



ISOTHERMAL AND KINETICS ASSESSMENT OF METAL IONS REMOVAL FROM LEACHATE USING CASSAVA PEEL DERIVED ADSORBENT

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ABSTRACT

Heavy metals are often present in leachate at concentrations exceeding discharge limits. They are persistent, non-biodegradable and harmful to human health. It is important that leachate is effectively treated before discharge into aqueous systems. Isothermal and kinetic studies were undertaken to evaluate the removal of Pb, Ni, Cr and Zn ions from synthetic leachate by a cassava peel-derived adsorbent (CPDA). Batch experiments were conducted at varied initial concentrations (23-150mg/l) and contact times(10-60 minutes) and the data were analysed using the non-linear Langmuir and Freundlich isotherms and the pseudo-first and second order kinetic models. The Freundlich isotherm provided a better description of the equilibrium process for all the metals. The maximum monolayer adsorption capacities were 50.95, 47.78, 44.72 and 22.26mg/g for Pb, Zn, Ni and Cr respectively. The pseudo-first order kinetic model provided a better fit for Pb and Cr, while Ni and Zn followed the pseudo-second order model. The results of this study have provided insight into the adsorption mechanisms and demonstrated the heavy metal removal capability of the adsorbent, while forming the basis for application to real leachate samples.

Keywords: Cassava peel, Heavy Metals, Adsorption, Kinetics, Isotherms



INTRODUCTION

Large volumes of agricultural processing wastes, such as cassava peels are an environmental nuisance due to inadequate disposal methods. In Nigeria, 450,000 tons of cassava peel waste are generated annually (FAO, 2006). However, conversion of these wastes to biosorbents is an economical value-added approach to simultaneously manage the solid wastes and treat aqueous waste streams, thus protecting the environment (Abia et al., 2003; Babel and Kurniawan, 2003; Horsfall and Abia, 2003). In comparison with conventional heavy metal removal techniques, adsorption is highly competitive and cost effective. This is due to the comparatively good performance, metal selectivity, regenerability, absence of sludge generation and associated secondary disposal problems, and possible metal recovery (Abia et al., 2003; Mathew et al., 2016). Some researchers have investigated the heavy metal removal performance of cassava wastes under different experimental conditions (Abia et al., 2003; Horsfall and Abia, 2003; Okoro and Abii, 2011; Ndlovu et al., 2013). Okoro and Abii (2011) investigated

the use of cassava peels amongst other wastes for the removal of cadmium from aqueous solutions, with a maximum adsorption capacity of 59.58mg/g obtained. The removal of cobalt, vanadium and chromium from waste effluent using thiolated cassava peels powder has also been studied (Ndlovu et al., 2013). In most developing countries, waste dumps and poorly designed landfills are prevalent. They receive large volumes of unsorted wastes daily, resulting in the uncontrolled discharge of leachate which is detrimental to human health, groundwater and the environment (Ayotamuno and Akuro, 2004; Aiyesanmi and Imoisi, 2011; Asibor et al., 2016). Heavy metals are often present in leachate at concentrations exceeding discharge limits. These metals are persistent, non-biodegradable, potentially carcinogenic and harmful to human health (Agbozu and Nwosisi, 2015). Hence it is important that leachate is properly treated before discharge into aqueous systems.

The aim of this study is to investigate the performance of cassava peel-derived adsorbent for the removal of metal ions (Pb^{2+} , Cr^{3+} , Zn^{2+} and Ni^{2+}) from single



solute synthetic leachate solutions in batch systems. Langmuir and Freundlich isotherms and pseudo-first and second order kinetic models were used to analyse the experimental data. The results of this study will form the basis for further applications of the adsorbent to real leachate samples.

Materials and Methods

Preparation and Characterization of Cassava Peel-Derived Adsorbent (CPDA) Cassava peels obtained from commercial factories in Auchi, Edo state were washed thoroughly with distilled water, air dried and oven dried at 65oC to constant weight. The dried peels were then crushed and ground to powdered form using an electric milling machine (Binatone model)

Table 1: Physical characteristics of cassava peel-derived adsorbent (CPDA)

Parameter	Cassava Peel-Derived Adsorbent
Fixed carbon (%)	79.8
Pore volume (cm ³)	1.11
Porosity (ml/g)	0.161
Bulk density (g/cm ³)	0.36

The powder was carbonized in a kiln at 350oC, cooled and stored in a dessicator (Gin et al., 2014). The carbonized powder was activated using Phosphoric acid (H₃PO₄) and Hydrochloric acid (HCL) (Yalc and Sevinc, 2000; Koby, et al., 2005). The physical characteristics of the adsorbent were determined according to standard procedures (ASTM, 2001) as shown in Table 1.

Preparation of Synthetic Leachate Samples

Synthetic metal solutions were prepared from their respective analytical grade salts (NiCl₂, ZnCl₂, Pb(NO₃)₂, and Cr₂Cl₃) using distilled water. The initial pH of each solution was adjusted to the optimum pH value by drop-wise addition of 0.1 M H₂SO₄. Metal concentrations in solutions were determined using a Flame Atomic Absorption Spectrophotometer (FAAS).



Isotherm Studies

Equilibrium isotherm studies were carried out by mixing 0.25g of adsorbent with 50 ml of each metal solution with concentrations varied from 25 to 150mg/l at pH 4. The solutions were agitated at 150rpm at 35°C for 60 minutes in order to reach equilibrium. The pH, agitation speed, temperature and contact time had earlier been determined from preliminary screening experiments. At the end of the experiments, samples were filtered using Whatman No. 40 filter paper, centrifuged for 5 minutes and analyzed using FAAS.

The amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g) was determined using the mass balance equation:

$$q_e = (C_o - C_e)V/m \quad (1)$$

Where C_o and C_e are the initial and equilibrium concentrations of adsorbate in solution respectively (mg/L), m is the mass of adsorbent (g) and V is the volume of solution (L).

The Langmuir isotherm is expressed as follows (Foo and Hameed, 2010):

$$q_e = q_{max}bC_e/(1 + bC_e) \quad (2)$$

Where C_e is the equilibrium concentration (mg/L), q_{max} is the maximum monolayer coverage capacity (mg/g), q_e is the amount of adsorbate adsorbed per unit mass

of adsorbent at equilibrium (mg/g) and b is the Langmuir isotherm constant (L/mg).

The Freundlich isotherm is expressed as follows (Foo and Hameed, 2010):

$$q_e = K(C_e)^{1/n} \quad (3)$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K is the Freundlich constant and n represents the adsorption intensity.

The natural language “R” statistical computer software was used to plot the experimental data and obtain the best fitting isotherm model.

Kinetic studies

The kinetic studies were conducted by mixing 0.25 g of adsorbent with 50 mL of each metal solution (250mg/L) at pH 4 and temperature 35°C for 10, 20, 30, 40, 50 and 60 minutes. At the end of the experiments, samples were filtered using Whatman No. 40 filter paper, centrifuged for 5 minutes and analyzed using FAAS. The linearized forms of the pseudo-first and pseudo-second order equations were plotted using Microsoft excel. The linear form of the pseudo-first order kinetic equation is:



$$\log(q_e - q_t) = \log q_e + k_1 t / 2.303 \quad (4)$$

Where q_e and q_t are the amount of adsorbate adsorbed at equilibrium and time t respectively. k_1 is the pseudo-first order rate constant. The constants q_e and k_1 were calculated from the intercept and slope of the plot of $\log(q_e - q_t)$ versus t (Akporie and Adebowale, 2015).

The linear form of the pseudo-second order kinetic equation is thus:

$$t/q_t = 1/V_0 + 1/q_e \quad (5)$$

$$V_0 = k_2 q_e^2 \quad (6)$$

Where V_0 (mg/g.min.) is the initial adsorption rate, K_2 is the pseudo-second order rate constant of adsorption and, q_e represents the amount of heavy metal adsorbed at equilibrium (mg/g). The constants q_e

and k_2 were calculated from the slope and intersection respectively of the plot of t/q_t versus t (Akporie and Adebowale, 2015).

Results and Discussion

Adsorption Isotherms

The Langmuir and Freundlich isotherm plots for Pb, Ni, Cr and Zn uptake by CPDA are shown in Figures 1a-1d. and the corresponding isotherm constants are presented in Table 2. The Freundlich isotherm had the least sum of squared errors (SSE) values and thus provided a better fit for the experimental data. The value of $1/n$ was less than 1 for all the metals studied, thus indicating favourable adsorption (Foo and Hameed, 2010). The maximum monolayer adsorption capacities of Pb, Zn, Ni and Cr were 50.95, 47.78, 44.72 and 22.26 mg/g respectively. Hence the order of selectivity of metal ions was $Pb > Zn > Ni > Cr$.

Table 2: Langmuir and Freundlich isotherm constants

Metals	Langmuir Constants			Freundlich Constants			
	q_m	b	SSE	n	$1/n$	k	SSE
Zn	47.7761	0.0183	0.0838	1.415	0.8734	1.4995	-0.2411
Cr	22.2683	0.1276	3.6745	6.974	0.1434	3.856	-0.0745
Pb	50.9518	0.0165	1.422	1.3645	0.7329	1.3645	-0.4625
Ni	44.7232	0.0104	1.2468	1.414	0.7072	0.9517	0.416

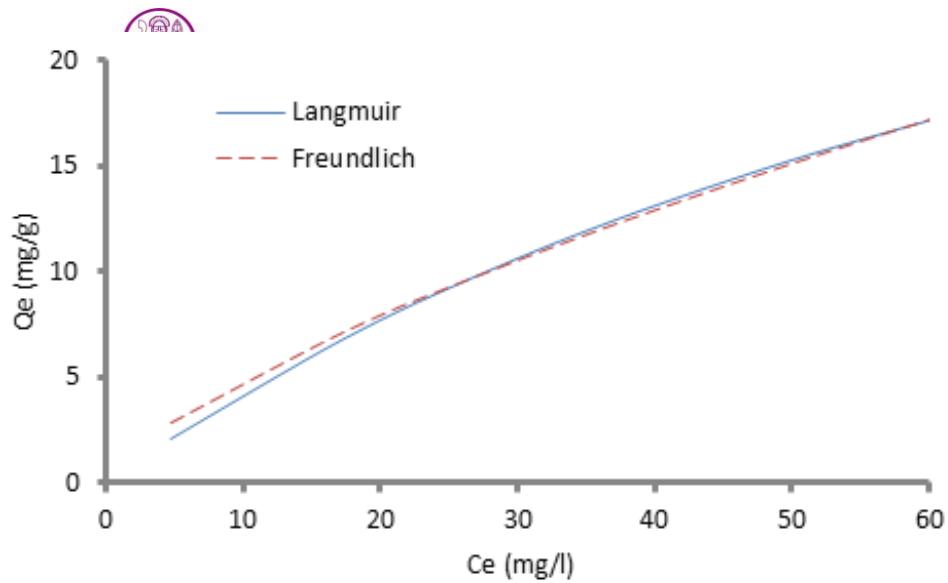


Figure 1a: Langmuir and Freundlich isotherm models for lead uptake by CPDA:
($pH=4$, $t=60\text{mins}$)

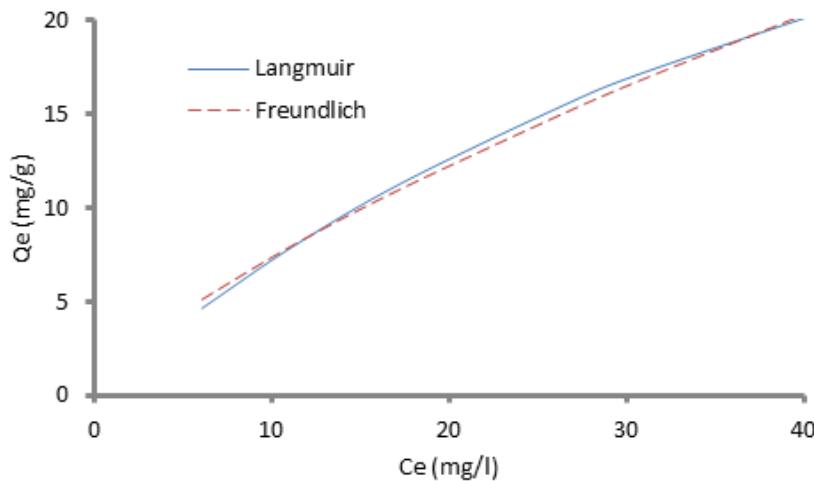


Figure 1b: Langmuir and Freundlich isotherm models for cadmium uptake by CPDA: ($pH=4$, $t=60\text{mins}$)

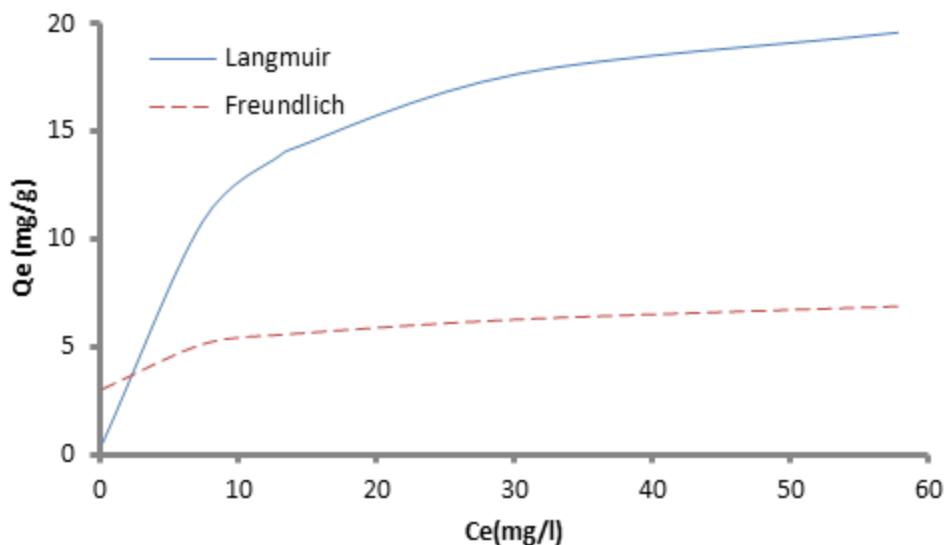


Figure 1c: Langmuir and Freundlich isotherm models for chromium uptake by CPDA: ($pH=4$, $t=60\text{mins}$)

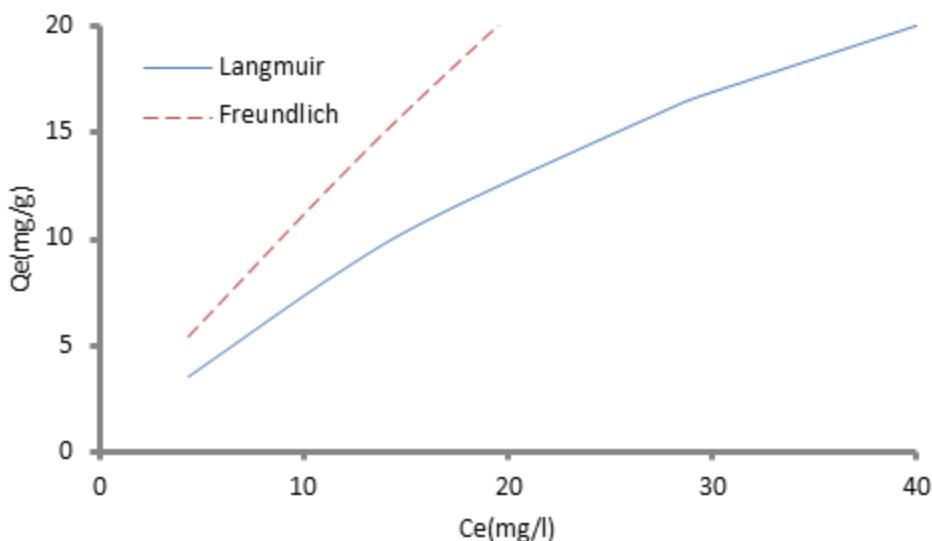


Figure 1d: Langmuir and Freundlich isotherm models for zinc uptake by CPDA: ($pH=4$, $t=60\text{mins}$)

Adsorption Kinetics

The adsorption kinetics describes the rate of uptake of metal ions and provides insight into the mechanisms of adsorption. The pseudo-first and second-order kinetics plots are shown in Figures 2 and 3. The kinetic rate constants obtained are presented in Table 3. The results indicate that the uptake of Pb and Cr followed the pseudo-first order kinetic model. This is based on their higher R^2 values. This indicates that the interaction between the metal ions and the adsorbent is reversible, as the ions can be easily desorbed (Sen Gupta and Bhattacharyya, 2011).

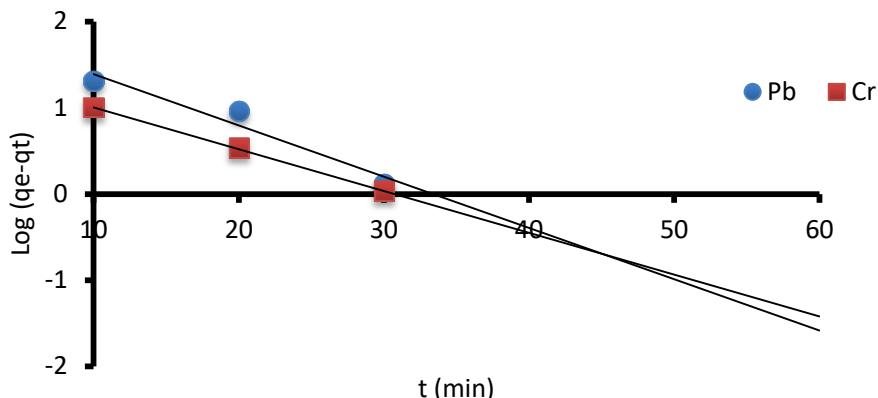


Figure 2: Pseudo-first order kinetic plots for Pb and Cr uptake by CPDA ($C_0=250\text{mg/l}$ $\text{pH}=4$)

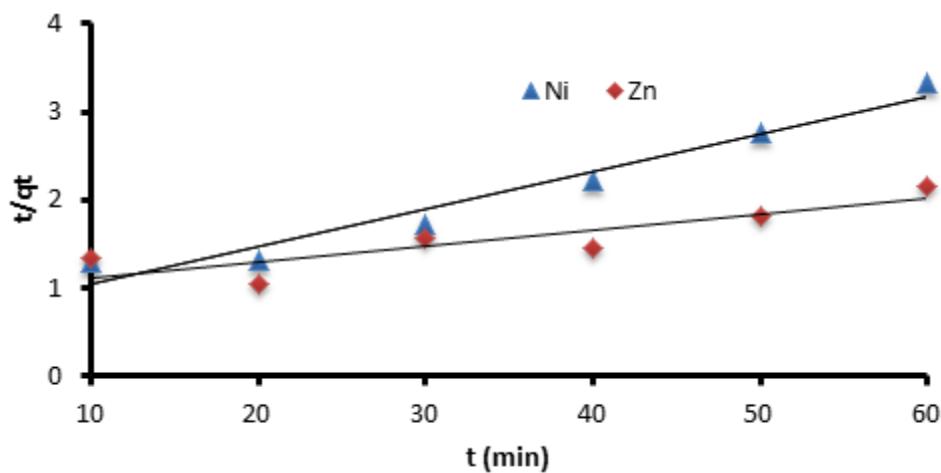


Figure 3: Pseudo-second order kinetic plots for Ni and Zn uptake by CPDA ($C_0=250\text{mg/l}$, $\text{pH}=4$)



The adsorption of Ni and Zn was best described by the pseudo-second order model which is based on the assumption that chemisorption may be the rate limiting step (Sen Gupta and Bhattacharyya, 2011).

Table 3: Pseudo-first and pseudo-second order kinetic rate constants

Metals	Pseudo-first order		Pseudo-second order		
	K _I	R ²	K ₂	q _e	R ²
Ni	-0.065	0.992	0.012	1.073	0.204
Pb	-0.059	0.946	0.02	0.592	0.874
Cr	-0.042	0.999	0.043	0.882	0.928
Zn	-0.185	0.75	0.185	0.926	0.75

Conclusion

The isotherm and kinetic parameters for the removal of selected metal ions from single component synthetic leachate solutions has been presented. The Freundlich isotherm provided a better fit for the experimental data, based on the lower sum of least square errors and 1/n was less than 1 which indicated favourable sorption. The maximum monolayer adsorption capacities for Pb, Zn, Ni and Cr were 50.95, 47.78, 44.72 and 22.26mg/g respectively. Kinetic modelling revealed that the pseudo first order kinetic model had a better correlation with the experimental data. The results suggest that cassava waste may potentially be developed, further tested and used in the treatment of landfill leachate.

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