REMOVAL OF LEAD FROM AQUEOUS SOLUTIONS BY ADSORPTION USING PEAT MOSS

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By

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Abstract

Presence of lead, a heavy metal in the environment has been a serious concern especially with rapid industrialization which has created new uses for lead. The actute toxicity of lead to aquatic life and humans and the stringent effluent standard to be met by industries as specified by regulatory organizations has necessitated the development of innovative, effective and economical methods for treating lead-bearing wastewater. An adsorption process using an inexpensive adsorbent such as peat moss is an attractive option for the removal of lead from wastewater.

In this study batch kinetic and isotherm studies were carried out om a laboratory scale to evaluate the adsorption capacity of peat. Effects of pH, contact time and dosage of adsorbent on lead removal was studied. Desorption studies were also conducted using deionized water to evaluate desorption of lead from peat.

Batch kinetic studies indicated that peat was effective in removing 95.5% of lead. The equilibrium time was determined to be 2 h and optimum pH range was found to be 5.5 to 6.0. The kinetics of adsorption of lead ions on peat can be adequately described by the Lagergren model and Ho's pseudo second order reaction rate model. The batch is otherm studies showed that the adsorption data can be described by the Langmuir, Freundlich and BET models. The Freundlich model was found to describe the adsorption data better im comparison with the Langmuir and BET models. The column study showed that peat was efficient in removing lead from an aqueous solution and the Thomas model adequately *described the column adsorption data. The Thomas constant qo was calculated to be 76.7 mgg/g. Desorption studies

using deionized water showed that a small amount of lead was desorbed from peat. The column study also indicated that adsorbed lead ions could be eluted from peat using 0.05N nitric acid solution.

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Notations

| b | amount of adsorbed per unit weight of adsorbent |
|----------------|---|
| В | constant relating to the energy of interaction with the surface |
| C_e | concentration of adsorbate in solution at equilibrium |
| C_0 | initial concentration of adsorbate |
| ${\mathcal C}$ | degree centigrade |
| C_s | saturation concentration of the adsorbate |
| E_s | sorption energy |
| h | hour |
| K | equilibrium constant indicative of adsorption capacity |
| K' | the second order reaction rate constant for adsorption |
| K_L | Lagergren rate constant for adsorption |
| k | Thomas rate constant |
| L | liter |
| L | length of the peat bed |
| M | molarity |
| m | mass of adsorbent |
| mg | milligram |
| min. | minute |
| mL | milliliter |
| n | adsorption equilibrium constant |
| N | normality |
| q | amount of adsorbate adsorbed per unit weight of adsorbent (adsorption density |
| Q | volumetric flow rate |

| q_e | amount of metal ion adsorbed at equilibrium | | |
|----------------|--|--|--|
| Q^{o} | constant related to the energy or net enthalpy of adsorption | | |
| q _o | maximum solid phase concentration of the solute | | |
| q_t | amount of metal ion adsorbed at any time | | |
| R | separation factor | | |
| rpm | revolutions per minute | | |
| T | absolute temperature | | |
| t | time | | |
| V | throughput volume | | |
| ν | linear flow velocity | | |
| x | depth of bed | | |
| X_m | maximum sorption capacity | | |

1. INTRODUCTION

1.1 Heavy metals definition and classification

Heavy metals can be defined in variety of ways, on the basis of their physical, chemical and biological properties. Metals with specific gravity of about 5g/cm³ or greater are generally defined as heavy metals and these include metals from group IIA, IIIB, IVB, VB and VIB of the periodic table. Lead, symbolized Pb is located in group IV of the periodic table, it has an atomic weight and number of 207.19 g and 82, respectively. It has a melting point of 327°C and a density of 11.4g/cm³ (11.4t/m³) and a remarkably high corrosion resistance to most acids, including sulphuric (H₂SO₄) and hydrochloric (HCl) acids with the exception of nitric acid (HNO₃). This corrosion resistance can be attributed to its ability to form a wide variety of oxides ranging from Pb₂O to PbO₂ thereby forming a protective film on the exposed surface (Royal Society of Canada, 1986).

1.2 Heavy metals in wastewater

Heavy metals such as lead can often be found in industrial wastewater and their discharge to the environment poses a serious threat due to their acute toxicity to aquatic and terrestrial life which includes humans. As a result of increasing industrialization more heavy metals are being continually released to the environment and this has prompted environmental engineers and scientists to investigate methods by which heavy metal-bearing wastewaters can be treated effectively and economically.

1.2.1 Sources of lead containing wastewater

Lead is a naturally occurring element chiefly buried in the earth crust in insoluble and biologically inoffensive forms. It is simply found as lead sulphide (galena, PbS) and in Canada it is found as complex ores composed mainly of lead and zinc sulphides, with small inclusions of silver or silver sulphide materials (National Research Council Canada, 1978). Enhanced industrialization and discovery of various uses for lead however have caused humans to disinter it, which has caused the release of large quantities of the by-product of this material into air, soils and surface waters. It is used as an industrial raw material in manufacturing of storage batteries, television tube, printing, paints, pigments, photographic materials, fuels, matches and explosives. The manufacturing process of these materials produces lead-bearing wastewaters, which have to be treated and disposed of. One of the largest consumers of lead is the storage battery industry followed by the petroleum industry in producing gasoline additives. Lead concentrations in wastewater from battery manufacturing, acid mine drainage, tailing pond and steel production plants range from 0.5 to 25 mg/L (Patterson, 1985)

1.2.2 Health effects and regulation in control of heavy metals

Physical and chemical agents generated by human activities may often have various adverse effects on both aquatic and terrestrial life. Lead is an ubiquitous material in the environment and its presence in varying concentrations can be found in diverse locations. The Royal Society of Canada (1986) reported that human exposure to lead has harmful effects on kidney, central nervous and reproductive systems. Air, food and water generally do not usually contain large amounts of lead, however excessive contamination of these natural

sources by industrial activities can result in continuous toxic levels of exposure and consequently clinical poisoning (Mahaffey et al., 1978). In order to develop poisoning from organic lead, one has to be continuously exposed to concentrations higher than those in the general environment for some week or months (Nriagu, 1978). Lead exposure has both acute and chronic effects (Davis, 1990). Another pertinent health problem of lead is bio-accumulation or magnification, which may elevate its concentration to toxic levels (Atkinson et al., 1998). National Research Council Canada (1978) reported that fish could absorb lead through their body surface and the food they consume. As a case study the liver of sea bass caught near California coast at Los Angeles was found to contain about 22 ppm Pb which is considerably higher than the permitted level of 10 ppm for human consumption and twice as high as the concentration in fishes found 300 km away; the majority of the lead was attributed to automotive aerosol (Chow, 1971).

The Canadian Council of Resources and Environment Ministers (1987) has developed guidelines for the discharge of wastewater containing lead and other heavy metals in order to protect freshwater aquatic life. Table 1.1 shows a summary of the guidelines for freshwater lead concentration.

Table 1.1: Summary of Canadian guidelines for protection of fresh water aquatic life (Canadian Council of Resource and Environment Ministers, 1987)

| Parameters | Guideline (μg/L) | Hardness in mg/L (as CaCO ₃) |
|------------|-------------------|--|
| Lead | 1 | 0 ~ 60 |
| | 2 | 60 ~ 120 |
| | 4 | 120 ~ 180 |
| | 7 | > 180 |
| Cadmium | 0.2 | 0 ~ 60 |
| | 0.8 | 60 ~ 120 |
| | 1.3 | 120 ~ 180 |
| | 1.8 | > 180 |
| Nickel | 25 | 0 ~ 60 |
| | 65 | 60 ~ 120 |
| | 110 | 120 ~ 180 |
| | 150 | > 180 |

Environment Canada (1977) also developed effluent limits for mining industry and the lead constituent summary is shown in Table 1.2

Table 1.2: Metal mining liquid effluent regulations for lead (Environment Canada, 1977)

| Parameter | Value (mg/L) |
|---|--------------|
| Maximum authorized monthly mean concentration. | 0.2 |
| Maximum authorized concentration on composite samples | 0.3 |
| Maximum authorized concentration in grab samples | 0.4 |

The maximum allowable concentration (MAC) level of lead in drinking water is 0.01 mg/L (Health Canada, 1996). The US EPA has recommended that the best available treatment technology for lead removal should be used in drinking water (Sawyer et al., 1994)

1.2.3 Treatment methods for heavy metal-bearing wastewater

There exists numerous techniques for the removal of heavy metals from wastewater and these include chemical precipitation, ion exchange, adsorption, electrolytic recovery, electrodialysis, solvent extraction, reverse osmosis, membrane separation, ultrafiltration, ozonation, foam floatation, vapour recovery, gamma irradiation, freeze crystallization, and photochemical methods (Patterson, 1985; Atkinson et al., 1998). Although some of these

treatment methods can be successfully used for treating most wastewaters, others are quite limited in use. The application of chemical precipitation to dilute solutions (low concentration) can be difficult unless the addition of flocculating agents such as lime, caustic and sodium carbonate is employed. However a bulky sludge is produced, and the disposal constitutes a problem (Thacktson et al., 1980). Ion exchange and activated carbon adsorption are quite expensive and require recharge of resin or spent activated carbon as well as the disposal of substantial volume of used regeneration solution. In addition to the fact that membrane technology is expensive, membranes are susceptible to attack by microorganisms, likewise other methods mentioned require elaborate and considerably high operation costs.

In general, factors to be considered in the choice of a method to be adopted for the treatment of heavy metal-bearing wastewater should include: high rate of removal, economic feasibility in terms of labour, materials, equipment and energy, applicability to small, intermediate and large scales, low productivity of highly enriched spent materials and capability of reducing heavy metal ion concentration to levels below established regulatory standards. Adsorption process is an effective process and adoption of economical and easily available adsorbents such as peat moss will make the process a considerably promising option by meeting the criteria stated above.

1.3 Rationale for using peat

It is established from literature that activated carbon is an effective adsorbent and is capable of removing organic compounds and a wide variety of heavy metals (Tan et al., 1987;

Annesini et al., 1986). However the high cost of activated carbon has resulted in limitation of its use as an adsorbent and thus the need to explore other cheaper adsorbents. The use of inexpensive adsorbents had been demonstrated to be effective in removing heavy metals from wastewater and such materials include: rice husk (Khalid et al., 1998), crab shell (Lee et al., 1998), fly ash (Gupta et al., 1998; Weng and Huang, 1994), zeolite (Groffman et al., 1992), bentonite (Viraraghavan and Kapoor 1993; Orumwense, 1996), peat (Gosset et al., 1984; Chaney and Hundemann, 1979) and discarded automotive tires (Netzer et al., 1974).

The use of peat as a soil moisture conditioner and in other agricultural and horticultural applications has been in existence for some time. Peat is also used in the manufacturing of resins, cellulose, humic acids and activated carbon; it's use in wastewater treatment has been the subject of many investigations recent years. Peat deposits cover a vast area of Canada, USSR, USA and other parts of the world (Kivinen and Pakarinen, 1980), Table 1.3 shows a summary of world peat producing countries. Peat is an inexpensive adsorbent and it is widely abundant, Canada has an estimated 500,000 square miles (1.295 million km²) of peatland (Radforth, 1968). Coupal and Lalancette (1976) reported that peat exhibits ion exchange capacity for metals like copper, lead and zinc effectively between pH of 3.0 and 8.5. Below pH 3 most metals will leak from peat and above pH 8.5 peat was unstable. This study was thus conducted to evaluate the effectiveness of peat in the removal of lead by adsorption.

Adsorption is the process whereby substances (e.g. dissolved solids) accumulate onto the surface of an adsorbent while absorption is further penetration of the accumulated substances

into the adsorbent. Since these two processes occurs simultaneously, the overall process is generally referred to as adsorption in the context of this study.

Table 1.3: World Peat producing countries (Kivinen and Pakarinen, 1980).

| Country | Peatland area (1000 ha) |
|-----------------|-------------------------|
| Canada | 170,000 |
| USSR | 150,000 |
| United States | 30,000 |
| Indonesia | 26,000 |
| Finland | 10,400 |
| Sweden | 7,000 |
| China | 3,480 |
| Norway | 3,000 |
| Malaysia | 2,360 |
| Great Britain | 1,580 |
| Poland | 1,350 |
| Ireland | 1,170 |
| West Germany | 1,110 |
| East Germany | 550 |
| The Netherlands | 250 |
| Denmark | 120 |
| France | 90 |
| Belgium | 18 |

1.4 Objective and scope of the study

The objectives of the study were as follows:

- (i) to investigate the effectiveness of horticultural peat in the removal of lead under varying experimental conditions;
- (ii) to examine effect of pH on adsorption of lead onto peat;
- (iii) to identify the mechanism involved in the removal of lead ions by peat;
- (iv) to examine the applicability of known adsorption kinetics models; and
- (v) to examine the applicability of various adsorption isotherms.

The scope of the study included the following tasks:

- (i) a review on use of peat in the removal of heavy metal from wastewater;
- (ii) laboratory batch kinetic and isotherm studies to evaluate the adsorption capacity of peat for lead;
- (iii) laboratory column study; and
- (iv) elution of metal ions from the peat after adsorption.

. . .

2. LITERATURE REVIEW

2.1 Impact of lead on aquatic ecosystems

The unique physical properties of lead, including low melting point, corrosion resistance, malleability and high density have led its use in a wide variety of industries and trade and consequently increased the potential of lead exposure in many occupations. Some of the occupations at the risk of lead exposure include battery makers, paint manufacturers, painters, lead miners and smelters, diamond polishers, electroplaters, musical instrument makers, pipe filters, match makers and welders among others (Kusnetz and Hutchinson, 1979)

Existence of lead in natural waters is greatly dependent on the atmosphere and earth surface that they are in direct contact (HMSO, 1974). The major sources of lead in aquatic ecosystem including the ocean are domestic wastewater effluent, coal burning power plants, non-ferrous metal smelters, iron and steel plants and dumping of sewage sludge (Nriagu and Pacyna, 1988). Leland et al. (1973) demonstrated that urban runoff and disposal of treated wastewaters had an adverse effect on a river ecosystem. They found acid extractable lead in river sediments in urban and rural drainage areas varied from 10 to 388 ppm respectively and that fishes were generally absent from urban drainage waters.

Pringle et al. (1968) demonstrated that oyster, *Crassostrea virginica*, could accumulate lead in concentrations of several hundreds to several thousand times greater than concentrations in seawater. Lead accumulating ability of shell fish thus made them very useful as a means of monitoring lead pollution (Navrot et al., 1974). Schultz-Balds (1972) found that absorption

and accumulation of lead by shell fish produced lethal and chronic effects even at 0.5 ppm in aqueous solution.

Other smaller aquatic organisms also have ability to accumulate lead from their food as well as from their surrounding medium and these may attain lethal concentrations. Aubert et al (1975) determined that the toxic threshold of Pb(NO₃)₂ in sea water for the aquatic worm Nereis diversicolour was 8.3 ppm for eight days. Brown and Ahsanullah (1971) also found that 50% mortality was reached in a group of 50 Ophyotrocha labronica maintained in sea water containing 1 ppm lead in about 600 hours. They also reported a linear relationship between lead concentration in sea water and the time required for 50% mortality in groups of 50 brine shrimp (Artenia salina).

Drifmeyer and Odum (1975) reported that fish taken from a marsh receiving dredge soil from a polluted industrialized harbor contained significantly higher levels of lead (4.5 ppm) than fish from a control marsh (0.2 -0.6 ppm). Carpenter (1925) showed that acute lead toxicity resulted in production of copious amounts of fish epidermal mucus which interfered with the gills and caused death by asphyxia. National Research Council Canada (1978) reported that under conditions of low pH and low water hardness, insoluble lead compounds can release Pb²⁺ to levels toxic to fish.

2.2 Use of peat for the removal of lead

Peat can be described as fibrous mass of fossilized plant matter in various decomposition

stages, it generally occurs in wet areas where there is a deficiency of oxygen thereby promoting the accumulation of plant matter over its decomposition. Peat is a complex material consisting predominantly of lignin and cellulose (Coupal and Lalancette, 1976). These constituents, especially lignin, bear polar functional groups such as alcohols, ketones, aldehydes, acids and phenolic residue which can be involved in chemical bonding and complexation roles during metal ion fixation from solutions (Coupal and Lalancette, 1976).

The use of peat in wastewater treatment has been extensively studied and it has been proven that peat is an effective adsorbent for the removal of heavy metals from wastewater. Peat has a natural capacity for exchange adsorption with heavy metals such as lead, zinc, chromium, nickel, copper and cadmium. Exchange adsorption takes place as a result of either solvent motivated force, which relates to surface tension, or adsorbent motivated force which combines chemical electrostatics and physical interaction between adsorbate and adsorbing surface. Adsorption is generally driven by the two forces (Weber and DiGiano, 1996). Peat strongly adsorbs various metal cations using their caboxylic, phenolic and hydroxylic functional group (Smith et al., 1977; Wolf et al., 1977).

Bunzl et al. (1976) studied the adsorption and desorption of lead, copper, cadmium, zinc and calcium on peat. The peat was pre-treated by washing with 1M HCl and then rinsed with deionized water. 1.00g of wet peat samples was then added to 200 mL of deionized water and stirred for some hours to establish the swelling equilibrium of the peat particles. The metal solution was then added for the adsorption study. This was followed by decanting of the supernatant which was replaced with 200 mL of dilute nitric acid. They found from their

studies that in the pH range of 3.5 to 4.5, the selective order of metal adsorption by peat was $Pb > Cu > Cd \approx Zn > Ca$. An initial increase in metal ion desorption rate was observed which subsequently decreased and followed a selective order similar to that of the adsorption.

Zhipei et al. (1984) conducted a study on the removal of lead, cadmium, zinc, nickel and chromium from wastewater using several Chinese peats with particle size ranging from 18 to 40 mesh sieves. 0.125 g of peat was mixed with 25 mL of heavy metal solutions, agitated for two hours and allowed to settle for seventy-two hours at room temperature. They found from their studies that the efficiency of heavy metal ion removal with various peats was related to composition and property of peat samples as well as the adsorbed ion. They also found that the equilibrium time was independent of the particle size. The desorption studies indicated that lead, cadmium, zinc and nickel could not be desorbed by refluxing with hot water but could be desorbed using 1M hydrochloric (HCl) or nitric (HNO₃) acids.

Coupal and Lalancette (1976) studied the treatment of wastewater containing mercury, cadmium, zinc, copper, iron, nickel, chromium (VI), silver, lead and cyanide, by circulating the wastewater over a mat of peat. Heavy metal concentration were initially reduced to the level of 1 mg/L by elevation of pH which resulted in precipitation of metals as sulfide and hydroxides. The precipitates were allowed to settle and the supernatant was then circulated through the mat of peat where majority of the remaining metal ions which were in form of suspended sulfide and hydroxide were then removed by adsorption to the surface of the mat of peat. The remaining metal ions were further removed by chemisorption onto the peat mat. The effluent metal concentration after the treatment fell below limits specified by the United

States Environmental Protection Agency (US EPA).

Ho and McKay (1999) studied the kinetics of lead (II) sorption on to peat based on the assumption of pseudo-second order mechanism and taking prominent cognisance of chemisorption. They developed a pseudo-second order model to predict the sorption rate constant, initial sorption and equilibrium capacity. Effects of initial concentration, temperature and particle size were investigated. From their study the rate constant decreased non-linearly with increasing initial concentration, increased with increasing temperature and increased with decreasing particle size.

McLellan and Rock (1988) investigated the removal of cadmium, chromium, copper and lead from landfill leachate with peat at a contact time of 1 and 24 hours. They observed that adsorption of metals increased with increasing concentration and longer contact time. They also found that metal interaction played an important role in the adsorption of metal from leachate, with various metals competing for adsorption sites on the peat. The desorption studies revealed a substantial final disposal problem as the application of deionized water to the peat after 76 days of operation showed that approximately 50 % of the adsorbed metal leached back into the solution. They thus concluded that ultimate disposal of the exhausted peat would require considerable attention and minimization of water infiltration to the final disposal site would be of pertinent importance to control leaching of metals.

2.3 Use of activated carbon for the removal of lead

Tan and Teo (1985) studied the combined effect of carbon dosage and initial concentration on the adsorption isotherm of lead and chromium onto activated carbon. They found that the Freundlich and Langmuir equations were unable to adequately describe the observed isotherm under combined influence of carbon dosage and initial adsorption concentration and this had to be modified. The activated carbons used were pre-conditioned by soaking in 6N HCl solution for twenty four hours, washed and then soaked in deionized water for twenty four hours before it was oven dried at 103° C. The contact times for the adsorption studies were 3 days. They concluded from their studies that adsorption of lead and chromium by activated carbon showed significant dependency on pH, carbon dosage and initial adsorbate concentration.

Netzer and Hughes (1984) studied the adsorption of copper, lead and cobalt by carbon. They used an initial concentration of 10 mg/L for each metal to evaluate and optimize process variables like pH, equilibrium, time, carbon type and carbon dosage. They found that when two or three metals were present in solution there seemed to be a competition for adsorption sites and the required time for complete adsorption was affected by the ratio of metal species to adsorption sites. Lead adsorption was hindered by the presence of other metals with copper having a greater hindrance effect on lead than cobalt. Also approximately twice as much lead was removed than copper and 10 times more lead was removed than cobalt. An optimum pH of 4 was obtained for the two metals.

Lee et al. (1998) studied the removal of lead in a fixed bed column packed with activated

carbon and crab shell. They found that the addition of 1g crab shell to a column packed with 10g of activated carbon lengthened breakthrough time from 380 bed volumes to 1500 bed volumes. This was attributed to the increases in CO₃²⁻ and OH⁻ ions available for bonding of lead. The stock solution used had concentrations of 10 to 50 mg/L and pH was fixed at 3 to minimize concentration of lead and the lead uptake doubled from 31.4 mgPb/g packing material to 62.7 mgPb/g packing material when the influent lead concentration increased from 10 to 50 mg/L. The major mechanism for lead removal was through dissolution of CaCO₃ in the crab shell followed by precipitation of lead in the form of Pb₃ (CO₃)₂OH₂.

Reed and Arunachalan (1994) studied the removal of lead and cadmium from metal bearing wastewaters containing lead and cadmium using granular activated carbon columns. Three synthetic wastewaters were simulated containing combinations of 10 and 50 mg/L concentrations of lead and cadmium, organic compounds and acetic acid. Column pH was a critical parameter for the column performance, there was significant increase in effluent metal concentrations with increasing pH. The granular activated carbon (GAC) was successfully regenerated by rinsing with 1L (\approx 8 bed volume) of 0.1 HNO₃, and the column performance was not adversely affected by the regeneration. The use of regeneration procedure for virgin carbon was recommended by the authors to enhance column performance since it increases OH available for surface and pore liquid precipitation, increases carbon pH and also increases sites available for adsorption.

Taylor and Kuennen (1994) studied removal of soluble and insoluble lead from drinking water using a point of use (POU), granular activate carbon (GAC), fixed bed adsorber (FBA).

The setup was composed of a pressed carbon block with five stages of filtration and a rated life of 500 gallons. The first two were made of non woven materials to remove large particles, the next two stages of carbon filtration consisted of first a coarse GAC followed by a fine GAC, and the final stage is a porous plastic made of sintered polyolefin. It was demonstrated that the setup adequately removed both insoluble and soluble lead from drinking water. They found from temperature studies that mechanisms other than adsorption such as hydrogen bonding and precipitation on carbon surface are also involved in the removal of lead. They also found that various carbons had a wide range of lead adsorption capacities and that adsorption also varied significantly with the pH of the water.

Wilczak and Keinath (1993) studied the kinetics of sorption and desorption of copper (II) and lead (II) on activated carbon. It was found that the sorption of lead (II) and copper(II) on activated carbon consisted of a rapid initial uptake followed by a slow approach to equilibrium which spaned over a period of several weeks. They found that sorption of copper and lead ions on activated carbon were fully reversible.

No general

3. MATERIALS AND METHODS

3.1 Peat

The sphagnum peat moss used in this study was supplied by Premier Peat Ltd., Carrot River, Saskatchewan, Canada. The porosity, surface area, moisture content and pH of the peat were determined. The peat was oven dried at 103 0 C for 24 h and the dried peat was then screened through ASTME: 11 # 20 mesh sieve prior to use in the experiments.

3.2 Stock and reference solutions

The lead nitrate salt and standard reference solution used in the experiment were supplied by Fisher Scientific Ltd., Edmonton, Canada. Lead nitrate (analytical grade Pb(NO₃)₂ 3.26 g/dm³) aqueous solutions were prepared in distilled, deionized (DDI) water supplied by Rainsoft Industries Regina, Canada.

3.3 Preparation of glassware

The glassware used in the experiments were first washed with detergent and properly rinsed with tap water, this was followed by the addition of 10% nitric acid to further rinse and get rid of any residual metal. The glassware was then finally rinsed with tap water and then distilled deionized water.

3.4 Batch adsorption studies

3.4.1 Batch kinetic studies

Approximately 10 mg/L stock solution of lead was prepared by dissolving 0.0159 g of lead in 1000mL of deionised water. The pH of the lead solutions was adjusted using 0.1N NaOH or HNO₃: 0.02 g of peat was then added to 100mL of lead solution in a 125 mL Erlenmeyer conical flask and sealed with PARAFILM M, manufactured by American National CAN, Greenwich, CT, USA. A control with no peat was also set up to determine the adsorption of lead on the glassware. Experiments were conducted in duplicate and mean values were used, variations in individual measurements were less than 10%.

The samples were then placed on a Labline orbital shaker manufactured by Labline Instrument Inc., Melrose Park, Illinois, USA and shaken at 125 rpm at a room temperature of 23±1°C. Fifteen samples were used for the batch kinetic studies and samples were withdrawn after 5,10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 150, and 180 min. The samples were measured for the remaining lead ion concentration in solution using Varian AA-10 atomic absorption spectrometer. Kinetic studies were used in determining the equilibrium time for the adsorption of lead onto peat.

3.4.2 Effect of pH on Adsorption

The optimum pH at which maximum amount of lead would be adsorbed by peat was determined by adjusting the pH of the stock solution using 0.1M HNO₃ or NaOH. 0.02g of

peat was added to each of the 125 mL Erlenmeyer flask containing 100 mL of lead solution with a concentration of about 10 mg/L. The lead solution pH was adjusted from 3.0 to 6.0 in an increment of 0.5 unit. The mixture was shaken at 125 rpm for a period of time i.e. equilibrium time; after equilibrium was reached the final pH of the mixture was recorded. The sample was then filtered and the lead concentration in the filtrate was then measured. The experiments were conducted in duplicate and mean values were used.

3.4.3 Batch isotherm studies

Isotherm experiments were conducted to investigate the relationship between the solid phase concentration of an adsorbate (i.e. the amount of adsorbate adsorbed per unit mass of adsorbent) and the solution phase concentration of the adsorbent at an equilibrium condition under constant temperature. 500 mL Erlenmeyer flasks containing 250 mL of lead solution with a concentration of about 10 mg/L at different pH values of 3.0, 4.0, 5.0, and 6.0. Eight samples containing varying amounts (0.01 to 0.06g) of peat were added to the lead solution at the various pH and the mixture was shaken at 125 rpm for a period of time (i.e. equilibrium time). The samples were then filtered and the filtrate lead ion concentrations were measured. These experiments were conducted in duplicate and mean values were used.

3.5 Desorption studies

Desorption studies were conducted to investigate if the adsorbed lead ions were leaching from the peat. Eight samples containing representative weights of peat (0.01 to 0.06g) were added to lead at pH values of 3.0, 4.0, 5.0 and 6.0 and mixed together for the equilibrium

time. After shaking for two hours, the peat samples were filtered and added to 250mL of deionized water and stirred at 125 rpm for two hours. The samples were then filtered and the filtrate lead ion concentrations were measured. These experiments were conducted in duplicate and mean values were used. A controlled study was also carried out to determine lead ion content of the peat used. This was done by adding representative weights of 0.01 to 0.06 g of fresh peat samples into 250 mL of deionized water.

3.6 Column Study

The column study was conducted using an acrylic pipe having an internal diameter of 44.45mm (1.75 inches) and a length of 400 mm. Fig 3.1 shows a schematic of the column set-up. 30.9g of peat was packed into the column to a density of 132.9 kg/m³ and a bed height of approximately 15cm was achieved. The glass wool layer in combination with a layer of gravel at the bottom and the top of the tube helped in even distribution of the lead solution through the top of the column and also prevented washing away of the peat at the bottom. (Figure 3.1). The lead solution of approximately 10 mg/L was pumped through the top of the column at a constant flow rate of 40.5 mL/min. (37.6 m/d) by means of a peristaltic Masterflex® pump. The pH of the lead solution was maintained at 6.0. Column effluent samples were collected at frequent time interval and analyzed for effluent lead concentration until the column achieved breakthrough, (i.e. effluent to influent concentration of 0.8 or higher). 0.05N HNO3 solution was then used to desorb the lead ions from the peat and samples were collected and analyzed for lead ion concentration. The elution experiment was terminated when the effluent concentration reached 1.0 mg/L or lower.

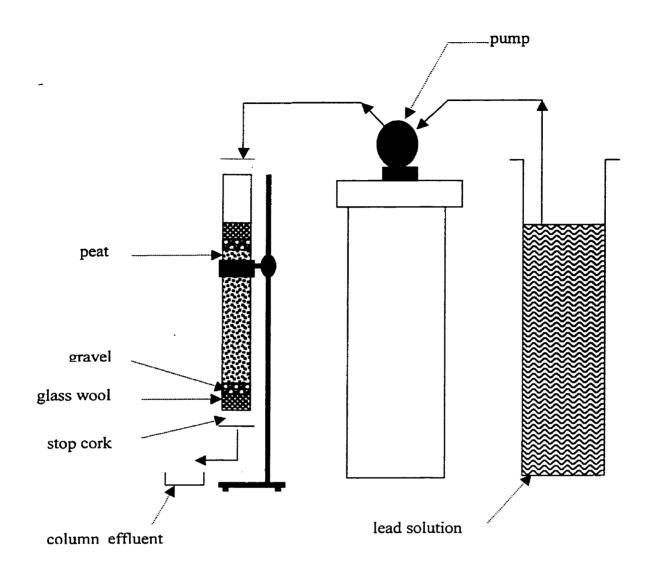


Figure 3.1: Schematic of column setup

3.7 Analytical procedures and methods adopted

The methods outlined in "Standard Methods" (1998) were used for analysis during the studies. The determination of pH was made electrometrically using Acument Selective Ion Analyzer (Model 750), manufactured by Fisher Scientific Limited, Edmonton, Canada.

The concentration of lead in the stock solution was verified by flame atomic absorption spectroscopy using Varian AA-10 Atomic absorption spectrometry (section 3111, Standard Methods 1998). The standard solutions were prepared using 1000 ppm reference solution supplied by Fisher Scientific Limited, the required concentrations were obtained by diluting with distilled deionised water to concentrations of 2.0 mg/L, 4.0 mg/L, 8.0mg/L, 12.0 mg/L and 15 mg/L. These were used in obtaining calibration curves for the concentration range used in the experiment. Single element hollow cathode lamp of lead was used as a light source while air -acetylene flame was used to atomize the samples. Lead ions were analyzed at 217 nm wavelength and the slit width was 1 nm. Three replicate readings of the same samples were taken with an integration time of 3 s and a delay time of 10 s.

The moisture content of the peat samples was determined using the procedure suggested by American Society for Testing and Materials (ASTM, 1971a) (D2974-71). A representative weight of throughly mixed peat samples was weighted and transferred to a pre-weighted porcelain dish. The peat samples were then oven dried at 105°C for 16 hours and then taken out to cool to room temperature and weighed again. The moisture content was then calculated

by taking the difference in weights before and after drying in an oven. An alternative procedure ASTM (1971a) (D2974-71) was also used in determining the moisture of the peat samples. Representative peat samples were thoroughly mixed and spread evenly on a flat surface and allowed to come to moisture equilibrium with room air for 24 hours. The sample was stirred occasionally to enhance maximum air exposure. The air-dried sample was then ground and a representative weight of the ground air-dried sample was further dried in an oven at 105°C for 24 hours. The oven-dried peat samples were then weighed again and the moisture content was determined.

The pH of the peat was determined by electrometric measurement (ASTM, 1971c). Air-dried samples (3g) was soaked in 350ml of deionized water for 30 minutes while stirring occasionally. The pH was then measured using an Acumet Selective Ion Analyzer (Model 750) manufactured by Fisher Scientific.

The surface area of the peat sample was determined using Flowsorb 2300 manufactured by Micrometrics Instrument Corporation, USA. A gas mixture of 30 mole percent nitrogen and 70 mole per cent helium was used in conducting a single-point surface area measurements. Liquid nitrogen was used in setting the adsorption of nitrogen gas by samples The peat samples were degassed at 100 °C for 30 minutes and were then cooled to liquid nitrogen temperature. The surface area of the sample under measurement was then read on the display meter. The value of the surface area recorded was then converted to specific surface area (m²/g) by dividing the reading on the display by the weight of the peat sample.

The particle size range of the peat was determined by the procedure recommended by ASTM (ASTM, 1971b) (D2977-71). 20g of air-dried peat sample was passed through 8 and 20 mesh sieves and shaken for 10 minutes with a bottom pan in place to collect samples finer than the two meshes. The fraction retained on the 8 mesh sieve, 20 mesh sieve and bottom pan was weighed and designated as coarse fiber, medium and finest respectively. The porosity of the peat sample was determined using the flooding technique. This method involves placing a known volume of peat sample in a measuring cylinder and flooding with water up to the top. The quantity of water that was required to fill the voids in the peat sample was measured and the porosity was determined.

4. RESULTS AND DISCUSSION

4.1 Characteristics of Peat

This study focussed on the use of commercial variety of peat (i.e. horticultural peat used in various agricultural and horticultural applications. Table 4.1 shows a typical analysis of sphagnum peat moss carried out by Premier Peat Ltd., Carrot River, Saskatchewan. The analysis of the peat samples for moisture content indicated a range of 47 to 68 percent by method 1 (ASTM, 1971a), which was comparable with the values indicated by Premier Peat Limited. The pH of the samples was found to be 6.2. The particle size analysis showed peat samples to be of 16 % coarse fiber, 31 % medium fiber and 53 % fines as compared with 0 to 20 % coarse fiber, 12 to 32 % medium fiber and 62 to 80 % fines by Premier Peat Ltd. The specific surface area was found to be 19.6 m²/g

4.2 Batch kinetic studies

Studies were conducted to determine the equilibrium time at pH values of 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0 in order to evaluate the effect of pH on equilibrium time. The raw data collected is presented in Appendix B (Tables B1 to B7)

Table 4.1: Typical analysis of sphagnum peat

| Parameter | Value |
|--------------------------|----------------------------------|
| Clasification | Type 1 - between class A & B |
| pH | 4.5 - 5.7 |
| Salinity | 0.3 - 0.8 m mhos/cm |
| Moisture | 40 - 70 % |
| Bulk density | $62.3 - 118.7 \text{ kg/m}^3$ |
| Organic matter | 90 - 95 % |
| Total Carbon | 44.3 - 45.61 % (w/w) |
| Total Hydrogen | 5.22 % (w/w) |
| Total Nitrogen | 1.01 - 1.32 % (w/w) |
| Nitrate | 118 - 397 mg/L |
| Dilute acid soluble iron | 80 - 250 mg/L |
| Phosphorus | 80 - 250 mg/L |
| Potassium | 650 - 2000 mg/L |
| Calcium | 12580 - 15510 mg/L |
| Magnesium | 4300 - 5550 mg/L |
| Boron | 3 - 10 mg/L |
| Manganese | 95 - 350 mg/L |
| Total Porosity | 70 - 85 % |
| Screen size 9.51 mm | % retained : 0 - 10 |
| Screen size 6.35 mm | % retained : 0 - 20 |
| Screen size 2.38 mm | % retained: 12 - 32 |
| Screen size 0.50 mm | % retained : 62 - 80 |
| Surface area | 57.41 - 108.53 m ² /g |
| Cation Exchange Capacity | 72.6 meq/100 g |

^{*}Source: Premier Peat Ltd., Carrot River, Saskatchewan

Note: surface area, total carbon, hydrogen, nitrogen and CEC values were determined at the University of Regina.

Figure 4.1 shows a profile of residual lead concentration versus agitation time. It can be seen that the adsorption process can be divided into three stages, the initial rapid phase, the intermediate phase and the slow phase. The three phases are more apparent at pH 4.0 to 6.0. Figure 4.2 shows a plot of percentage lead removal versus contact time. From the two plots it can be observed that the rapid phase was fast and accounted for a majority of lead adsorption (between 55 to 60 %) and the time used for this phase is about 20 minutes. After the initial rapid phase the rate of lead removal slowed down and this was followed by the slow phase which contributed relatively a small part to the adsorption process.

The equilibrium time can be defined as the time interval in which a system reaches a chemical equilibrium and the instance at which the concentration of the product and the reactants cease to change with time (USEPA, 1991). In a batch adsorption experiment this is the time interval required at which the concentration of the solute in solution ceases to change with time. The USEPA suggests that the equilibrium time be the minimum amount of time needed to establish a change in the solute concentration of less than five percent.

1

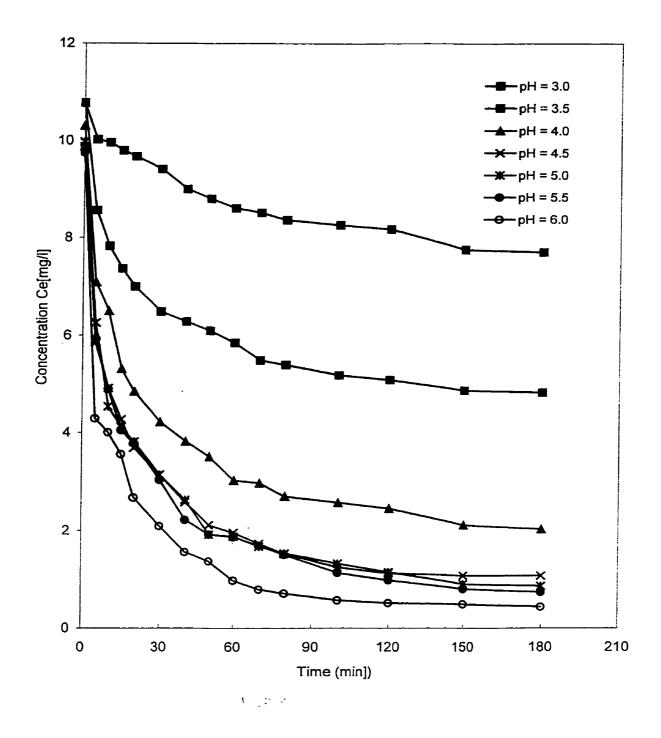


Figure 4.1: Plot of lead concentration versus contact time at pH 3, 3.5, 4, 4.5, 5, 5.5 and 6.

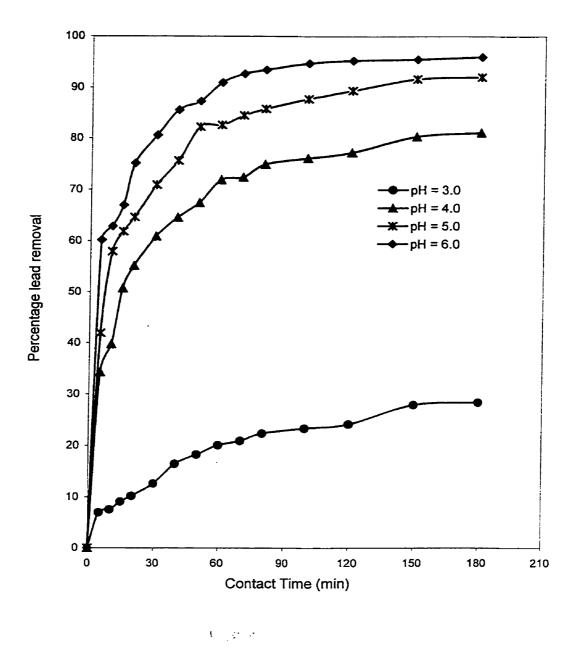


Figure 4.2: Plot of percentage lead removal versus contact time at pH 3.0, 4.0, 5.0 and 6.0

From Figure 4.2 it can be observed that equilibrium was reached in two hours and no significant adsorption was noted beyond two hours.

Lagergren (1898) developed the first model for adsorption kinetics based on the first order reaction rate and has the form:

$$\frac{dq_t}{dt} = K_L(q_e - q_t) \tag{4.1}$$

This can be integrated for the boundary conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t to give:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_L}{23}t \tag{4.2}$$

Equation 4.2 can be rearranged to obtain the non-linearized form

$$q_t = q_e - q_e \exp(-K_L t) \tag{4.3}$$

where,

 K_L = Lagergren rate constant for adsorption (h⁻¹);

 q_e = amount of metal ion adsorbed at equilibrium (mg/g);

 q_t = amount of metal ion adsorbed (mg/g) at any given time t (h).

Ho et al. (1996) developed a pseudo second order reaction rate equation to study the

adsorption of heavy metals onto peat and this can be expressed in the form:

$$\frac{t}{q_t} = \frac{1}{2K'q_t^2} + \frac{t}{q_t} \tag{4.4}$$

where,

K' = second order reaction rate constant for adsorption (g/mg.h);

 q_e = Amount of metal ion adsorbed at equilibrium (mg/g);

 q_t = Amount of metal ion adsorbed (mg/g) at any given time t (h).

The Lagergren reaction rate model and Ho's pseudo second order reaction rate model were used in describing the adsorption kinetics of lead onto peat. The batch kinetic studies data were fitted to the Lagergren and Ho's models by non-linear regression analysis using software package STATISTICA (Release 5.0), the model equations of the data fit were derived using Quasi-Ne wton algorithm. The Lagergren and Ho's model equations are presented in Tables 4.2 and 4.3 respectively. The model plots for Lagergren and Ho are shown in Figure 4.3 and 4.4 respectively. From Figure 4.3 and Table 4.2 it can be observed that the Lagergren model described the adsorption of lead adequately. All the model equations showed very good correlation and were statistically significant using t- test at 95% confidence level.

From Figure 4.4 and Table 4.3 it can also be observed that Ho's pseudo second order reaction rate model adequately described the adsorption of lead. All the model equations showed very good correlation and were statistically significant using t-test at 95% confidence level.

A comparison of the two models is presented in Table 4.4 and from the table it can be observed that the two models adequately described the sorption of lead onto peat with the Ho's model having a higher correlation than that of Lagergren. From Table 4.4 it can be observed that the effect of pH was significant, the sorption capacity (q_e, i.e. mg of lead adsorbed per g of peat) values increased with increasing pH. For the Lagergren model the values of q_e were 15.22, 28.11, 39.27, 42.60, 42.17, 42.97 and 45.86 and for the Ho's model there were 18.58, 30.75, 42.92, 45.78, 45.57 and 46.45 at pH 3.0, 4.0, 4.5, 5.0, 5.5 and 6.0 respectively.

Table 4.2: Lagergren model equations for lead adsorption kinetics.

| pН | Equation | Correlation |
|-----|---------------------------------|---------------|
| | | Coefficient R |
| 3.0 | $q_t = 15.2 - 15.2 EXP(-1.0 t)$ | 0.98* |
| 3.5 | $q_t = 28.1 - 28.1 EXP(-2.3t)$ | 0.97* |
| 4.0 | $q_t = 39.3 - 39.3EXP(-2.4t)$ | 0.98* |
| 4.5 | $q_t = 42.6 - 42.6EXP(-2.8t)$ | 0.97* |
| 5.0 | $q_t = 42.2 - 42.2 EXP(-2.7t)$ | 0.98* |
| 5.5 | $q_t = 43.0 - 43.0 EXP(-2.7t)$ | 0.98* |
| 6.0 | $q_t = 45.9 - 45.9 EXP(-3.4t)$ | 0.93* |

Note: * Indicates that correlation is statistically significant (using t-test at 95% confidence level);

Table 4.3: Ho's pseudo second order reaction rate equations for lead adsorption

| pH | Equation | Correlation |
|-----|--|---------------|
| | | Coefficient R |
| 3.0 | $\frac{t}{q_t} = \frac{1}{2(0.04)(18.6)^2} + \frac{t}{18.6}$ | 0.99* |
| 3.5 | $\frac{t}{q_t} = \frac{1}{2(0.08)(30.8)^2} + \frac{t}{30.8}$ | 0.99* |
| 4.0 | $\frac{t}{q_t} = \frac{1}{2(0.06)(42.9)^2} + \frac{t}{42.9}$ | 0.99* |
| 4.5 | $\frac{t}{q_t} = \frac{1}{2(0.08)(45.8)^2} + \frac{t}{45.8}$ | 0.99* |
| 5.0 | $\frac{t}{q_t} = \frac{1}{2(0.07)(45.6)^2} + \frac{t}{45.6}$ | 0.99* |
| 5.5 | $\frac{t}{q_t} = \frac{1}{2(0.07)(46.5)^2} + \frac{t}{46.5}$ | 0.99* |
| 6.0 | $\frac{t}{q_t} = \frac{1}{2(0.11)(48.2)^2} + \frac{t}{48.2}$ | 0.99* |

Note: * Indicates that correlation is statistically significant (using t-test at 95% confidence level);

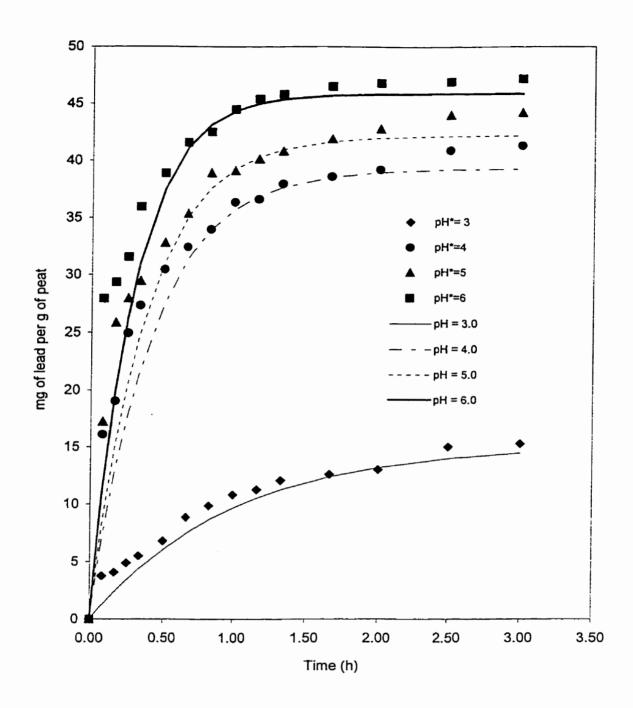


Figure 4.3: Experimental data points and prediction curves for the Lagergren model applied to adsorption of lead onto peat at pH 3.0, 4.0, 5.0 and 6.0

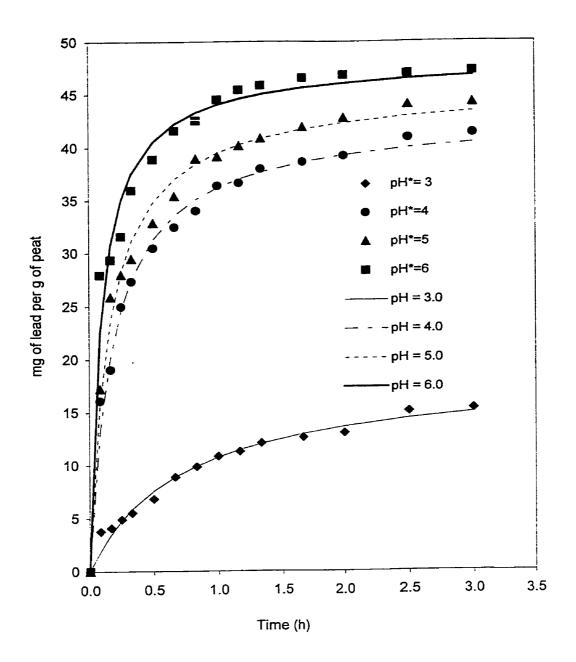


Figure 4.4: Experimental data points and prediction curves for the Ho's model applied to adsorption of lead onto peat at pH 3.0, 4.0, 5.0 and 6.0

Table 4.4: Comparison of constants values calculated using Lagergren model and Ho's model for adsorption of Pb onto peat

| | Lagergren model | | | Ho's model | | |
|------------|-----------------|----------------|----------------|----------------|------|-------|
| Initial pH | q _e | K _L | R ² | q _e | K' | R^2 |
| 3.0 | 15.2 | 1.0 | 0.96 | 18.6 | 0.04 | 0.98 |
| 3.5 | 28.1 | 2.3 | 0.94 | 30.8 | 0.08 | 0.99 |
| 4.0 | 39.3 | 2.4 | 0.95 | 42.9 | 0.06 | 0.99 |
| 4.5 | 42.6 | 2.8 | 0.94 | 45.8 | 80.0 | 0.99 |
| 5.0 | 42.2 | 2.7 | 0.95 | 45.6 | 0.07 | 0.99 |
| 5.5 | 43.0 | 2.7 | 0.94 | 46.5 | 0.07 | 0.99 |
| 6.0 | 45.9 | 3.4 | 0.93 | 48.2 | 0.11 | 0.97 |

Note: R^2 denotes coefficient of determination.

1 ...

4.3 Batch isotherm studies

Three of the most widely used adsorption isotherms are the Langmuir, Freundlich and BET (Brunauer, Emmet and Teller) isotherms. The Langmuir adsorption isotherm is derived from consideration based upon an assumption of maximum monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The Langmuir adsorption isotherm equation is represented in equation 4.4 (Metcalf and Eddy, 1991)

$$q = \frac{Q^0 b C_e}{1 + b C_e} \tag{4.4}$$

and the linearized form can be represented as

$$\frac{1}{a} = \left(\frac{1}{O^0}\right) + \left(\frac{1}{bO^0}\right)\left(\frac{1}{C}\right) \tag{4.5}$$

where,

q = amount of adsorbate adsorbed per unit weight of adsorbent (g/mg);

 Q^0 = Constant related to the energy or net enthalpy of adsorption;

b = Amount of adsorbate adsorbed per unit weight of adsorbent (mg/g);

 C_e = Concentration of adsorbate in solution at equilibrium (mg/L).

Hall et al (1966) introduced a dimensionless equilibrium term R, also known as the separation factor to express the Langmuir constant b. The significance of the R term is based

upon an initial assumption of the applicability of the given data to Langmuir isotherm model, beyond which the value of R provides important information about the nature of the adsorption isotherm (see Table 4.5).

Table 4.5: Use of separation factor R in in obtaining information about the nature of adsorption (Hall et al., 1966)

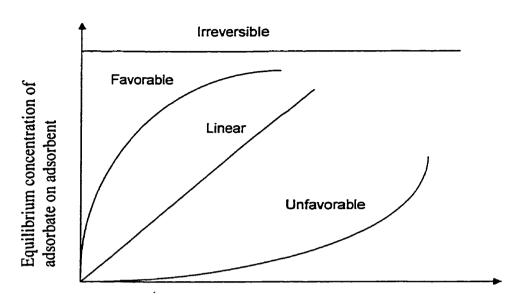
| Value of R | Information about the |
|------------|-----------------------|
| | adsorption |
| R > 1 | Unfavorable |
| R = 1 | Linear |
| 0 < R < 1 | Favorable |
| R = 0 | <i>Irreversible</i> |

The separation factor, R can be calculated using the equation below:

$$R = \frac{1}{1 + bC_0} \tag{4.6}$$

where, C_0 = initial concentration of adsorbate (mg/l).

Figure 4.5 can be used to determine the shape of an isotherm from information in Table 4.5.



Equilibrium concentration of adsorbate in liquid phase

Figure 4.5: Plot of various kinds of isotherms



The Freundlich isotherm model describes a multi-layer adsorption with the assumption of heterogeneous surface in which the energy, a term in the Langmuir equation varies as a function of the surface coverage. The model can be presented as

$$q = KC_{\epsilon}^{1/n} \tag{4.7}$$

and the linearized form can be represented as

$$\log q = \log K + \left(\frac{1}{n}\right) \log C_{\epsilon} \tag{4.8}$$

where,

q = amount of adsorbate adsorbed per unit weight of adsorbent (g/mg);

K = equilibrium constant indicative of adsorption capacity;

n = adsorption equilibrium constant;

 C_e = concentration of adsorbate in solution at equilibrium (mg/L).

The BET isotherm is an expression of the Langmuir isotherm describing multilayer adsorption at the adsorbent surface with an assumption that Langmuir isotherm applies to each layer, it also assumes that adsorption on subsequent layers can be initiated even before a given layer is completely formed (Weber, 1972). The BET isotherm has the form:

$$q = \frac{BQ^{0}C_{e}}{(C_{s} - C_{e})\left[1 + (B - 1)\left(\frac{C_{e}}{C_{s}}\right)\right]}$$

$$(4.9)$$

and the linearized form can be represented as

$$\frac{C}{q(C_{\epsilon} - C_{\epsilon})} = \left(\frac{1}{BQ^{0}}\right) + \left(\frac{B - 1}{BQ^{0}}\right) \left(\frac{C_{\epsilon}}{C_{\epsilon}}\right) \tag{4.10}$$

where,

 C_s = saturation concentration of the adsorbate (mg/L);

 Q^0 = amount of adsorbate adsorbed per unit weight of adsorbent for monolayer adsorption (mg/g);

B = constant relating to the energy of interaction with the surface.

Batch isotherm studies were conducted using different representative weights of peat to study the adsorption of lead onto peat at pH 3.0, 4.0, 5.0 and 6.0. An equilibrium time of two hours was used for isotherm study based on knowledge obtained from the batch kinetic studies. The raw data collected is presented in Appendix B (Tables B.8 to B.11).

The Langmuir, Freundlich and BET models were used to describe the adsorption isotherm. The data were fitted to the isotherm models by non-linear regression analysis using software package STATISTICA (Release 5.0). The model equations were derived using Quasi - Newton and simplex algorithms. Figures A1 to A10 in Appendix A show the Langmuir,

Freundlich and BET isotherm plots for pH 3.0, 4.0, 5.0 and 6.0. Figure 4.6, 4.7 and 4.8 shows the combined plots (for pH 3.0, 4.0, 5.0 and 6.0) for the Langmuir, Freundlich and BET isotherm models respectively. The Langmuir, Freundlich and BET model equations are presented in Tables 4.5, 4.6 and 4.7 respectively,

From Figures 4.6 and 4.7 and Tables 4.5 and 4.6, it can be observed that the Langmuir and Freundlich equations can be used to describe the adsorption data with the Freundlich having a better correlation. The separation factor R for the Langmuir model equations at pH 3.0, 4.0, 5.0 and 6.0 was greater than zero and less than one indicating that the Langmuir isotherm was favorable for describing the dynamics of lead adsorption by peat. The Langmuir model had a poor correlation value of 0.59, at pH 3.0 the model parameters were also not statistically significant at 95% confidence level for pH 3.0, 4.0 and 5.0. The model parameter obtained for the Freundlich model were statistically significant at 95% confidence level for all pH except at pH 3. From Figure 4.8 and Table 4.8, it can be observed that the BET model could not be used to model the adsorption data for pH 3.0 and 4.0. The BET model can be used to describe the adsorption data at pH 5.0 and 6.0, but the model parameters were not statistically significant at 95% confidence level for pH 5.0. The Langmuir, Freundlich and BET model adequately described the adsorption data for pH 6.0 and the model parameter were statistically significant at 95% confidence level.

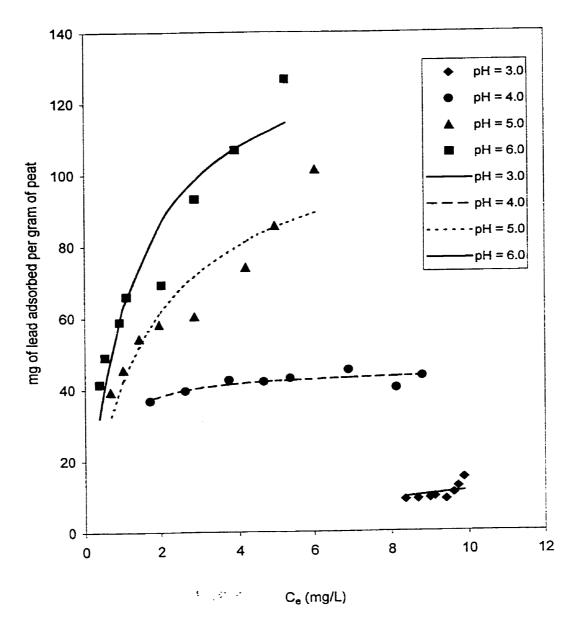


Figure 4.6: Langmuir model plots adsorption of lead onto peat at pH 3.0, 4.0, 5.0 and 6.0

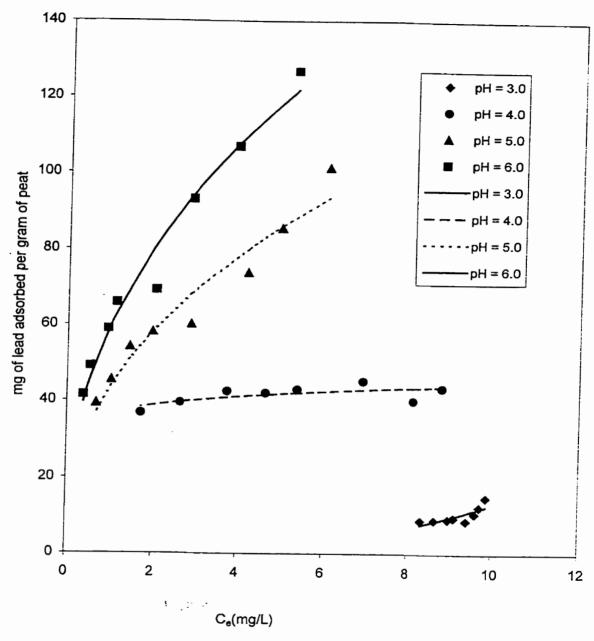


Figure 4.7: Freundlich model plots adsorption of lead onto peat at pH 3.0, 4.0, 5.0 and 6.0

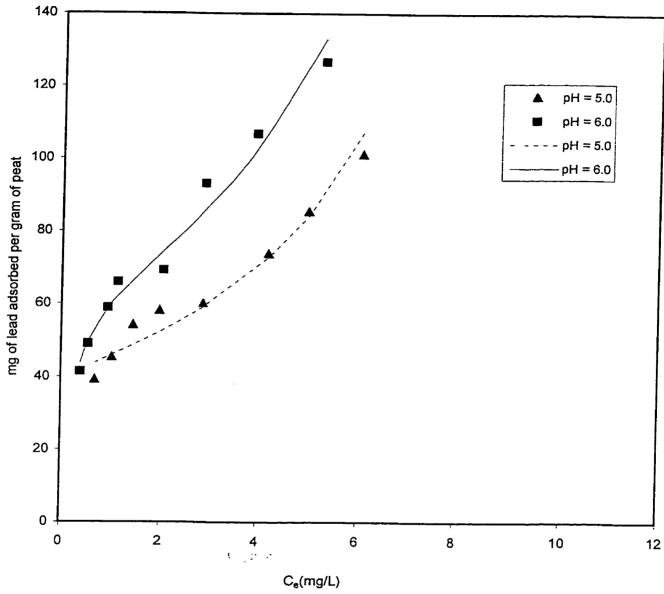


Figure 4.8: BET model plots adsorption of lead onto peat at pH 3.0, 4.10, 5.0 and 6.0

Table 4.6: Langmuir isotherm model equations for adsorption of lead on peat

| Initial pH | Equation | Separation | R ² | Correlation |
|------------|--|-------------------------|----------------|-------------------|
| | | factor R | | coefficient |
| 3 | $q_{\epsilon} = \frac{(1540)(0.0008)C_{\epsilon}}{1 + (0.0008)C_{\epsilon}}$ | 6.20 x 10 ⁻⁵ | 0.34 | 0.59 ⁺ |
| 4 | $q_e = \frac{(45)(2.74)C_e}{1 + (2.74)C_e}$ | 2.09 x 10 ⁻³ | 0.65 | 0.81+ |
| 5 | $q_{e} = \frac{(115)(0.58)C_{e}}{1 + (0.58)C_{e}}$ | 8.62 x 10 ⁻⁴ | 0.87 | 0.93+ |
| 6 | $q_e = \frac{(143)(0.76)C_e}{1 + (0.76)C_e}$ | 6.75 x 10 ⁻⁴ | 0.90 | 0.95* |

Note: * Indicates that correlation is statistically significant (using t-test at 95% confidence level);

⁺ Indicates that correlation is not statistically significant (using t-test at 95% confidence level).

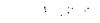


Table 4.7: Freundlich isotherm model equations for adsorption of lead on peat

| Initial pH | Equation | R^2 | Correlation |
|------------|-------------------------------|-------|-------------|
| | | | coefficient |
| 3 | $q_e = (0.02)C_e^{(1/0.35)}$ | 0.63 | 0.79+ |
| 4 | $q_e = (36.7)C_e^{(1/12.18)}$ | 0.54 | 0.73* |
| 5 | $q_e = (43.6)C_e^{(1/2.36)}$ | 0.94 | 0.96* |
| 6 | $q_e = (59.9)C_e^{(1/2.34)}$ | 0.96 | 0.98* |
| | | | |

Note:

- * Indicates that correlation is statistically significant (using t-test at 95% confidence level);
- ⁺ Indicates that correlation is not statistically significant (using t-test at 95% confidence level).



Table 4.8: BET isotherm model equations for adsorption of lead on peat

| Initial pH | Equation | R^2 | Correlation |
|------------|---|-------|-------------|
| | | | coefficient |
| 5 | $q = \frac{(359)(42.41)C_e}{(C_s - C_e)\left[1 + (359 - 1)\left(\frac{C_e}{C_s}\right)\right]}$ | 0.96 | 0.97⁺ |
| 6 | $q = \frac{(48)(64)C_e}{(C_s - C_e)\left[1 + (48 - 1)\left(\frac{C_e}{C_s}\right)\right]}$ | 0.97 | 0.99* |

Note: * Indicates that correlation is statistically significant (using t-test at 95% confidence level);

⁺ Indicates that correlation is not statistically significant (using t-test at 95% confidence level).

BET isotherm model is not applicable at pH values of 3 and 4.

Table 4.9: Comparison of adsorption parameters calculated using the Langmuir and Freundlich isotherms for adsorption of Pb onto peat

| Initial | Langmuir model | | | Freundlich model | | | BET model | | |
|---------|----------------|-------------------|-------|------------------|-------|-------|-----------|------------------|-------|
| pН | Q^0 | b | R^2 | K' | n | R^2 | Q^0 | В | R^2 |
| 3 | 1540 | 8x10 ⁴ | 0.34 | 0.02 | 0.35 | 0.63 | (N | (Not applicable) | |
| 4 | 45 | 2.74 | 0.65 | 36.7 | 12.18 | 0.54 | (N | (Not applicable) | |
| 5 | 115 | 0.58 | 0.87 | 43.6 | 2.36 | 0.94 | 42 | 359 | 0.96 |
| 6 | 143 | 0.76 | 0.90 | 59.9 | 2.34 | 0.96 | 64 | 48 | 0.97 |

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4.4 Desorption studies

Desorption studies conducted at various pH values showed that a small amount of lead was desorbed from peat in deionized water. The raw data collected is presented in Tables B.12, B.13, B.14 and B.15. The desorbed lead ions were not significant in comparison to the lead adsorbed and thus did not necessitate fitting of the data to any known adsorption isotherm. In the controlled study carried out using fresh peat samples and 250 mL of deionized water which was shaken for two hours at 125 rpm, no lead ions were detected.

4.5 Effect of pH

Batch studies were conducted by contacting peat with approximately 10 mg/L lead solution with initial pH values of 3.0, 4.0, 5.0 and 6.0. After two hours the pH was measured and it was found that the variation between the initial pH and final pH for the studies was less than 5 percent.

The adsorption of lead to peat can be explained on the basis of the constituent of peat. The major constituent of peat are lignin and cellulose which have polar functional groups that are particularly effective in bonding trace elements such as lead, nickel and zinc (Channey and Hundemann 1979; Zhipei et al., 1984). Lignin is a polymeric substance which has hydroxyl groups that can exert repulsive force on the approaching anion thereby aiding adsorption of lead to peat.

Metal ions adsorption from aqueous an solution is affected by pH, properties of adsorbent, adsorbate concentration and presence of co-ions in solution (Zhang et al. 1998). From the Freundlich isotherm which best described the data for the batch isotherm studies, it can be observed that low k value of 0.017 was obtained at pH 3 which suggested that peat had low lead adsorption capacity at pH 3. The low adsorptive capacity can be attributed to hydrogen ions that compete with the lead ions on sorption sites (Huang et al., 1991). A sharp increase in adsorption was observed within a pH range of 4.0 and 6.0 and maximum adsorption occurred at pH 6.

At low pH some functional groups may be positively charged and their interaction with metal ions can be highly reduced (Fourest et al., 1994; Tobin et al., 1984). Figure 4.9 shows the effect of pH on the adsorption of lead.

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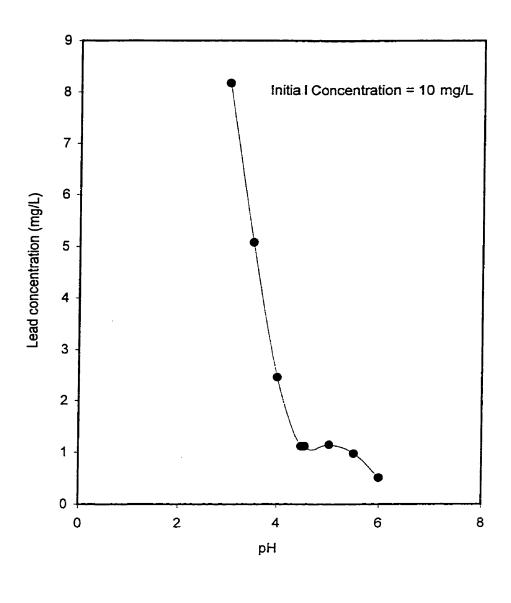


Figure 4.9: Effect of pH on lead adsorption onto peat

4.6 Column study

A column study was conducted for 202 h using a lead solution with an influent concentration of about 10.07 mg/L, an influent pH of 6.0 and a flow rate of 40.5 mL/min. A Plot of the ratio of effluent to influent lead ion concentration versus bed volume for the column study is shown in Figure 4.10. The column achieved complete removal (zero effluent concentration) for 355 bed volumes and 50% removal for about 900 bed volumes. The column effluent pH ranged from 5.95 to 6.2 during the column operation; the raw data collected is presented in Appendix B (Table B.12). For the continuous flow adsorption system, the Thomas model can be used to describe the concentration-time profile and can be written in the form (Reynolds and Richards, 1996):

$$\frac{C_{e}}{C_{0}} = \frac{1}{1 + \exp\left[\frac{k}{Q}(q_{0}m - C_{0}V)\right]}$$
(4.11)

where,

 C_e = effluent adsorbate concentration (mg/L);

 C_0 = influent adsorbate concentration (mg/L);

k = Thomas rate constant (L.min.mg);

 q_0 = maximum solid phase concentration of the solute (mg/g);

m = mass of the adsorbent (g);

V = throughput volume (mL);

Q = volumetric flow rate (mL/min).

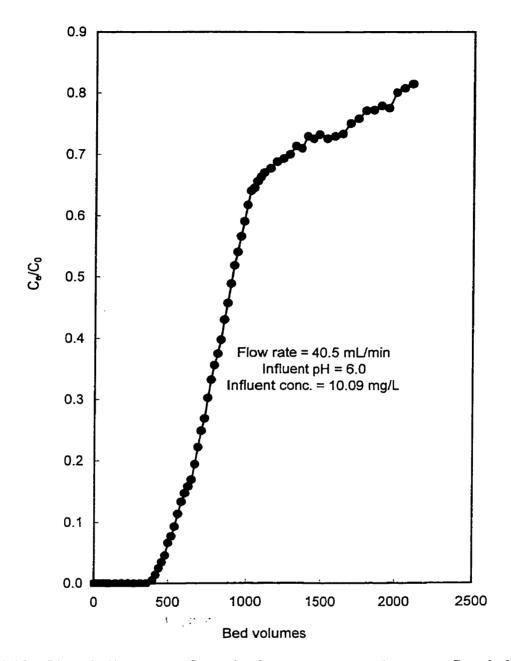


Figure 4.10: Plot of effluent to influent lead concentration ratio versus flow in bed volumes.

and the linearized form can be expressed as:

$$\ln\left(\frac{C_0}{C_c} - 1\right) = \frac{kq_0 m}{Q} - \frac{kC_0}{Q}V$$
(4.12)

The Thomas model was used in describing the adsorption kinetics and evaluating the maximum solid phase concentration (q_0) and the Thomas rate constant (k). The data obtained were fitted to the Thomas model using software package STATISTICA (Release 5.0), and the model equation was derived using Quasi-Newton algorithm. The non-linear Thomas model plot is shown in Figure 4.11 and the linearized Thomas model plot is shown in Figure 4.12. From the two plots the Thomas rate constant k and the maximum solid phase concentration of the solute q_0 were calculated and Table 4.10 shows a comparison of the linearized and non-linear Thomas model parameters. From Table 4.10, it was observed that the non-linear regression analysis gave higher R² values and a good correlation R (coefficient of determination) of 0.96. The non-linear model parameters were statistically significant at 95% confidence level. Comparing the batch and column study, it was observed that column experiment produced higher lead ion removals. The explanation to this is that batch experiment is driven by concentration of adsorbate in solution which diminished as the experiment progressed while in column operations adsorbent in column experiment were continuously in contact with a relatively constant concentration of adsorbate (Weber, 1972).

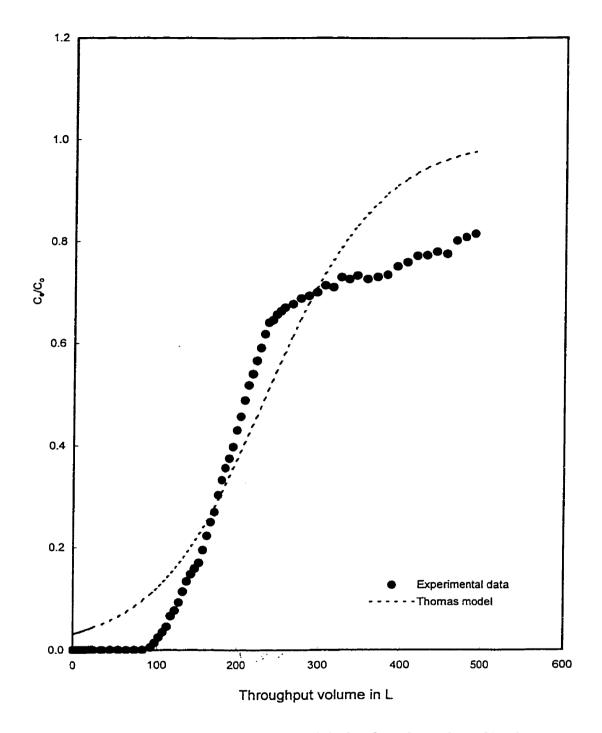


Figure 4.11: Non-linearized Thomas model plot for adsorption of lead on peat

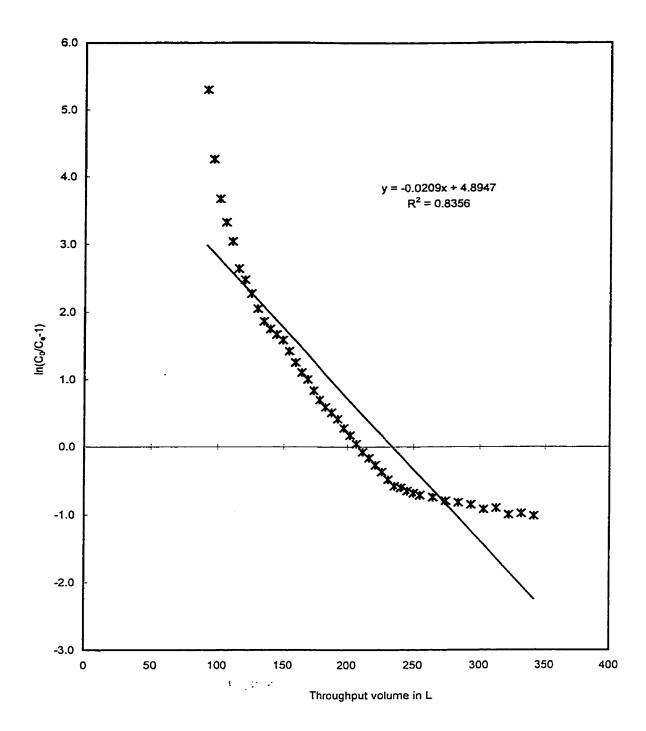


Figure 4.12: Linearized Thomas model plot for adsorption of lead on peat.

Table 4.10: Comparison of Thomas linearized and non-linear model parametrs.

| Parameter | Linear | Non-linear |
|----------------|---|--|
| Equation | $\ln\left(\frac{C_0}{C_e} - 1\right) = 4.9 - 0.02V$ | $\frac{C_e}{C_0} = \frac{1}{1 + \exp[3.42 - 0.015V)]}$ |
| K | 0.084 mL/mg-min | 0.059 mL/mg-min |
| q_0 | 76.3 mg/g | 76.7 mg/g |
| R ² | 0.84 | 0.92 |
| R | | 0.96* |

Note: * Indicates that correlation is statistically significant (using t-test at 95% confidence level);

;

The passage of lead solution was terminated after the peat was exhausted and the lead ions were eluted using 0.05N nitric acid solution. The raw data for the elution studies is presented in Table B.13 and a plot of effluent lead concentration versus bed volume nitric flow through the column is shown in Figure 4.13. It can be observed from Figure 4.13 and Table B.13 that majority of the lead ions were desorbed in about 95 bed volumes.

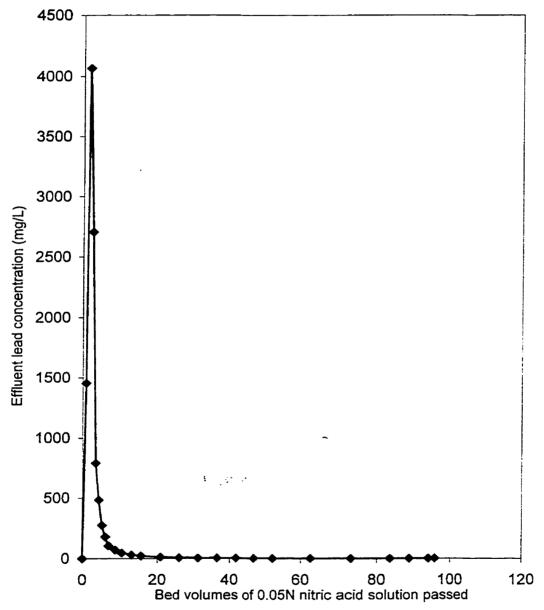


Figure 4.13: Elution of adsorbed lead from peat in column studies

4.7 General discussion

The advantages of using peatmoss for the removal of lead include: simplicity in system design, effectiveness and it is relatively cheap. Batch adsorption and column studies have shown that lead can effectively remove lead from an aqueous solution.

The contact time necessary for maximum adsorption was found to be two hours, this compares well with Ho and Mckay, (1999). The pH level of the solutions was an important factor in the removal of lead, the reaction rate (k') increased with increasing pH and reached an optimum of 59.9 at pH value of 6.0 (Table 4.9). Peat dosage was also an important factor, Figure 4.14 shows a plot of adsorption densities and the percentage removal for a range of peat dosage. The removal efficiency increased from 49% to 96% when the peat dosage was increased from 0.01 g to 0.06 g at pH value of 6.0 and this is consistent with the results of Sharma and Forster (1993). The drop in adsorption density (Figure 4.14) can be attributed to an increase in available adsorption sites for lead ions.

Practical application based on the result of this study and a knowledge of the initial concentration and desired final concentration of lead can be implemented by developing a system (a tank) filled with peat to treat wastewater containing lead, this can be similar to a sand filter system but proper characterization of the allowable flow must be done. The pH should be adequately adjusted since lead adsorption occurs at an optimal pH value of 6.0.

The final disposal of peat after use need to be carefully considered. Peat can be used as fuel and can also be incinerated, however the remaining ash after incineration will be highly

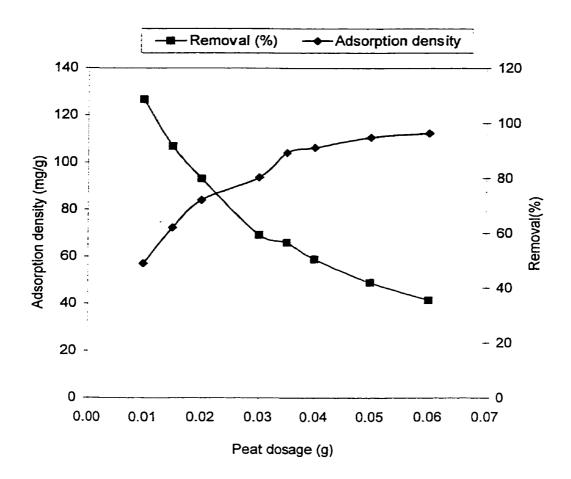


Figure 4.14: Effect of peat dosage on the adsorption of lead onto peat at pH 6

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5. CONCLUSIONS

5.1 Summary

Laboratory batch kinetic and isotherm studies were conducted to evaluate the potential of peat moss for the adsorption of lead from aqueous solution. The studies investigated the effect of initial pH on adsorption process as well as how well the Lagergren and Ho's adsorption kinetics models and the Langmuir, Freundlich and BET isotherm models described the data obtained. A column study was also carried out and applicability of the Thomas model was investigated.

5.2 Conclusions

The following conclusions can be drawn from the study:

- i) The kinetic studies indicated that the equilibrium time required for the adsorption of lead from aqueous solution by peat was two hours.
- The Lagergren reaction rate and Ho's pseudo second order reaction rate models described the adsorption data adequately with good and statistically significant correlation coefficient. The Ho's model represented the adsorption kinetics better than the Lagergren model. The reaction rate constants increased with increasing pH for the two kinetic models used.
- iii) The sorption capacity of peat increased with increasing pH for both the Lagergren and Ho's model.
- iv) The optimum pH range for lead adsorption onto peat was 5.5 to 6.0.

- v) The Langmuir and Freundlich and BET isotherm models can be used to represent the adsorption data. The BET could not be used to model the adsorption data at pH 3.0 and 4.0. The Freundlich model represented the adsorption process better than the Langmuir and BET models, while the Langmuir model represented the adsorption data better than the BET model.
- vi) The adsorption capacity of peat increased with increasing pH as indicated by the Freundlich equilibrium constant k. The values of k were 0.002, 36.7, 43.6 and 59.9 at pH 3.0, 4.0, 5.0 and 6.0 respectively.
- vii) Desorption using deionized water indicated that only a small amount of lead were desorbed from peat.

5.3 Further research needs

This study was conducted to determine the feasibility and effectiveness of peat in the removal of lead from aqueous solution. Further research needs are identified in the following areas:

- i) the effect of particles of peat on the adsorption of lead;
- ii) the effect of carbon content of peat on the adsorption of lead;
- iii) batch kinetic studies at various temperatures may be conducted to determine thermodynamic parameter for lead adsorption on peat;
- iv) batch studies using acid pre-treated peat;
- v) column studies using industrial wastewater containing lead ions and other metals to investigate effect of competitive adsorption on lead and other metals; and
- vi) column studies using a mixture of peat and sand to enhance porosity and allow a greater application rate.

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Appendix A - Figures

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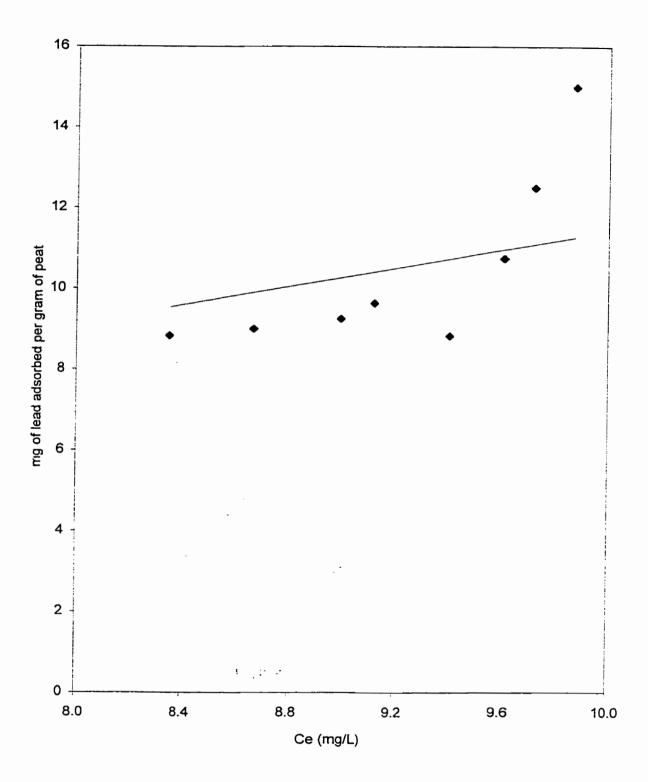


Figure A.1: Langmuir isotherm for adsorption of lead on peat at pH 3.0

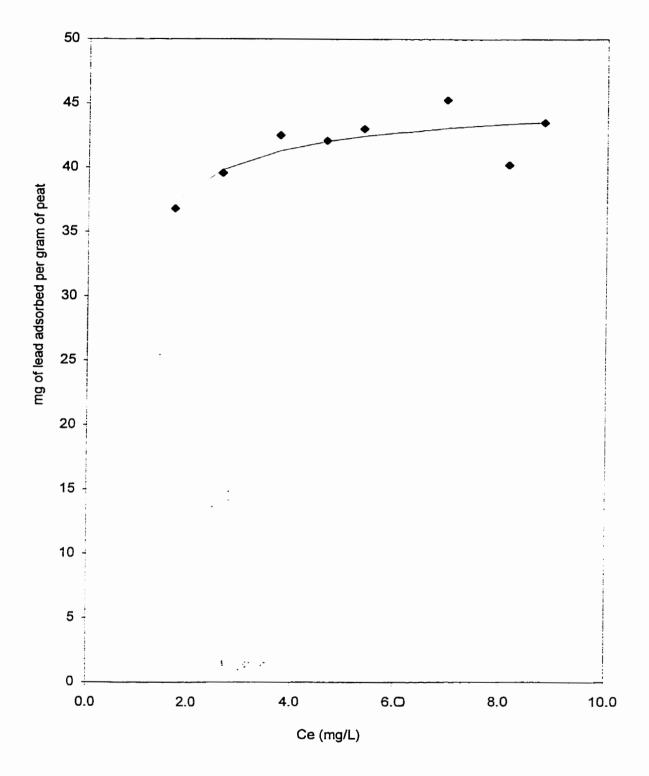


Figure A.2: Langmuir isotherm for adsorption of lead on peat at pH 4.0

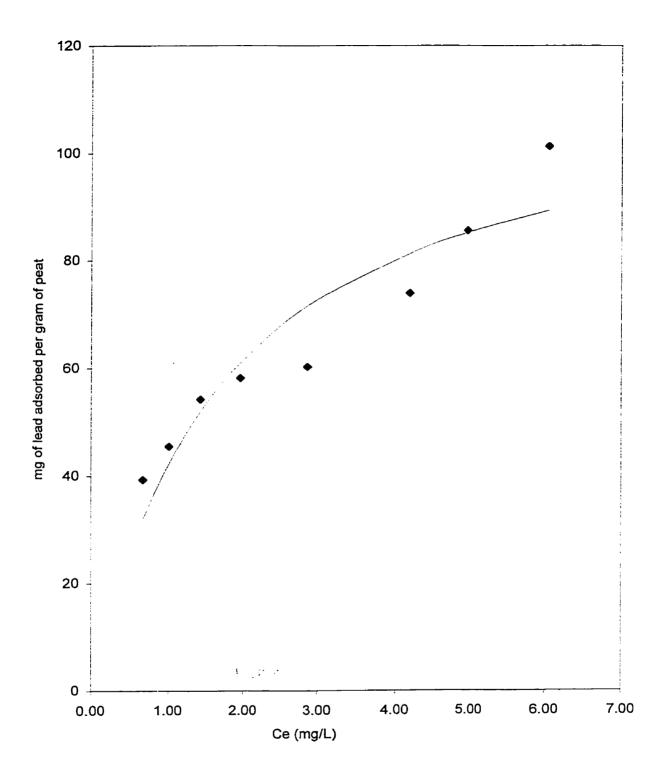


Figure A.3: Langmuir isotherm for adsorption of lead on peat at pH 5.0

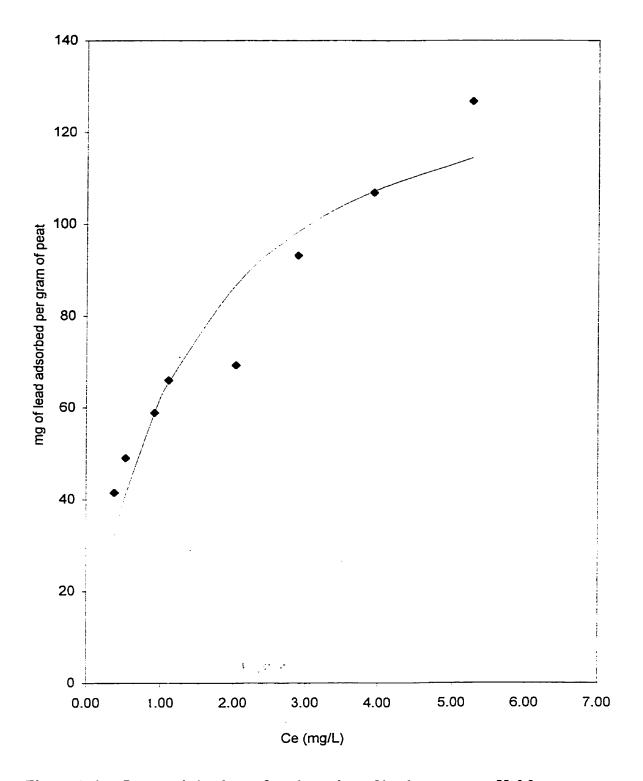


Figure A.4: Langmuir isotherm for adsorption of lead on peat at pH 6.0

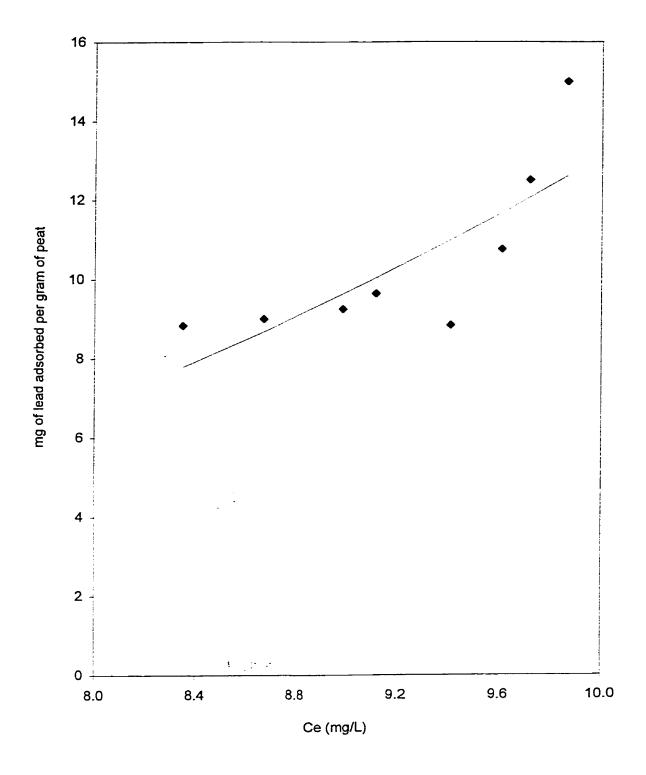


Figure A.5: Freundlich isotherm for adsorption of lead on peat at pH 3.0

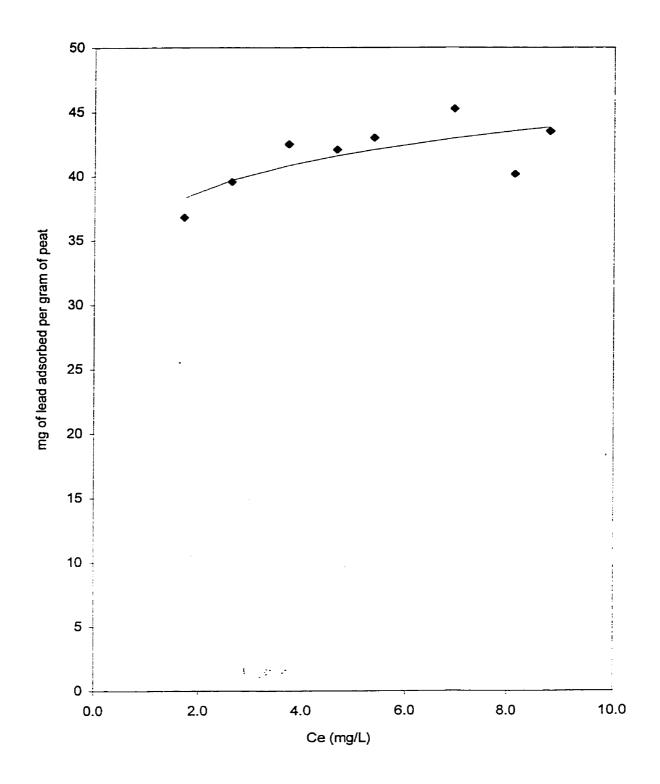


Figure A.6: Freundlich isotherm for adsorption of lead on peat at pH 4.0

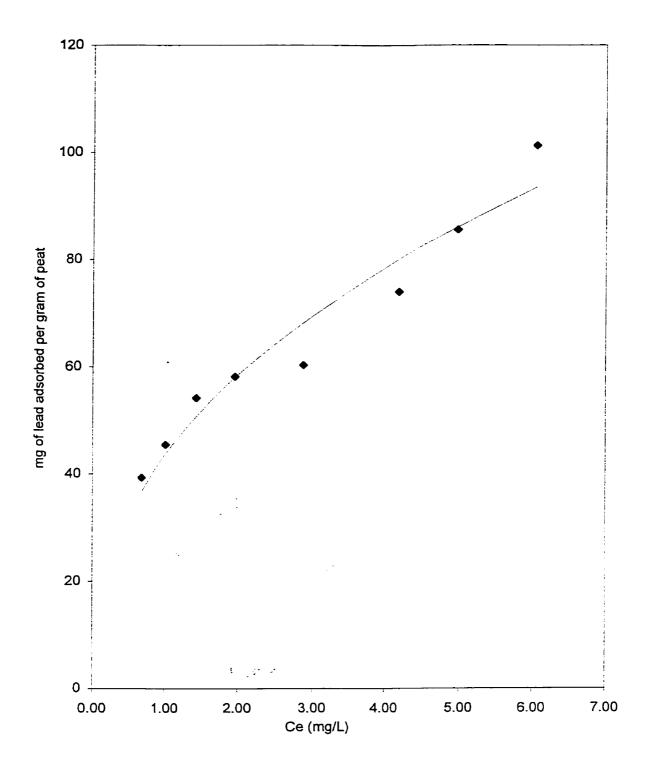


Figure A.7: Freundlich isotherm for adsorption of lead on peat at pH 5.0

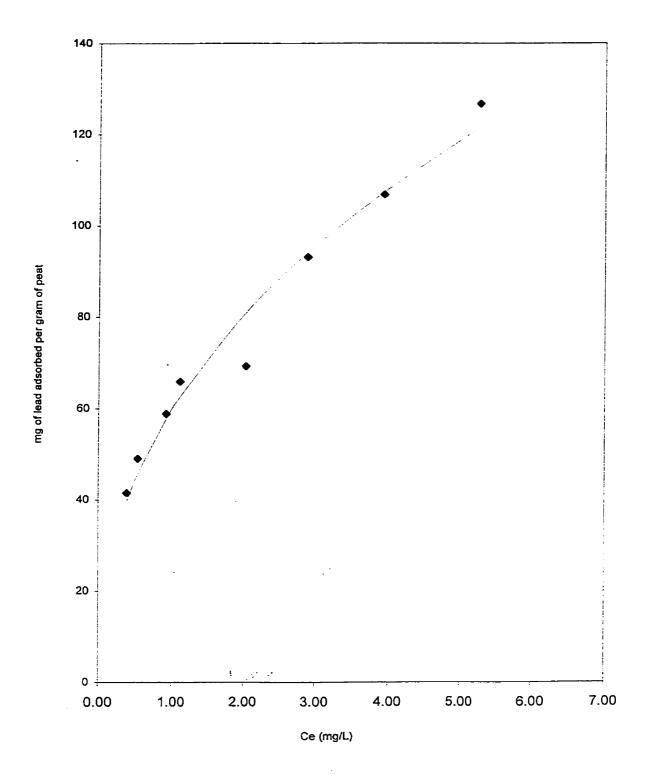


Figure A.8: Freundlich isotherm for adsorption of lead on peat at pH 6.0

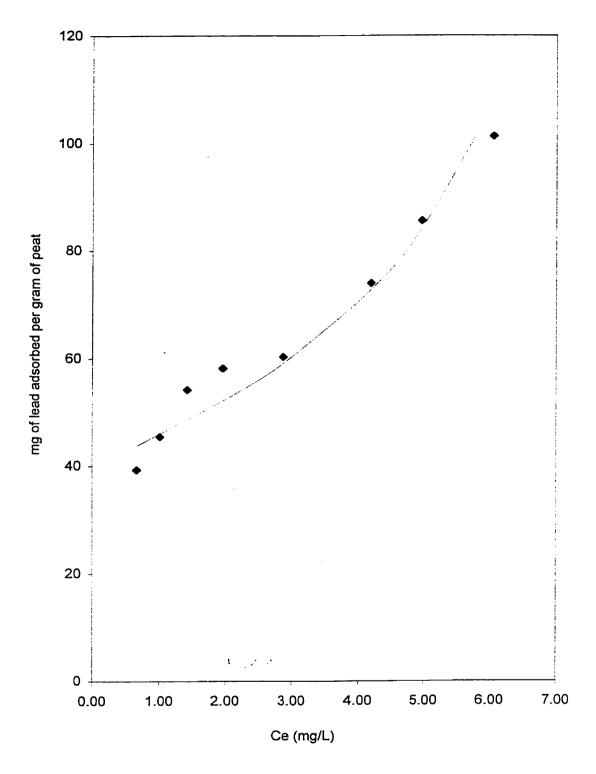


Figure A.9: BET isotherm for adsorption of lead on peat at pH 5.0

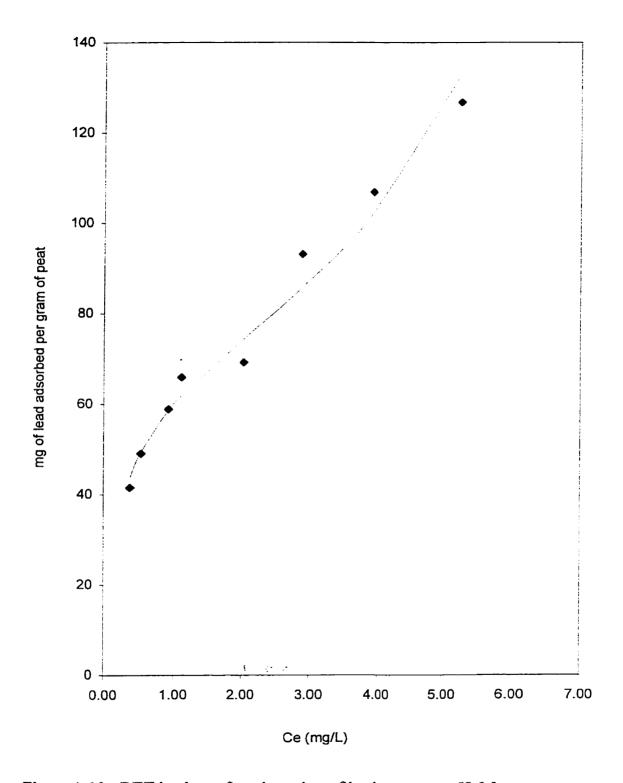


Figure A.10: BET isotherm for adsorption of lead on peat at pH 6.0

Appendix B - Raw experimental data

t jorde

Table B.1: Kinetic study for adsorption of lead onto peat at pH 3.0

Reaction volume = 100 mL, mass of peat = 0.02 g

| Contact | Residual | lead concentra | ation [mg/l] | Final pH |
|------------|----------|----------------|--------------|----------|
| Time (min) | Trial 1 | Trial 2 | Mean | Mean |
| 0 | 10.77 | 10.77 | 10.77 | 3.00 |
| 5 | 9.99 | 10.05 | 10.02 | 3.00 |
| 10 | 9.97 | 9.94 | 9.96 | 3.00 |
| 15 | 9.85 | 9.74 | 9.79 | 3.10 |
| 20 | 9.64 | 9.70 | 9.67 | 3.20 |
| 30 | 9.38 | 9.44 | 9.41 | 3.10 |
| 40 | 8.92 | 9.07 | 9.00 | 3.20 |
| 50 | 8.77 | 8.83 | 8.80 | 3.10 |
| 60 | 8.64 | 8.57 | 8.61 | 3.00 |
| 70 | 8.49 | 8.54 | 8.52 | 3.00 |
| 80 | 8.37 | 8.35 | 8.36 | 3.00 |
| 100 | 8.33 | 8.18 | 8.25 | 3.20 |
| 120 | 8.15 | 8.19 | 8.17 | 3.10 |
| 150 | 7.78 | 7.75 | 7.76 | 3.15 |
| 180 | 7.65 | 7.77 | 7.71 | 3.20 |
| | | | ! | |

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Table B.2: Kinetics study for adsorption of lead onto peat at pH 3.5 Reaction volume = 100 mL, mass of peat = 0.02 g

| Contact | Residual | lead concentra | tion [mg/l] | Final pH |
|------------|----------|----------------|-------------|----------|
| Time (min) | Trial 1 | Trial 2 | Mean | Mean |
| 0 | 10.76 | 10.76 | 10.76 | 3.55 |
| 5 | 8.55 | 8.58 | 8.56 | 3.60 |
| 10 | 7.87 | 7.78 | 7.82 | 3.50 |
| 15 | 7.38 | 7.35 | 7.36 | 3.40 |
| 20 | 7.02 | 6.97 | 6.99 | 3.60 |
| 30 | 6.45 | 6.51 | 6.48 | 3.60 |
| 40 | 6.27 | 6.28 | 6.28 | 3.60 |
| 50 | 6.11 | 6.08 | 6.09 | 3.45 |
| 60 | 5.95 | 5.74 | 5.85 | 3.65 |
| 70 | 5.44 | 5.53 | 5.49 | 3.50 |
| 80 | 5.37 | 5.42 | 5.39 | 3.60 |
| 100 | 5.20 | 5.15 | 5.18 | 3.60 |
| 120 | 5.01 | 5.16 | 5.08 | 3.60 |
| 150 | 4.88 | 4.86 | 4.87 | 3.55 |
| 180 | 4.84 | 4.81 | 4.82 | 3.50 |
| | | | | |

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Table B.3 : Kinetic study for adsorption of lead onto peat at pH 4.0 Reaction volume = 100 mL, mass of peat = 0.02 g

| Contact | Residual | lead concentra | ation [mg/l] | Final pH |
|------------|----------|----------------|--------------|----------|
| Time (min) | Trial 1 | Trial 2 | Mean | Mean |
| 0 | 10.30 | 10.30 | 10.30 | 4.10 |
| 5 | 7.14 | 7.02 | 7.08 | 4.15 |
| 10 | 6.48 | 6.51 | 6.49 | 4.10 |
| 15 | 5.33 | 5.29 | 5.31 | 4.20 |
| 20 | 4.88 | 4.79 | 4.84 | 4.10 |
| 30 | 4.22 | 4.21 | 4.21 | 4.10 |
| 40 | 3.78 | 3.85 | 3.82 | 4.10 |
| 50 | 3.45 | 3.56 | 3.51 | 4.25 |
| 60 | 3.12 | 2.94 | 3.03 | 4.20 |
| 70 | 2.87 | 3.08 | 2.98 | 4.1 |
| 80 | 2.77 | 2.64 | 2.71 | 4.20 |
| 100 | 2.61 | 2.54 | 2.58 | 4.20 |
| 120 | 2.40 | 2.52 | 2.46 | 4.10 |
| 150 | 2.15 | 2.10 | 2.12 | 4.25 |
| 180 | 2.08 | 1.99 | 2.04 | 4.25 |
| | | | | |

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Table B.4: Kinetic study for adsorption of lead onto peat at pH 4.5 Reaction volume = 100 mL, mass of peat = 0.02 g

| Contact | Residual | lead concentra | tion [mg/l] | Final pH |
|------------|----------|----------------|-------------|----------|
| Time (min) | Trial 1 | Trial 2 | Mean | Mean |
| 0 | 9.87 | 9.87 | 9.87 | 4.55 |
| 5 | 5.79 | 5.92 | 5.85 | 4.55 |
| 10 | 4.84 | 4.98 | 4.91 | 4.60 |
| 15 | 4.29 | 4.24 | 4.27 | 4.60 |
| 20 | 3.63 | 3.74 | 3.69 | 4.40 |
| 30 | 3.08 | 3.21 | 3.14 | 4.60 |
| 40 | 2.61 | 2.56 | 2.58 | 4.60 |
| 50 | 2.14 | 2.09 | 2.12 | 4.70 |
| 60 | 1.85 | 2.07 | 1.96 | 4.60 |
| 70 | 1.77 | 1.69 | 1.73 | 4.50 |
| 80 | 1.53 | 1.52 | 1.53 | 4.55 |
| 100 | 1.26 | 1.23 | 1.24 | 4.60 |
| 120 | 1.09 | 1.16 | 1.12 | 4.60 |
| 150 | 1.09 | 1.06 | 1.08 | 4.60 |
| 180 | 1.08 | 1.07 | 1.07 | 4.65 |
| ; | | : | | |

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Table B.5: Kinetic study for adsorption of lead onto peat at pH 5.0 Reaction volume = 100 mL, mass of peat = 0.02 g

| Contact | Residual | lead concentra | ation [mg/l] | Final pH |
|------------|----------|----------------|---------------------------------------|----------|
| Time (min) | Trial 1 | Trial 2 | Mean | Mean |
| 0 | 9.97 | 9.97 | 9.97 | 5.10 |
| 5 | 6.32 | 6.19 | 6.26 | 5.10 |
| 10 | 4.59 | 4.48 | 4.53 | 5.20 |
| 15 | 4.09 | 4.14 | 4.11 | 5.20 |
| 20 | 3.77 | 3.86 | 3.81 | 5.20 |
| 30 | 3.19 | 3.09 | 3.14 | 5.20 |
| 40 | 2.66 | 2.60 | 2.63 | 4.90 |
| 50 | 1.91 | 1.93 | 1.92 | 5.15 |
| 60 | 1.85 | 1.91 | 1.88 | 5.10 |
| 70 | 1.62 | 1.73 | 1.67 | 5.30 |
| 80 | 1.57 | 1.50 | 1.53 | 4.95 |
| 100 | 1.39 | 1.25 | 1.32 | 5.25 |
| 120 | 1.24 | 1.05 | 1.15 | 5.20 |
| 150 | 1.14 | 0.67 | 0.90 | 5.20 |
| 180 | 0.82 | 0.90 | 0.86 | 5.20 |
| | | | · · · · · · · · · · · · · · · · · · · | |

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Table B.6: Kinetic study for adsorption of lead onto peat at pH 5.5 Reaction volume = 100 mL, mass of peat = 0.02 g

| Contact | Residual | lead concentra | ation [mg/l] | Final pH |
|------------|----------|----------------|--------------|----------|
| Time (min) | Trial 1 | Trial 2 | Mean | Mean |
| 0 | 9.75 | 9.75 | 9.75 | 5.50 |
| 5 | 5.95 | 5.90 | 5.93 | 5.55 |
| 10 | 4.96 | 4.83 | 4.90 | 5.55 |
| 15 | 3.99 | 4.10 | 4.05 | 5.60 |
| 20 | 3.61 | 3.95 | 3.78 | 5.40 |
| 30 | 3.07 | 3.01 | 3.04 | 5.55 |
| 40 | 2.18 | 2.26 | 2.22 | 5.60 |
| 50 | 1.86 | 1.99 | 1.92 | 5.45 |
| 60 | 1.89 | 1.85 | 1.87 | 5.50 |
| 70 | 1.74 | 1.65 | 1.69 | 5.65 |
| 80 | 1.58 | 1.43 | 1.51 | 5.60 |
| 100 | 1.09 | 1.17 | 1.13 | 5.70 |
| 120 | 1.11 | 0.85 | 0.98 | 5.75 |
| 150 | 0.87 | 0.74 | 0.80 | 5.80 |
| 180 | 0.68 | 0.79 | 0.74 | 5.65 |
| | | | <u>:</u> | |

Table B.7: Kinetic study for adsorption of lead onto peat at pH 6.0 Reaction volume = 100 mL, mass of peat = 0.02 g

| Contact | Residual | lead concentra | ation [mg/l] | Final pH |
|------------|----------|----------------|--------------|----------|
| Time (min) | Trial 1 | Trial 2 | Mean | Mean |
| 0 | 9.87 | 9.87 | 9.87 | 6.10 |
| 5 | 4.33 | 4.24 | 4.29 | 6.20 |
| 10 | 3.97 | 4.04 | 4.00 | 6.30 |
| 15 | 3.60 | 3.52 | 3.56 | 6.25 |
| 20 | 2.69 | 2.67 | 2.68 | 6.20 |
| 30 | 2.04 | 2.15 | 2.09 | 6.20 |
| 40 | 1.62 | 1.49 | 1.56 | 6.15 |
| 50 | 1.44 | 1.30 | 1.37 | 6.10 |
| 60 | 0.99 | 0.96 | 0.97 | 6.25 |
| 70 | 0.76 | 0.82 | 0.79 | 6.25 |
| 80 | 0.74 | 0.67 | 0.71 | 6.20 |
| 100 | 0.55 | 0.58 | 0.57 | 5.90 |
| 120 | 0.53 | 0.49 | 0.51 | 5.90 |
| 150 | 0.47 | 0.50 | 0.49 | 6.20 |
| 180 | 0.44 | 0.43 | 0.44 | 6.20 |
| | | | ! ! | |

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Table B.8: Isotherm study for adsorption of lead on peat at pH 3.0•

Reaction volume = 250 mL

| Mass of | Residual | lead concentra | tion [mg/l] | Final pH |
|----------|----------|----------------|-------------|----------|
| peat (g) | Trial 1 | Trial 2 | Mean | Mean |
| 0.000 | 10.47 | 10.47 | 10.47 | 3.10 |
| 0.010 | 9.93 | 9.81 | 9.87 | 3.10 |
| 0.015 | 9.69 | 9.75 | 9.72 | 2.95 |
| 0.020 | 9.55 | 9.67 | 9.61 | 3.10 |
| 0.030 | 9.42 | 9.40 | 9.41 | 3.00 |
| 0.035 | 9.07 | 9.17 | 9.12 | 3.20 |
| 0.040 | 8.92 | 9.06 | 8.99 | 3.10 |
| 0.050 | 8.74 | 8.60 | 8.67 | 3.10 |
| 0.060 | 8.36 | 8.34 | 8.35 | 3.10 |
| | | | | |

Table B.9 : Isotherm study for adsorption of lead on peat at pH 4.0 Reaction volume = 250 mL

| Mass of | Residual | Final pH | | |
|----------|----------|----------|-------|------|
| peat (g) | Trial 1 | Trial 2 | Mean | Mean |
| 0.000 | 10.54 | 10.54 | 10.54 | 4.00 |
| 0.010 | 8.73 | 8.87 | 8.80 | 4.15 |
| 0.015 | 8.16 | 8.10 | 8.13 | 4.10 |
| 0.020 | 6.90 | 6.94 | 6.92 | 4.10 |
| 0.030 | 5.32 | 5.44 | 5.38 | 4.20 |
| 0.035 | 4.61 | 4.69 | 4.65 | 4.30 |
| 0.040 | 3.80 | 3.68 | 3.74 | 4.25 |
| 0.050 | 2.55 | 2.71 | 2.63 | 4.20 |
| 0.060 | 1.76 | 1.66 | 1.71 | 4.20 |
| | 1 1 | | | |

Table B.10: Isotherm study for adsorption of lead on peat at pH 5.0

Reaction volume = 250 mL

| Mass of | Residual | Residual lead concentration [mg/l] | | | |
|----------|----------|------------------------------------|-------|------|--|
| peat (g) | Trial 1 | Trial 2 | Mean | Mean | |
| 0.000 | 10.10 | 10.10 | 10.10 | 5.00 | |
| 0.010 | 6.15 | 5.95 | 6.05 | 5.10 | |
| 0.015 | 4.89 | 5.05 | 4.97 | 5.20 | |
| 0.020 | 4.17 | 4.21 | 4.19 | 5.20 | |
| 0.030 | 2.82 | 2.92 | 2.87 | 5.30 | |
| 0.035 | 1.99 | 1.93 | 1.96 | 5.20 | |
| 0.040 | 1.50 | 1.36 | 1.43 | 5.10 | |
| 0.050 | 1.11 | 0.91 | 1.01 | 5.30 | |
| 0.060 | 0.73 | 0.61 | 0.67 | 5.25 | |
| | | , | | | |

Table B.11: Isotherm study for adsorption of lead on peat at pH 6.0

Reaction volume = 250 mL

| Mass of | Residual | lead concentra | tion [mg/l] | Final pH |
|----------|----------|----------------|-------------|----------|
| peat (g) | Trial 1 | Trial 2 | Mean | Mean |
| 0.000 | 10.34 | 10.34 | 10.34 | 6.10 |
| 0.010 | 5.24 | 5.30 | 5.27 | 6.15 |
| 0.015 | 3.99 | 3.87 | 3.93 | 6.20 |
| 0.020 | 2.83 | 2.95 | 2.89 | 6.15 |
| 0.030 | 2.12 | 1.94 | 2.03 | 6.25 |
| 0.035 | 1.18 | 1.04 | 1.11 | 6.20 |
| 0.040 | 1.04 | 0.80 | 0.92 | 6.20 |
| 0.050 | 0.57 | 0.49 | 0.53 | 6.20 |
| 0.060 | 0.35 | 0.41 | 0.38 | 6.25 |
| | | | | |

Table B.12: Desorption study of lead from peat at pH 3.0

Reaction volume = 250 mL

| Mass of | Residual | lead concentra | tion [mg/l] |
|----------|----------|----------------|-------------|
| peat (g) | Trial 1 | Trial 2 | Mean |
| 0.010 | 0.17 | 0.19 | 0.18 |
| 0.015 | 0.25 | 0.23 | 0.24 |
| 0.020 | 0.25 | 0.27 | 0.26 |
| 0.030 | 0.29 | 0.33 | 0.31 |
| 0.035 | 0.43 | 0.41 | 0.42 |
| 0.040 | 0.41 | 0.45 | 0.43 |
| 0.050 | 0.52 | 0.46 | 0.49 |
| 0.060 | 0.64 | 0.66 | 0.65 |
| | | _ | |

Table B.13: Desorption study of lead from peat at pH 4.0

Reaction volume = 250 mL

| Mass of | Residual lead concentration [mg/l] | | |
|----------|------------------------------------|---------|------|
| peat (g) | Trial 1 | Trial 2 | Mean |
| 0.010 | 0.52 | 0.50 | 0.51 |
| 0.015 | 0.73 | 0.69 | 0.71 |
| 0.020 | 1.04 | 1.06 | 1.05 |
| 0.030 | 1.59 | 1.47 | 1.53 |
| 0.035 | 1.75 | 1.81 | 1.78 |
| 0.040 | 2.10 | 2.00 | 2.05 |
| 0.050 | 2.31 | 2.27 | 2.29 |
| 0.060 | 2.62 | 2.48 | 2.55 |
| | 1 | | |

Table B.14: Desorption study of lead from peat at pH 5.0

Reaction volume = 250 mL

| Mass of | Residual | lead concentra | tion [mg/l] |
|----------|----------|----------------|-------------|
| peat (g) | Trial 1 | Trial 2 | Mean |
| 0.010 | 1.25 | 1.19 | 1.22 |
| 0.015 | 1.56 | 1.50 | 1.53 |
| 0.020 | 1.72 | 1.66 | 1.69 |
| 0.030 | 2.14 | 2.20 | 2.17 |
| 0.035 | 2.40 | 2.50 | 2.45 |
| 0.040 | 2.55 | 2.63 | 2.59 |
| 0.050 | 2.73 | 2.69 | 2.71 |
| 0.060 | 2.81 | 2.77 | 2.79 |
| | | | |

Table B.15: Desorption study of lead from peat at pH 6.0

Reaction volume = 250 mL

| Mass of | Residual | lead concentra | tion [mg/l] |
|----------|----------|----------------|-------------|
| peat (g) | Trial 1 | Trial 2 | Mean |
| 0.010 | 1.49 | 1.57 | 1.53 |
| 0.015 | 1.89 | 1.85 | 1.87 |
| 0.020 | 2.31 | 2.19 | 2.25 |
| 0.030 | 2.42 | 2.56 | 2.49 |
| 0.035 | 2.67 | 2.83 | 2.75 |
| 0.040 | 2.84 | 2.78 | 2.81 |
| 0.050 | 2.95 | - 2.91 | 2.93 |
| 0.060 | 3.08 | 2.94 | 3.01 |
| | | | |

Table B.16 : Column study for adsorption of lead on peat. $pH=6.0 \label{eq:pH}$

| Time (min) | Effluent lead concentration [mg/l] |
|--------------------|------------------------------------|
| 0.00 | 10.07 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 15.00 | 0.00 |
| 30.00 | 0.00 |
| 45.00 | 0.00 |
| 60.00 | 0.00 |
| 90.00 | 0.00 |
| 120.00 | 0.00 |
| 150.00 | 0.00 |
| 180.00 | 0.00 |
| 210.00 | 0.00 |
| 240.00 | 0.00 |
| 270.00 | 0.00 |
| 300.00 | 0.00 |
| 360.00 | 0.00 |
| 420.00 | 0.00 |
| 480.00 | 0.00 |
| 540.00 | 0.00 |
| 600.00 | 0.00 |
| 840.00 | 0.00 |
| 1080.00 | 0.00 |
| 1320.00 | 0.00 |
| 1560.00 1800.00 | 0.00 |
| 2040.00 | 0.00 0.00 |
| 2280.00 | 0.05 |
| 2400.00 | 0.14 |
| 2520.00 | 0.25 |
| 2640.00 | 0.35 |
| 2760.00 | 0.46 |
| 2880.00 3000.00 | 0.67 0.78 |
| 3000.00 | 0.76 |

Table B.16 Column study Table for adsorption of lead on peat. (continued..) pH = 6.0

| Time (min) | Effluent lead concentration [mg/l] |
|--------------------|------------------------------------|
| 3120.00 | 0.94 |
| 3240.00 | 1.15 |
| 3360.00 | 1.35 |
| 3480.00 | 1.49 |
| 3600.00 | 1.60 |
| 3720.00 | 1.71 |
| 3840.00 | 1.96 |
| 3960.00 | 2.24 |
| 4080.00 | 2.51 |
| 4200.00 | 2.71 |
| 4320.00 | 3.05 |
| 4440.00 | 3.35 |
| 4560.00 | 3.59 |
| 4680.00 | 3.78 |
| 4800.00 | 4.01 |
| 4920.00 | 4.34 |
| 5040.00 | 4.61 |
| 5160.00 | 4.93 |
| 5280.00 | 5.23 |
| 5400.00 | 5.45 |
| 5520.00 | 5.71 |
| 5640.00 | 5.96 |
| 5760.00 5880.00 | 6.23 6.46 |
| 6000.00 | 6.46 6.51 |
| 6120.00 | 6.62 |
| 6240.00 | 6.69 |
| 6360.00 | 6.76 |
| 6600.00 | 6.83 6.94 |
| 6840.00 7080.00 | 6.99 |
| 7320.00 | 7.06 |
| 7560.00 | 7.20 |
| 7800.00 | 7.16 |
| | |

Table B.16 Column study Table for adsorption of lead on peat. (continued..) pH = 6.0

| Time (min) | Effluent lead concentration [mg/l] |
|------------|------------------------------------|
| 8040.00 | 7.36 |
| 8280.00 | 7.32 |
| 8520.00 | 7.39 |
| 8820.00 | 7.32 |
| 9120.00 | 7.36 |
| 9420.00 | 7.40 |
| 9720.00 | 7.57 |
| 10020.00 | 7.65 |
| 10320.00 | 7.78 |
| 10620.00 | 7.79 |
| 10920.00 | 7.86 |
| 11220.00 | 7.82 |
| 11520.00 | 8.08 |
| 11820.00 | 8.15 |
| 12120.00 | 8.22 |
| | |

Table B.17: Elution of lead from peat using 0.05N nitric acid solution.

| Time (min) | Effluent lead concentration |
|------------|-----------------------------|
| 5.00 | 1454.00 |
| 10.00 | 4066.67 |
| 15.00 | 2705.00 |
| 20.00 | 791.67 |
| 25.00 | 484.17 |
| 30.00 | 275.60 |
| 35.00 | 180.28 |
| 40.00 | 104.79 |
| 50.00 | 71.83 |
| 60.00 | 46.64 |
| 75.00 | 30.95 |
| 90.00 | 21.65 |
| 120.00 | 11.86 |
| 150.00 | 8.08 |
| 180.00 | 5.83 |
| 210.00 | 5.24 |
| 240.00 | 4.08 |
| 270.00 | 3.45 |
| 300.00 | 2.86 |
| 360.00 | 2.15 |
| 420.00 | 1.69 |
| 480.00 | 1.41 |
| 510.00 | 1.23 |
| 540.00 | 1.04 |
| 550.00 | 0.98 |
| | |