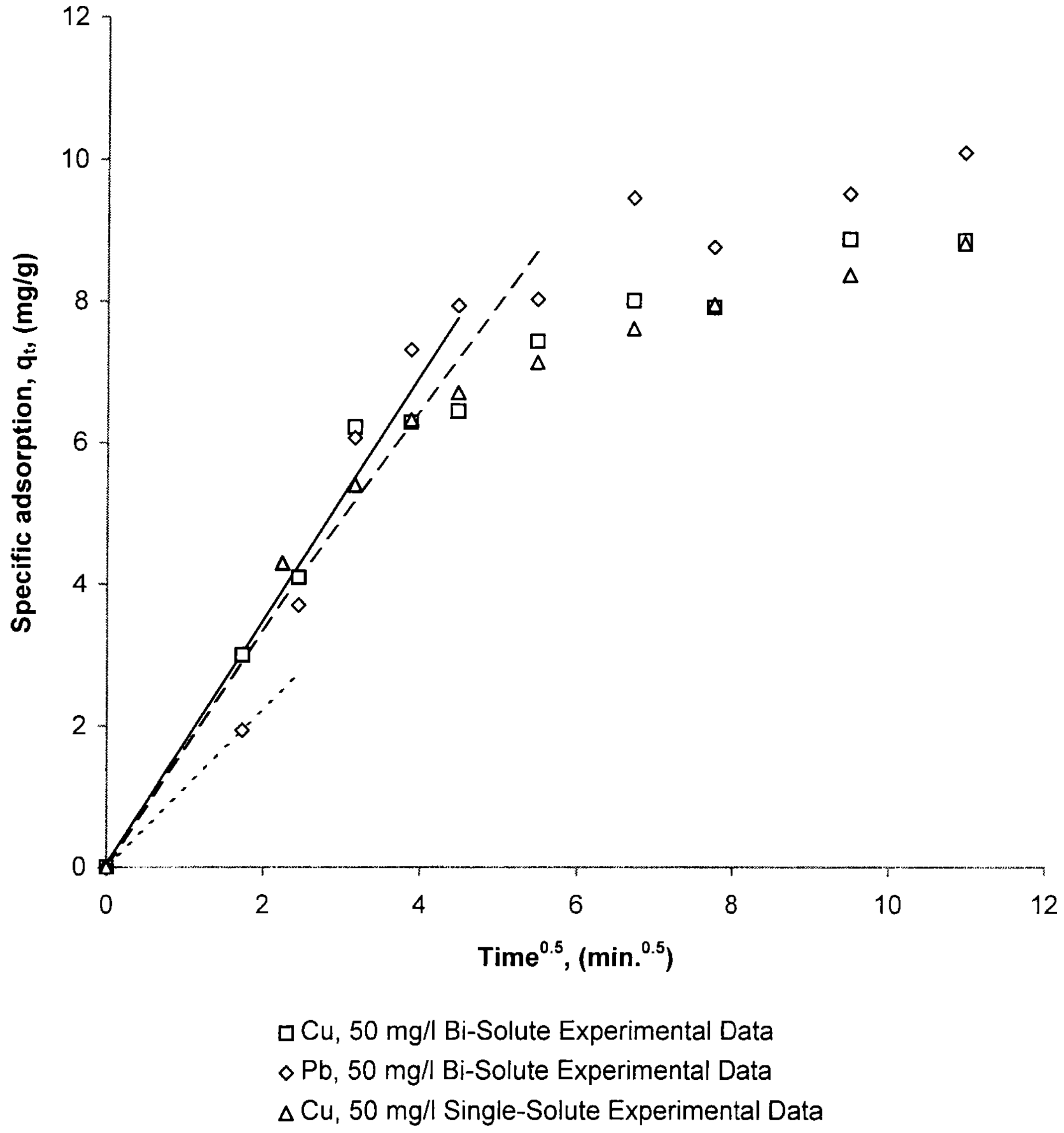


Figure 5.3.1-8: The effect of copper on the pore diffusion model for lead (50 mg/l).



The second order model could be used for copper and lead bi-solute system as copper and nickel. Values for these constants are given in **Table 5.3.1-9** and comparisons between the data and the predictions made by the equation are shown in **Figure 5.3.1-9**. The data in this Figure show that the second order equation does provide a realistic description of the adsorption process.

The initial adsorption rate of copper is affected by additional metal ions. In a copper and nickel bi-solute system, the initial adsorption rate of copper is lower than in the mono-solute system. However, it is higher in the copper and lead bi-solute system.

TABLE 5.3.1-7: Initial (5 minute) Sorption Rates (1/min) for Copper Based on $\left[\left(1-\frac{C_5}{C_0}\right)\Big/5\right]$.

	Copper/Lead System		Copper/Nickel System	
Mono-Solute	Bi-Solute	Δ (%)	Bi-Solute	Δ (%)
0.0689	0.0597	13.4	0.0520	24.5

TABLE 5.3.1-8: Initial Rate Parameters for Copper (mg/gmin$^{-0.5}$).

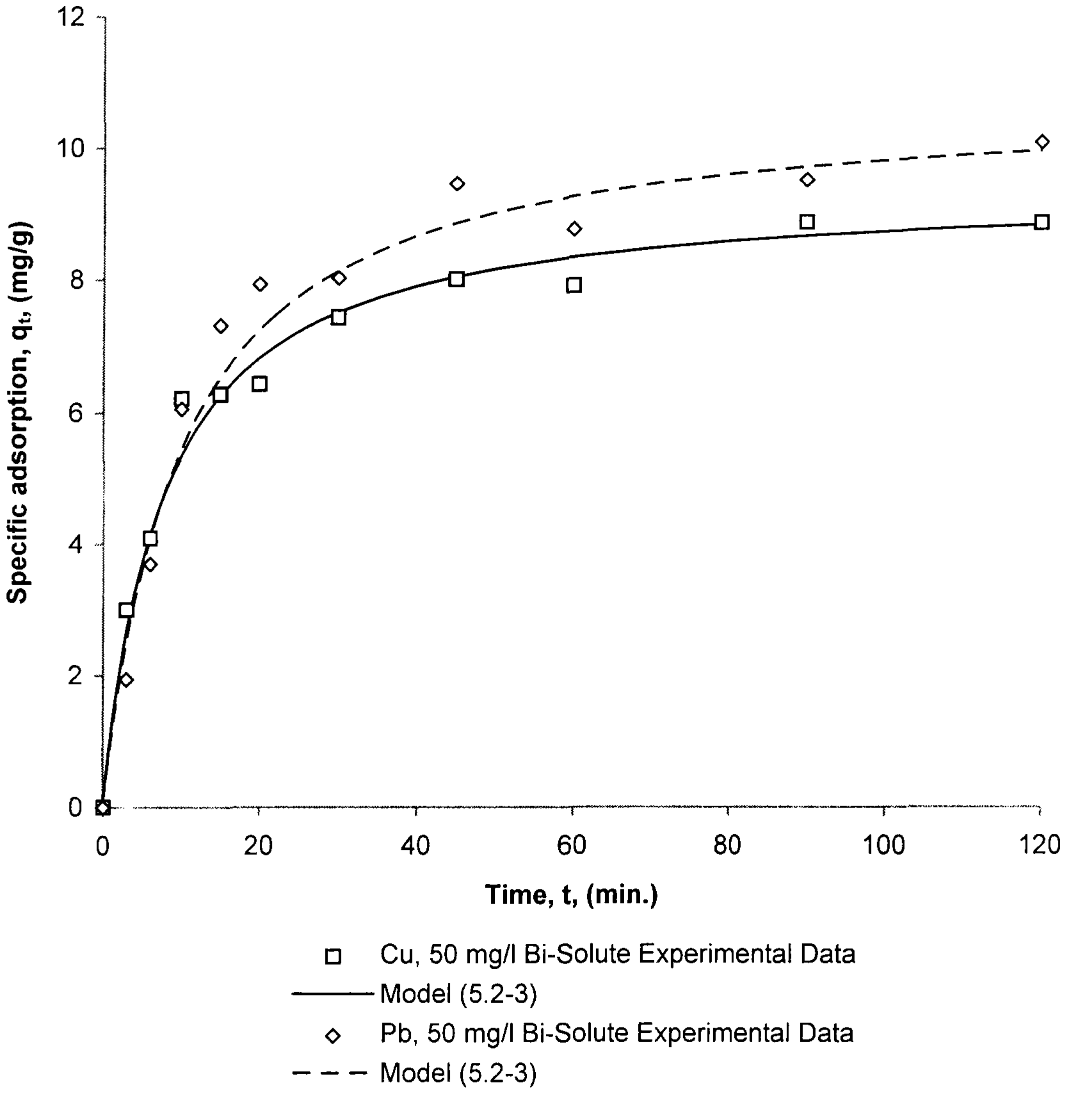
	Copper/Lead System		Copper/Nickel System	
Mono-Solute	Bi-Solute	Δ (%)	Bi-Solute	Δ (%)
1.53	1.73	-13.1	1.17	23.5

TABLE 5.3.1-9: Second Order Constants for Copper Adsorption.

(q_e = mg/g; K = g/mgmin; h = mg/gmin)

Mono-Solute			Cu/Ni System			Cu/Pb System		
q_e	K	h	q_e	K	h	q_e	K	h
9.36	0.00640	1.12	8.13	0.00497	0.657	9.39	0.0709	1.25

Figure 5.3.1-9: Data (points) and predictions (curves) for the 2nd-order rate model applied to the bi-solute systems for copper (50 mg/l) and for lead (50 mg/l).



5.3.2. Kinetics of Triple-Solute System

There are difficulties in describing the adsorption of metal ions from wastewater which contains not one but many metal ions. In order to obtain the parameters for the design of the processing equipment and to determine the optimum operating conditions, mathematical models are of importance. This section describes the results of an examination into the adsorption by peat of copper, lead and nickel from triple-solute systems. The results showed that the kinetics of adsorption were best described by a second order expression.

Experimental results for the triple-solute system are given in **Figure 5.3.2-1**. The adsorption order is the same as single- and bi-solute system as Pb(II) > Cu(II) > Ni(II). With triple-solute system, the equilibrium concentrations of the primary metal in the liquid phase were lower than in their respective single-solute systems and it can be seen that each metal appears to have an effect as the "contaminant" of the other.

The second order model could be used for triple-solute system. Values for these constants were derived from a regression analysis of (t/q_t):t and are given in **Table 5.3.2-1** and comparisons between the data and the predictions made by the equation are shown in **Figure 6.3.2-2**. From the results it seen that the heavy metals are adsorbed fairly rapidly, and that there is a relatively good fit between experimental data and the second order model for copper, lead and nickel. The data in this Figure shows that the second order equation does indeed provide a realistic description of the adsorption process.

Figure 5.3.2-1: Experimental results for batch kinetic adsorption for copper, lead and nickel.

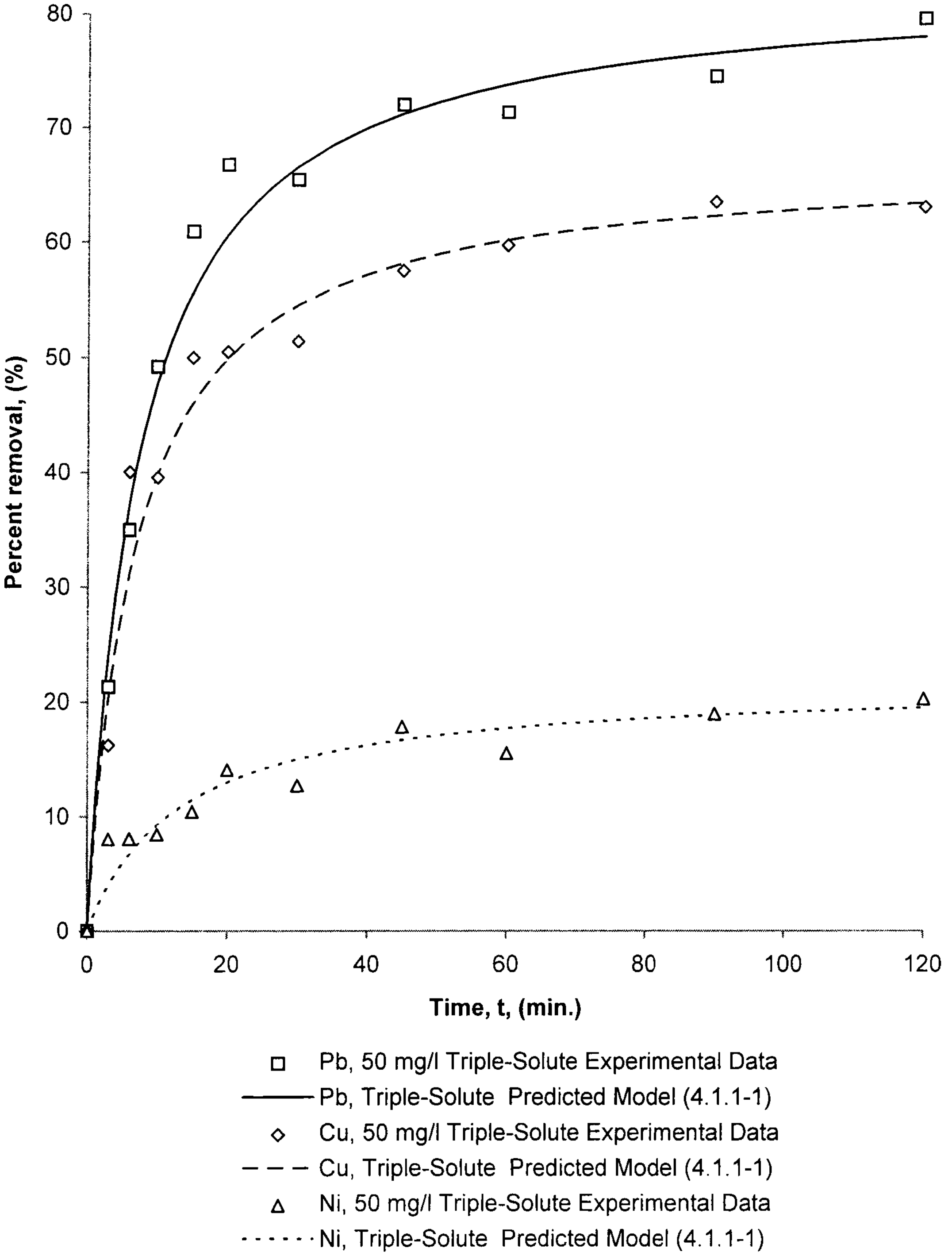


Figure 5.3.2-2: Data (points) and predictions (curves) for the 2nd-order rate model applied to the triple-solute systems for copper (50 mg/l), for lead (50 mg/l) and nickel (50 mg/l).

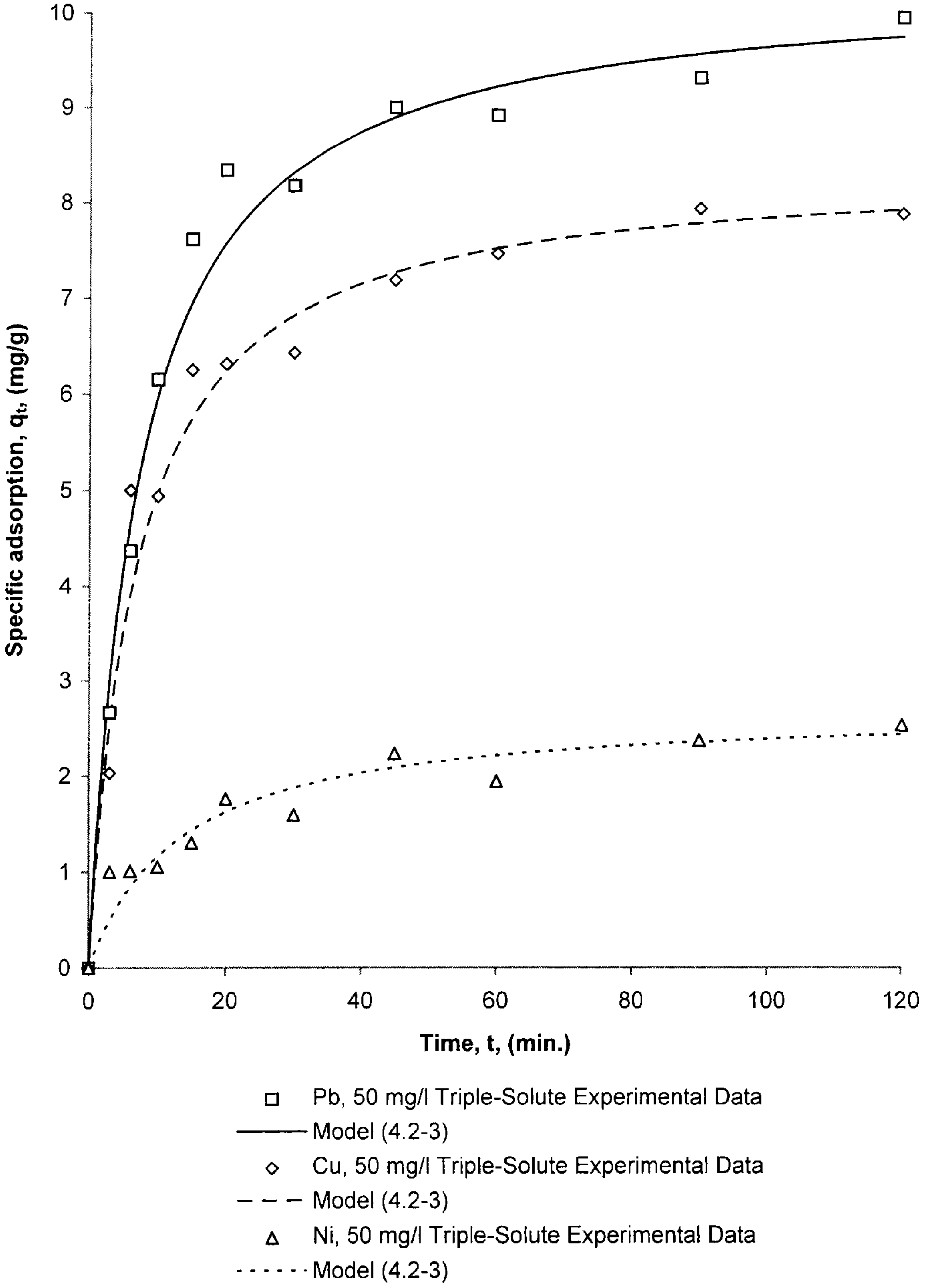


TABLE 5.3.2-1: Second Order Constants for Copper, Nickel and Lead Adsorption in Triple-Solute System.

(q_e = mg/g; K = g/mgmin; h = mg/gmin)

		Copper	Nickel	Lead
Mono-Solute	q_e	9.36	6.20	-
	K	0.00640	0.0131	-
	h	1.12	1.01	-
Cu/Ni System	q_e	8.13	2.46	-
	K	0.00497	0.0141	-
	h	0.657	0.171	-
Cu/Pb System	q_e	9.39	-	10.8
	K	0.0709	-	0.00477
	h	1.25	-	1.11
Triple-Solute	q_e	8.37	2.70	10.3
	K	0.00873	0.0139	0.00663
	h	1.22	0.203	1.42

The ionic radius of divalent copper and nickel is almost the same, but the capacity is quite different. This binding of nickel to bio-surfaces is typical. Indeed, Gould and Genetelli (1978) have suggested that, with anaerobic sludges, there are some sites which, although suitable for other metals, are not available to nickel. Rudd *et al.* (1984) have noted that extracellular polymer (ECP) from *Klebsiella aerogenes*, continued to bind copper, cadmium and cobalt even after the complexation capacity had been reached, whereas with nickel it did not. This implies that peat possesses strong complexing agents which dominate the ion-exchange capabilities of the metals listed, and the ion-exchange capacity differs for different metal ions (Tummavuori and Aho, 1980). The behaviour of nickel in relation to peat is, therefore, understandable if not explainable.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

6.1. CONCLUSIONS

Irish sphagnum moss peat is an inexpensive and readily available biosorbent for the removal of copper(II), nickel(II), and lead(II) from aqueous solution. Of the three heavy metals studied, lead is most readily adsorbed. In other words, the peat has highest adsorption capacity for lead, intermediate for copper and lowest for nickel.

Effective copper(II) removal from aqueous solution can be achieved by adsorption using sphagnum moss peat. Sorption of copper is pH dependent and the best results are obtained in the pH range 4.0 to 5.0. Regression analysis of the observed data resulted in the model of Langmuir and Freundlich isotherms. Percent copper removal at equilibrium increased with increasing adsorption dose. Thus, sphagnum moss peat can be used for the treatment of waste effluents containing copper.

Irish sphagnum moss peat is also a suitable adsorbent for the removal of nickel(II) from aqueous solution. However, its removal is poor compared with other metals. Sorption of nickel is pH dependent and the best results are obtained in the pH range 4.0 to 7.0. Regression analysis showed that the experimental data fitted closely the Langmuir and Freundlich isotherms. Percent nickel removal at equilibrium increased with increasing adsorption dose.

The use of sphagnum moss peat in removing lead from aqueous solution was studied in batch experiments. The adsorption equilibria data can be approximated to a Langmuir isotherm. The maximum adsorption capacity for sphagnum moss peat was found at 30.7 mg/g of peat, when peat dose is 4 g/l, and the initial adjusted pH was 5.0 at 37°C. Freundlich isotherms were also found for the range of the initial lead concentrations from 20 to 80 mg/l at the given temperatures (12 to 37°C) and initial pH values (4.0 to 6.0). It is evident that sphagnum moss peat, a natural, commercially available material, is a good adsorbent for lead(II) from aqueous solutions and can be suggested for the removal of lead(II) from wastewater. The efficiency of removal of lead(II) using sphagnum moss peat as adsorbent was only very slightly dependent on reaction temperature (12 to 37°C) and initial pH (4.0 to 6.0). Kinetic data suggested that the adsorption process is endothermic and transport of adsorbate from solution to the particle solution interface and therefore to the lead bonding reaction are equally responsible in determining the rate. The data therefore obtained might be helpful to environmental engineering for designing and establishing a continuous water pollution control for lead(II).

A kinetic model has been developed and fitted for the adsorption of the divalent metal ions onto sphagnum moss peat. The parameter which has the influence on the kinetics of the adsorption reaction was adsorption equilibrium, q_e, is a function of temperature, initial metal ion concentration, peat dose and nature of solute.

The adsorption capacities of copper(II) and nickel(II) from bi-solute solution onto moss peat were each affected by the presence of the other metal ion. Copper(II) is more strongly adsorbed by peat than nickel(II) in the bi-solute competitive adsorption system. A predictive mathematical model was used successfully in competitive adsorption.

Adsorption without competition has been considered based on the Langmuir theory for binary adsorbate systems and a coefficient for this study was calculated, based on the ratio of solute in the solution. The mathematical model was used successfully to predict results for various ratios of concentrations in competitive adsorption.

During adsorption of copper(II) and of nickel(II) from aqueous solutions by peat as well as ionic competition, there are also sites which are specific for copper(II) and for nickel(II), respectively. These are also considered for bi-solute adsorption systems. The ratio of adsorption capacity of bisolute/single solute systems is almost constant at around 0.8, for copper, that for nickel increases from zero as peat dose is increased. The peat dose effect on the uptake of metals on peat has also been studied for the description of bi-solute adsorption systems. The results indicate that adsorption capacity of copper decreased with increased peat dose. However, adsorption capacity of nickel increased with increased peat dose. A mathematical model was used to predict metal removal and adsorption capacity by adding peat dose.

Lead and copper bi-solute as well as lead and nickel bi-solute systems have also been studied for competitive adsorption. Copper had a greater effect on lead adsorption than did nickel. Nickel removal was reduced by 25.3% when lead was also in solution. The amount of lead adsorbed when other metals were present was less than when only lead was in solution. However, the amount of copper adsorbed when lead was present was only slightly less than when copper alone was in solution. In both of bi-solute systems, the two metal ions shared most of active sites and there are only a few specific sites on the surface which are for copper and nickel, with more specific sites for copper than for nickel.

A copper, lead and nickel triple-solute system has also been studied. The adsorption of any single metal studies such as copper, lead and nickel was hindered by the presence of the other metals. The competitive effect appears to have affected the three ions in the order nickel > lead > copper with nickel affected most; the adsorption capacities for each solute from the mixed solution was 15.9, 57.4, and 71.5% of that of a single-solute system for copper, lead and nickel, respectively.

A kinetic model was developed and fitted for adsorption of divalent metal ions onto sphagnum moss peat. The parameter which had most influence on the kinetics of the adsorption reaction was adsorption equilibrium. This is a function of temperature, initial metal ion concentration, peat dose and nature of solute. It is important to note that adsorption equilibrium is influenced by so many conditions, for this makes the overall reaction pseudo second order.

The adsorption of metal ions onto peat at various initial concentrations of metal ions, temperatures, peat doses and nature solutes shows that the amount of metal adsorbed increases rapidly with time in the beginning, but only very slowly towards the end of the reaction. Indeed, a large fraction of the total amount of metal was removed within a short time.

The results clearly establish that a pseudo second order model provides a more appropriate description of the single-, bi- and triple-solute binding of copper, nickel, and lead to peat than a first order equation. When the second order reaction equation was used to describe kinetic behaviour of metal adsorption onto sphagnum moss peat, the adsorption capacity was predicted well. Again, these results also imply that nickel behaves differently from other metals, particularly when a second metal is present. The precise reason for this, currently, is unclear but it is a behaviour which has been noted previously and is one which has been attributed to the size of the nickel ion and to the chemical nature of the binding sites. The data also confirm that both chemical bonding and pore diffusion are important in determining the adsorption rates and that their relative significance depends on the temperature, initial metal ion concentration, peat dose and nature of solute.

Kinetic expressions developed in batch experiments can be employed to predict the performance of continuous-flow adsorption reactors. The results therefore obtained might be helpful to environmental engineering for designing and establishing a continuous water pollution control for copper(II), nickel(II), and lead(II).

6.2. RECOMMENDATIONS FOR FUTURE RESEARCH

These studies provide us with an initial understanding of the phenomenon of adsorption of heavy metals on sphagnum moss peat, as a model biosorbent, either as single metals ions, or as mixtures. However there still remains much to be done.

The outstanding problems relate to five areas. Firstly, there is the problem of the nature of the organic adsorbent. Do all bio-adsorbents behave similarly, or are there differences? If so, can one classify them, or is there a smooth graduation from one to other? Much work on testing such adsorbants remains. Secondly, there is still much work to be done before the material we have used, sphagnum moss peat, is fully characterised. In particular, continuous column studies are needed. Thirdly, there is the possibility of surface modification of the adsorbent. So far, only a little work has been done. However, until we are able to describe and characterise more readily the range of biosorbents available, as indicated above. There are limitations on what can be done. Fourthly, and more seriously, there is little published work on desorption, disposal, and metal recovery and little serious thought seems to have been given to this subject or its implications, particularly in environmental or economic terms. Does one re-use the adsorbent, or is it merely dumped, thus merely moving the problem, or burned, or is it better to recover the metal? Finally, there is the construction of pilot plant for sanitary and effluent treatment. Will this merely remove metals? Can it filter out biochemical oxygen demand (BOD) and chemical oxygen demand (COD)? There are many laboratory studies of many sorts in the literature, but very few seem to have been converted into the design of a real-life pilot plant. This must change soon.

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