

KINETIC AND EQUILIBRIUM STUDIES ON THE ADSORPTION OF Pb^{2+} AND Zn^{2+} FROM AQUEOUS SOLUTION USING COCO-PEAT BY BATCH EXPERIMENT

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Abstract

The presence of heavy metals in surface water, which is common in mining area pose harmful effect to human health and the environment. Recently, coco-peat has been studied as an effective sorbent material for removing heavy metals from wastewater. In this study, kinetic was done by analyzing the distribution of the heavy metal in sorbent material and liquid phase after mixing 50 mg/L solution of lead (Pb^{2+}) and zinc (Zn^{2+}) in single solute system with 0.1 g of coco-peat, that were consequently shaken at 5, 10, 15, 30, 60, 120, 180 and 360 minutes. To determine the equilibrium adsorption isotherm for each heavy metal, the solutions of 10, 20, 30, 40 and 50 mg/L of Pb^{2+} and Zn^{2+} were prepared separately. Two different pH levels (natural pH, and pH 4) were set to describe the sorption behavior of Pb^{2+} and Zn^{2+} of each heavy metal. Using data from batch experiments, appropriate kinetic (time dependency) and equilibrium (isotherm) models were fitted on the sorbent material and liquid phase concentrations to determine adsorption parameters. Pseudo second-order kinetic model fitted well to the kinetic data due to chemisorption that happened during experiments. In other hand, Langmuir model fitted well to the equilibrium, this indicates that the sorption of lead and zinc on coco peat is monolayer and that the adsorbent's surface is homogenous. The increase of

heavy metals adsorption following the increase of pH might be due to negative charge of coco peat surface. Pb^{2+} adsorbed more than Zn^{2+} because ion with high hydration enthalpy will have smaller amount of ion adsorbed. The hydration enthalpies for Pb^{2+} and Zn^{2+} are 23 kJ/kg and 113 kJ/kg, respectively. Considering all the factors that we have discussed, coco-peat has high efficiency to remove the heavy metals from wastewater.

Keywords: Coco-peat, adsorption, batch experiment, kinetic, equilibrium.

1 Introduction

The Presence of heavy metals in environment, especially aquatic environment and soil is a major concern due to their toxicity towards humans, aquatic life, other animals and the environment itself. Although various treatment techniques have been employed to remove the heavy metal from wastewater include chemical precipitation, ion exchange, membrane filtration, electrochemical processes and adsorption on activated carbon, but most of these methods are ineffective due to high cost, generation of secondary pollution and ineffectiveness for low metal concentration. Easy implementation, high adsorption percentage, low cost and easy obtainable material should be considered for the development of a heavy metals removal method.

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Nowadays, removal of heavy metals using bio-sorption materials were investigated in many researches due to low cost, abundantly available in tropic countries as agricultural waste and renewable (Macedo *et al*, 2006). One of the effective sorbents within heavy metal removal is coco-peat. Researches have been done using coco-peat from coconut husks as a sorbent material to quantify the efficiency of removal heavy metals that are common in wastewater such as Lead (Pb^{2+}) and Zinc (Zn^{2+}) using batch and/or column studies. Adsorption studies have shown that coco-peat can effectively bind lead and zinc ions (Conrad and Hansen, 2007; Ong, 2010; Quek, 1998). However, these studies have not investigated the parameters such as the increasing of pH.

Sorption is a major process influencing the transport of pollutants in soils (Clark, 1996). Sorption can be further categorized into adsorption, absorption, ion exchange, diffusion and precipitation. These types of sorption have different processes and characterizations. Adsorption is the process whereby solutes bind to surfaces of soil particles to form outer or inner sphere solute-surface site complexes (Selim *et al*, 1990) and absorption is the process of a solute compound attaching itself or chemically bond within a soil particle (Loll and Moldrup, 2000).

Ion exchange is the process whereby charged solutes replace ions on soil particles (Selim *et al*, 1990). This study investigated the use of natural coco-peat on heavy metals removal in a synthetic wastewater by adsorption through batch experiment set up. The different solutions were prepared to highlight the effect of ion competition on equilibrium and kinetic studies. In addition, the effect of pH on the adsorption of Pb and Zn as single species and when both species are present is further considered. Previous adsorption studies have shown it to have good metal binding ability (Macedo *et al*, 2006; Parcon, 2010).

Studying the effects of metal ion competition on equilibrium and kinetic studies yields results that are valuable for future adsorption

Table 1: Physical and chemical characteristics of coco-peat for this research (Parcon, 2010).

Properties	Unit	Value
Moisture content	%	17.47
Ash Content	%	7.45
pH	%	5.70
Lignin	%	48.71
Hemicellulose	%	7.20
Extractive (with alcohol-benzene)	%	1.85
Cation Exchange Capacity (CEC)	meq g ⁻¹	151
Anion exchange capacity	meq g ⁻¹	0.068
Total organic matter	%	80
Trace metal concentration		
Cu	mg/kg	3.9
Specific surface area	m ² /g	0.1159

researches and in the design of adsorbent systems.

2 Materials and Methods

2.1 Sample preparation

Coco-peat was taken from Soriano Integrated Fiber Corporation located in Sariaya, Quezon City, Philippines. The samples were taken from the top of a fresh mound of coco-peat. The coco-peat was passed through sieve no. 10 in order to eliminate the larger particles and impurities, and then stored in a cool and dry place. Table 1 shows the physico-chemical characteristics of the coco-peat used in this study.

$Pb(NO_3)_2$ and $Zn(NO_3)_2$ standard solutions were used as stock solutions. Solutions with different concentrations were prepared by diluting the stock solution with deionized water. In order to adjust the pH of heavy metals solutions, 0.1 M of HNO_3 and or NaOH were added.

2.2 Batch adsorption studies

Batch experiments were conducted by mixing 100 mL heavy metal solution with 0.100 g coco-peat in a 250 mL Erlenmeyer flask. The solutions were placed in an orbital shaker at 150 rpm for a specified contact time. The resulting solution was filtered and the filtrate was an-

alyzed for metal concentration using a Flame Atomic Absorption Spectrophotometer (AAS).

2.3 Kinetic studies

Using an initial metal concentration of 50 ppm and initial natural pH and adjusted pH of 2,4 and 4, batch experiments were performed using the following contact times: 5 minutes, 10 minutes, 15 minutes, 30 minutes, 60 minutes, 120 minutes, 180 minutes and 360 minutes.

The amount of solute adsorbed per unit weight of sorbent at any time t , q_t (expressed in mg metal/g coco-peat), is computed using the following equation.

$$q_t = \frac{(C_o - C_t) V}{W} \quad (1)$$

where C_o is the initial metal concentration in mg/L; C_t is the measured metal concentration at time t expressed in mg/L; V is the volume of metal solution used in L; and W is the weight of adsorbent in grams.

Kinetic models

In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. The kinetic models used in this experiment are the pseudo-first order kinetic equation and the pseudo second order equation (Ho and McKay, 1998).

The pseudo-first order kinetic model proposed by Lagergren (1898) is expressed as follows:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2)$$

where, q_t and q_e are the sorption capacity (amount adsorbed) at equilibrium time and at any time t , respectively; expressed in mg of metal per gram of coco-peat; k_1 is the kinetic rate constant expressed in min^{-1} .

After integration and applying boundary conditions $q_t = 0$ and $t = 0$ and $q_t = q_t$ at $t = t$, the equation can be expressed in linearized form of the pseudo-first order kinetic equation:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

A plot of $\log (q_e - q_t)$ versus t should yield a straight line from which k_1 and q_e can be estimated.

Many studies on adsorption have kinetic data that fitted well with the pseudo-second order kinetic model. This model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption which involves valency forces through sharing or exchange of electrons between sorbate and sorbent.

The pseudo-second order chemisorptions kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (4)$$

where, q_t and q_e are the sorption capacity (amount adsorbed) at equilibrium and at time t , respectively, expressed in mg of metal per grams of coco-peat and k_2 is the kinetic rate constant expressed in min^{-1} for pseudo-second order sorption.

After a process of integrating the original equation, the following is now the linearized form:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e} \right) t \quad (5)$$

where $h = k_2 q_e^2$ and is the initial sorption rate as $q_t/t = 0$ and k_2 is the pseudo-second order rate constant in $\text{g mg}^{-1} \text{min}^{-1}$. Plotting t/q_t versus t yields a linear relationship, the slope and intercept of which can be used to compute for h and q_e .

2.4 Equilibrium studies

Using the equilibrium time that was obtained in the kinetic studies, adsorption isotherm data were generated by using different initial metal concentrations. The concentrations used were 10, 20, 30, 40 and 50 ppm for each heavy metal and adjustment of pH was done up to pH 4.

Adsorption isotherm models

The adsorption isotherms were obtained from the equilibrium data. The change in the concentration of solute at the interface when solute concentration is increased is known as an isotherm (Clark, 1996). In terms of the adsorption of metal in aqueous solutions, an isotherm shows the amount of metal adsorbed by the adsorbent as the concentration of the metal in the solution is increased. Freundlich and Langmuir isotherms are the the simplest known relationships describing the adsorption equation. These two isotherm models were used to assess the different isotherms and their ability to correlate the experimental data (Igwe and Abia, 2007).

The Langmuir isotherm model is based on a kinetic principle, which is the rate of adsorption at the surface is equal to the rate of desorption from it. This model is applicable for monolayer adsorption. It is used to obtain a maximum adsorption capacity based on complete monolayer coverage of adsorbent surface [11]. This model is the most basic isotherm model and assumes that surface is homogeneous. The isotherm equation is represented as:

$$\frac{q_e}{Q_m} = \frac{bC_e}{1 + bC_e} \quad (6)$$

where b is the adsorption equilibrium constant (in $L\ mg^{-1}$) and is related to the apparent energy of adsorption; Q_m is the monolayer adsorbent capacity, described as the quantity of adsorbate required to form a single monolayer on a unit mass of adsorbent and is expressed in $mg\ g^{-1}$; q_e is the amount of component adsorbed on the adsorbent ($mg\ g^{-1}$) when the concentration of that component in the solution at equilibrium is C_e ($mg\ L^{-1}$). Equation (6) can be rearranged to obtain the linear form, expressed as:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right) C_e \quad (7)$$

a plot C_e/q_e versus C_e should yield a straight line if the adsorption process follows Langmuir's theory. The Freundlich isotherm was derived empirically for solid-liquid systems (Clark, 1996). The model describes that the

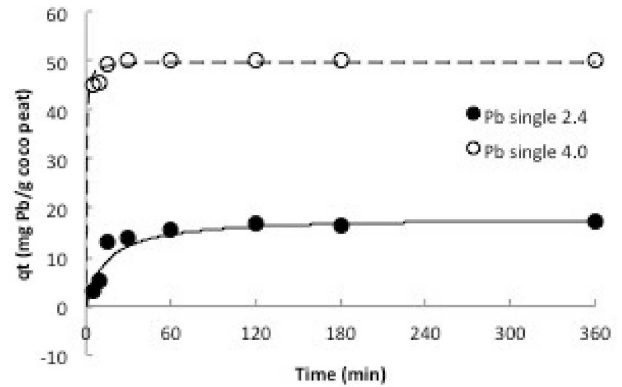


Figure 1: Adsorption behavior of lead (Pb^{2+}) over time at different pH.

ratio of the amount of solute adsorbed to a certain mass of adsorbent to the concentration of solute in the solution is not constant at different concentrations (Gupta and Babu, 2009). It is given by the equation:

$$q_e = K_f C_e^{1/n} \quad (8)$$

where K_f is an empirical constant associated to the capacity of the adsorbent to adsorb the adsorbate and is expressed in $(mg\ g^{-1})(L\ mg^{-1})^{1/n}$. The higher the value of K_f , the more adsorbate is potentially sorbed; n is the Freundlich constant and describes the deviation of the adsorption from linearity. q_e and C_e has the same connotation as that in Langmuir isotherm. The coefficients can be obtained by plotting the linear form of the model:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (9)$$

3 Results

The adsorption of metal ions is affected by the contact time between the sorbate and the sorbent. Hence the sorption of all metal ions onto coco peat was studied as a function of contact time from 5 minutes to 360 minutes. The effect of pH was also observed to the amount of heavy metals absorbed. The results are illustrated in Figures 1–2.

It can be seen from Figure 1 that the adsorption of Pb^{2+} for both pH (2.4 and 4.0) increased with increasing contact time. There is a rapid

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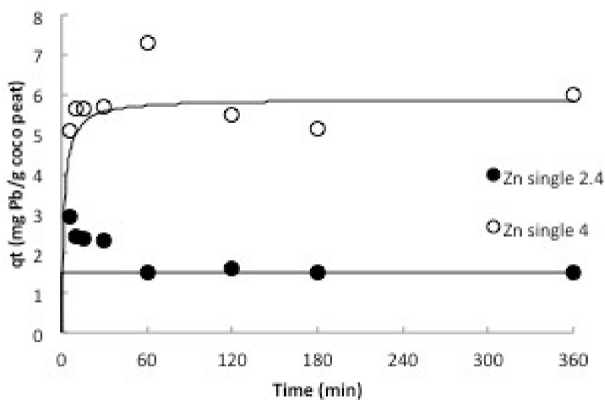


Figure 2: Adsorption behavior of zinc (Zn^{2+}) over time at different pH.

increase for the first 30 minutes and followed by a constant value beyond 60 minutes. Thus, the 60 min equilibrium time was employed for the equilibrium time for experiments. Another study has observed the same equilibrium period of 1 hour using unground coir for the same heavy metals (Conrad and Hansen, 2007). The highest equilibrium adsorption capacity, q_e for lead was obtained at pH 4.0 with 100% removal or 50 mg/g cocopeat of Pb^{2+} removed.

The sorption of Zn^{2+} as shown in Figure 2 followed the same trend of increasing sorption with increasing contact time except the zinc solutions at pH 2.4. The 60 min equilibrium time is also used for further experiments for zinc in single and binary solute system. It can be observed that q_e , the amount of metal ions adsorbed at equilibrium time, increased as the pH is increased for all systems. Experimental results have shown that Pb was fully removed at pH 4.0. Zinc, however, was only removed at 7.292 mg/g at pH 4.0.

3.1 Kinetic studies

Experiments on sorption kinetics are important to determine the type of sorption between a heavy metal and its sorbent. The pseudo first order kinetic model, assumes the rate of uptake is limited to one mechanism that is acting on a single class of sorbing sites. The pseudo second order kinetic model states that the rate-limiting step of reaction involves an exchange or sharing of electrons between the heavy metal and

Table 2: Correlation coefficients (r^2) for pseudo first order and pseudo second order kinetic models for single solution of Pb and Zn.

	Pb (II)		Zn (II)	
	r^2 Pseudo 1 st Order	r^2 Pseudo 2 nd Order	r^2 Pseudo 1 st Order	r^2 Pseudo 2 nd Order
pH 2.4	0.347	0.99	0.07	0.99
pH 4.0	0.12	1	0.04	0.99

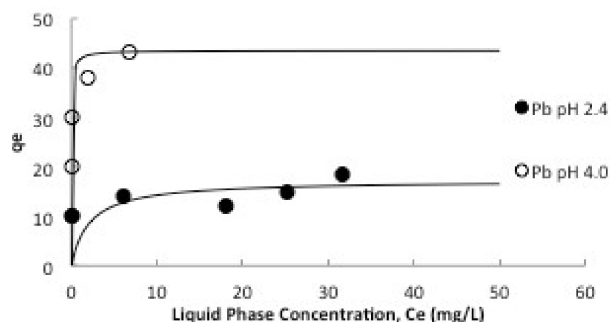


Figure 3: Fitted Adsorption Isotherm Model (Langmuir) of Lead at different pH.

sorbent – the process is also called chemisorption (Ho and McKay, 1998).

However, when the data was fitted to the pseudo first order kinetic model, the correlation is poor to describe the sorption behavior between the given heavy metals and coco-peat for this experiment. It is more likely that the experiment data well suited for the pseudo second order kinetic model as shown in Table 2.

The r^2 values for pseudo-second order kinetic model are close to unity indicating that the rate-limiting step in the adsorption of lead and zinc on coco-peat is chemisorption.

3.2 Equilibrium studies

The equilibrium data fitted more satisfactorily to Langmuir isotherm model than Freundlich isotherm model (Table 3). This indicates that monolayer coverage of sorption between the heavy metals and coco-peat is more likely to occur. Table 3 showed the r^2 of the graphs and confirms that the Langmuir isotherm is the more adequate sorption isotherm model for lead and zinc than the Freundlich isotherm model as illustrated in Figure 3 and 4.

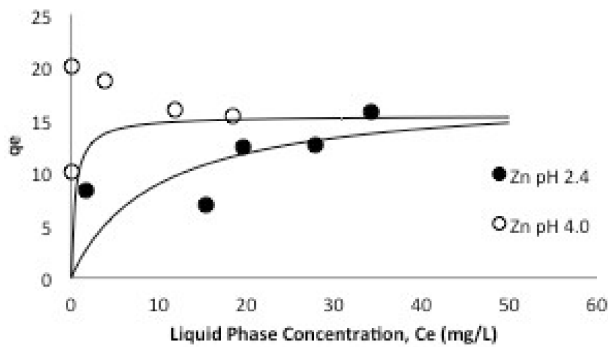


Figure 4: Fitted Adsorption Isotherm Model (Langmuir) of Zinc at different pH.

Table 3: Correlation coefficients (r^2) for Langmuir and Freundlich isotherm models.

	Pb (II)		Zn (II)	
	r ² L Model	r ² F Model	r ² L Model	r ² F Model
pH 2.4	0.92	0.66	0.67	0.37
pH 4.0	0.99	0.43	0.98	0.79

L: Langmuir Isotherm Model

F: Freundlich Isotherm Model

4 Conclusions

Based on the results of this study, the following conclusions are drawn:

- The kinetic data fitted were satisfactory to the pseudo second order kinetic model. The rate of uptake of the heavy metals in coco-peat is described as chemisorption.
- The effect of an increase in pH in the kinetics, as well as in the isotherms, is evident and showed an increase in the Sorption Capacity of coco-peat.
- The Langmuir isotherm fits better in Pb²⁺, therefore the sorption between the heavy metal and coco-peat is of monolayer coverage.
- The amount of Pb (II) adsorbed in coco-peat was greater in comparison to Zn (II) adsorbed because higher hydration enthalpy will have smaller amount of ion adsorbed. The hydration enthalpies for Pb²⁺ and Zn²⁺ are 23 kJ/kg and 113 kJ/kg, respectively.

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