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Kinetics Studies for the Adsorption of Aqueous Cu (II) and Pb (II) Ions onto Chicken Feather

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ABSTRACT

Adsorption kinetic studies are of great significance to evaluate the performance of a given adsorbent and to gain insight into the underlying mechanism. The sorption kinetics of Pb(II) onto chicken feathers (CF) was investigated. In order to understand the mechanisms of the biosorption process and the potential rate controlling steps, kinetic models were used to fit the experimental data. The results indicated that kinetic data were best described by the pseudo second-order model with a correlation coefficient (R^2) of 0.999 and 0.998 for Pb(II)/CF and Cu(II)/CF respectively. The experimental uptakes, q_{exp} were much consistent with those calculated/obtained from the pseudo second order model. Biosorbents- Pb(II) kinetics follow the order: pseudo-second order > pseudo-first order > Weber-Moris intra particle diffusion model. The biosorbents also show a good reusability after simple elution with EDTA and HNO_3.

Keywords: *Kinetics, first order, second order, lead, copper*

INTRODUCTION

One of the most critical problems of developing countries is improper management of vast amount of wastes generated by various anthropogenic activities. More challenging is the unsafe disposal of these wastes into the ambient environment. Water bodies especially freshwater reservoirs are the most affected. This has often rendered these natural resources unsuitable for both primary and/or secondary usage (Fakayode, 2005). Industrial effluent contamination of natural water bodies has emerged as a major challenge in developing and densely populated countries like Nigeria. Estuaries and inland water bodies, which are the major sources of drinking water in Nigeria, are often contaminated by the activities of the adjoining populations and industrial establishments (Sangodoyin, 1995).

Copper and lead are some of the most toxic metals apart from mercury and cadmium. They have been known to cause Wilsons disease, hepatic cirrhosis, brain damage, demyelization and renal diseases. The removal of Pb(II) and Cu(II) from wastewater has become imperative globally as a result of their toxicity (Olawale et al, 2018a) because prolonged consumption of lead and copper contaminated water will be of health risk overtime (Olawale et al, 2016). Conventional technologies for the removal of metal ions from industrial effluents are less efficient, very costly and generate toxic sludge (Aravind et al, 2013). Among these processes include chemical precipitation, membrane filtration, adsorption, ion exchange, reverse osmosis and coagulation. The search for new techniques for the removal of toxic metals directed attention towards adsorption. Due to the presence of surface functional groups such as acetamido, alcoholic, carbonyl, phenolic, amido, amino, and sulfhydryl groups, cellulosic agricultural waste materials act as an important source for metal biosorption (Aravind et al, 2013). In addition adsorption has gained a lot of credibility currently because of its eco- friendly nature, excellent performance and cost-effectiveness (Amboga, 2014). Specifically, chicken feathers are among natural adsorbents with high potential for water treatment. Chicken feathers make up 4 – 6% of the weight of mature chickens and as a result, large quantities are produced as waste from poultry farms (Olawale et al, 2018b)

The aim of this study was to investigate the mechanism behind removal of Cu (II) and Pb

(II) ions from aqueous solutions using chicken feathers (CF), hence, the adsorption kinetics was evaluated.

MATERIALS AND METHODS

All the chemicals used in this work were of analytical grade. Preparation of adsorbate was carried out by preparing 1000 mg/L stock solution of Pb(II) and Cu(II) which were later diluted to the aqueous feed for each experiment. Sodium hydroxide (0.1M) and nitric acid (0.1M) were alternately used for the pH adjustment of the feed solution prior to commencing the biosorption experiments.

Chicken feathers (CF) were collected from slaughter point in Gwagwalada area council of the FCT and were washed several times with distilled water and then left to dry at room temperature (25±2^{0}C). The feathers were cut into smaller sizes using a scissors. The smaller sized feathers were used in the biosorption experiments.

The feathers were characterized by determining the following parameters: moisture content, loss of mass on ignition, pH and bulk density using standard procedures:

Determination of Moisture Content

This was done by weighing 5g of CF into a crucible. This was placed in the oven and heated for 4 hours at constant temperature of 105°C. The sample was then removed and put rapidly into a desiccator in order to prevent more moisture uptake from atmosphere. The sample was re-weighed. This procedure was repeated several times until a constant weight was obtained. The difference in the mass constitutes the amount of moisture content of the adsorbent (Langmuir, 1918)

$$\frac{W_2 - W_3}{W_2 - W_1} \text{ X } 100$$

W_1 = Weight of crucible W_2 = Initial weight of crucible with sample W_3 = Final weight of crucible with sample

Determination of Loss on Ignition

The determination of loss of mass on ignition was done by weighing 10g of the adsorbent (CF) and put inside furnace at constant temperature of 600°C for 2 hours. After roasting, the sample was removed and put in a desiccator for cooling. The residual product is then weighed and the difference in mass represented the mass of organic material present in the sample. This operation was repeated four times

Ph Determination

The determination of pH of the samples was done by weighing 1g each of CF, boiled in a beaker containing 100 cm^3 of distilled water for 5 minutes, the solution was diluted to 200 cm^3 with distilled water and cooled at room temperature, the pH of each was measured using a pH meter and the readings were recorded (Abdel-Halim, 2006)

Determination of Bulk Density

The bulk density of each of the samples of CF was determined using Archimedes‘s principle by weighing a 10 cm^3 measuring cylinder before and after filling with the samples. The measuring cylinder was then dried and the sample was packed inside the measuring cylinder, leveled and weighed. The weight of the sample packed in the measuring cylinder was determined from the difference in weight of the filled and empty measuring cylinder. The volume of water in the container was determined by taking the difference in weight of the empty and water filled measuring cylinder. The bulk density was determined using the equation below (Toshiguki and Yukata, 2003)

$$\text{Bulk density} = \frac{W_2 - W_1}{V}$$

W_1 = Weight of empty measuring cylinder W_2 = Weight of cylinder filled with sample V = Volume of cylinder

Biosorption Experiment

Biosorption isotherm studies were conducted at 25±1^{O}C in single metal (Pb(II)) aqueous solution varying the initial metal concentration. 50 mL of Pb(II) aqueous solution at pH 4.0 were agigated by a stirrer at 250 rpm with 0.05 g of each biosorbent for 3 hours. The mixture was filtered and the filtrate analyzed for metal ions concentration using AAS. The data was fitted into the following isotherms: Langmuir Freudlich, Temkin and Dubinin-Raduskevich. The metal uptake (Q, in mg/g) is the concentration of adsorbed metal ion per unit mass of biosorbent (in mg/g), which was calculated using the equation:

$$Q \text{ (mg/g)} = \frac{(C_I - C_f) \times V}{W}$$

Where C_i and C_f are the initial and the final concentration of metal ions in the aqueous solution respectively (in mg/L), V is the total volume of the solution (in L) and W is the total amount of biosorbent used (in g).

In this study, all the experiments were carried out in duplicate and average values are presented.

Results and Discussion

The results for physico-chemical analysis of CF is given in table 1 below

Table1. *Physico-chemical analysis of CF*

Properties	CF
pH	8.10
Moisture content (%)	8.54
Loss on ignition (%)	85.97
Bulk density (g/cm^3)	0.037

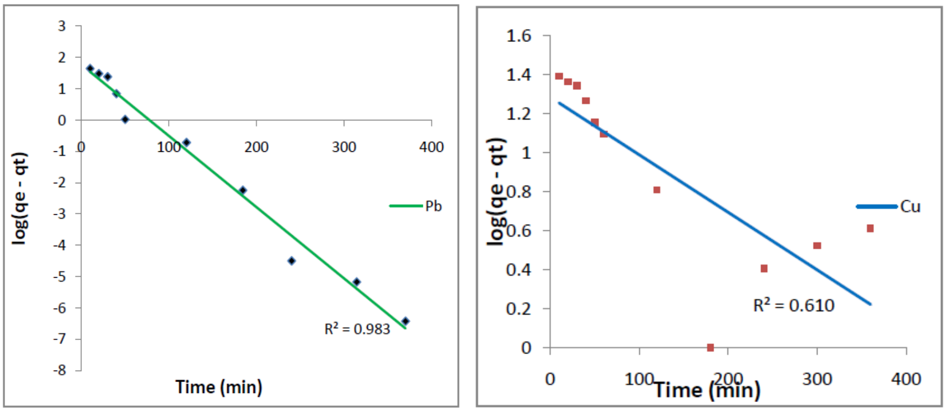

Figure1. *Pseudo First Order Kinetics Plots for the adsorption of Pb(II) and Cu(II) onto CF*

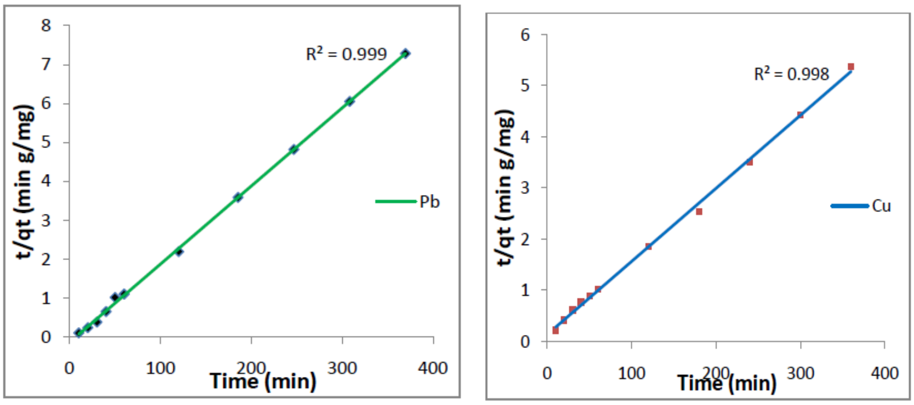

Figure2. *Pseudo Second Order Kinetics Plots for the adsorption of Pb(II) and Cu(II) onto CF*

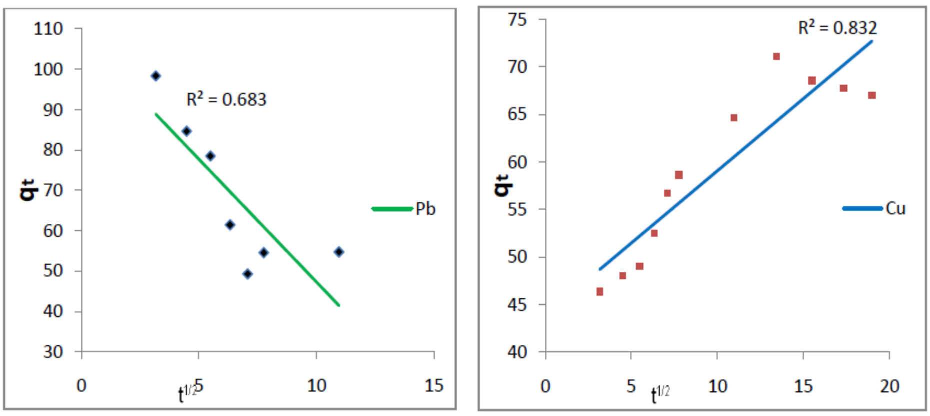

Figure3. *Weber Moris Intraparticle Plots for the adsorption of Pb(II) and Cu(II) onto CF*

Table2. *Pseudo first order kinetics constants for the adsorption of Pb(II) and Cu(II) ion onto CF*

Metal	K_1 (min^{-1})	q_e (mg/g)	R^2	q_{exp}(mg/g)

Pb	4.84×10^{-2}	74.99	0.983	50.91
Cu	6.91×10^{-3}	19.28	0.610	67.77

Table3. *Pseudo second order kinetics constants for the adsorption of Pb(II) and Cu(II) ion onto CF*

Sorbents	K_2 ($mgg^{-1}.min^{-1}$)	q_e (mg/g)	R^2	h (mg/g.min)	q_{exp}(mg/g)
Pb	3.25×10^{-3}	50.63	0.999	8.33	50.91
Cu	1.50×10^{-3}	71.43	0.998	7.65	67.77

Table4. *Weber Morisintra particle diffusion constants for the adsorption of Pb(II) and Cu(II) ion onto CF*

Sorbents	K_{id}	C	R^2
Pb	6.082	108	0.683
Cu	1.518	43.89	0.832

Table5. *Elution of sorbed metal using 0.1M EDTA and 0.1M HNO_3*

Metal	% metal adsorbed	Elution efficiency (%) using 0.1M EDTA	Elution efficiency (%) using 0.1M HNO_3
Pb	90.23	95.54	91.65
Cu	84.39	68.65	69.18

Discussion

A comparison between pseudo first order, pseudo second order and Weber Moris intra-particle diffusion kinetic parameters suggested that Pb(II) and Cu(II) biosorption by CF pursued the pseudo-second order kinetics than pseudo-first order and Weber-Moris intra particle diffusion model kinetics since the value of predicted qe, 50.63 mg/g and 71.43 mg/g for Pb and Cu respectively obtained from pseudo-second order model was in close accordance with the experiment values qexp, 50.91 mg/g and 67.71 mg/g whereas the value of qe computed from pseudo first order model did not agree with the experimental values unlike in pseudo second order kinetic model, where the q_{exp} were much consistent with the calculated ones. This indicates that pseudo-first order model might be insufficient to interpret the mechanism of Pb(II) and Cu(II) biosorption (Ho *et al.*, 2001). Kinetic data evaluation of these biosorbents also revealed that the correlation coefficient R^2 values for the pseudo second order models are 0.999 and 0.998 for Pb(II)/CF and Cu(II)/CF systems respectively. These results imply that the adsorption systems studied could well be explained by pseudo second order kinetic model at all time intervals in comparison to pseudo-first order and Weber Moris intra particle diffusion model.

The correlation coefficient R^2 obtained from the Pb(II) and Cu(II) kinetic data for the biosorbent, follow the order: pseudo-second order > pseudo-first order > Weber-Moris intraparticle diffusion model. Hence pseudo first order model cannot provide an accurate fit to the experimental data. Since Ho and McKay (1998a) had corroborated this fact.

A number of earlier workers proposed pseudo second order kinetic model for describing the sorption of Pb (II) on keratinous materials (Helan, 2014), cations on peat (Ho and McKay, 2000), on dried activated sludge (Wang and Chen, 2006), rose waste (Javed*et al.*, 2007), tree fern (Ho, 2006), palm kernel fiber (Ho and Ofomaja, 2006), tea waste (Amarasinghe and Williams, 2007), protonated rice bran (Zafar *et al.*, 2007), waste distillery sludge from sugar-cane industry (Nadeem *et al.*, 2008) and distillation waste of rose petals (Nasir*et al.*, 2007).

These kinetics informations are of significant practical value for technological applications (Ho and McKay, 1998b; Deng *et al.*, 2006; Loukidou *et al.*, 2004) and can be adopted to find significant parameters for a bioreactor design (Cruz *et al.*, 2004).

Desorption of Pb(II) and Cu(II) adsorbed onto CF was investigated. The solution of 0.1M HNO_3 performed reasonably well but not as good as EDTA solution at the same concentration. The elution efficiencies of HNO_3 and EDTA for the metal loaded CF are given in Table 5.

Conclusion

Kinetic parameters suggested that Pb(II) and Cu(II) biosorption by chicken feather (CF) followed the pseudo-second order kinetics. The experimental uptakes, q_{exp} were much consistent with those calculated from the pseudo second order model.

Desorption experiments prove that 0.1 M EDTA and HNO_3 solutions are efficient eluents for the recovery of Pb(II).

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