

Equilibrium and Kinetics of Adsorption of Ni (II) and Pb (II) Ions on Cow Bone ASH

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Abstract: The adsorption capacity of cow bone ash for Ni (II) and Pb (II) ions in aqueous solution was studied as functions of initial metal ion concentration and time in a batch system. Results showed that adsorption increased with Ni (II) and Pb (II) concentration. Adsorption isotherms such as Langmuir, Freundlich, Dubinin-Radushkevich, Harkins-Jura and Henry's isotherms were applied to the adsorption data. Isotherm parameters showed that the data for Ni (II) sorption was better correlated than Pb(II) data. Ni (II) sorption correlated at 0.986, 0.945, 0.903, 0.884 and 0.768 for Langmuir, Freundlich, Harkins-Jura Dubinin-Radushkevich and Temkin isotherms respectively. The maximum adsorption capacity was found to be 0.079mg/g and 0.236 mg/g for Pb(II) and Ni(II) respectively. The kinetic behaviour of Ni (II) and Pb (II) ions towards the adsorbent was studied with two rate models: pseudo first-order and pseudo second-order equation. The pseudo-first order rate model fitted the Pb (II) sorption ($R^2 = 0.941$) while the pseudo second order rate model correlated the Ni (II) data ($R^2 = 0.999$). Maximum percent removal efficiency was 99.5% at 50 minutes for Pb (II) while that of Ni (II) was 32.83% at 60 minutes.

Keywords: adsorption isotherms, sorption kinetics

1. Introduction

Separation science and technology taken as an aspect of environmental safety and control may not have a terminal date in the pursuit of better and cheaper methods even as aqueous end-of-pipe industrial effluents may have no expiry dates. It is a subject that will continue to draw the attention of investigators as no single method of pollutant removal and remediation may be unilaterally applied to both organic and inorganic effluents. The fact that heavy metals are not ecologically friendly is longer a new information and the pursuit of their elimination, removal or remediation add to the weight of the investigations on their separation. Several competing technologies for heavy metal removal or remediation exist: high gradient magnetic separation (Anand et al., 1985) super critical fluid extraction (Murphy and Erkey, 2004), electrocoagulation (Golder et al., 2007), ion exchange (Lin and Juang, 2008), micellar enhanced ultrafiltration (Kim et al., 2008). However, high capital investment and operational cost puts the suitability of some of these methods outside of industrial scale applications. Adsorption as a technique of fluid phase separation has been applied to a large extent using synthetic, agricultural and vegetable materials. This technique has proved to be very effective and versatile for heavy metal removal even at very low concentrations.

2. Materials and Methods

The main material used for this work was cow bone ash. Cow bones (femur and humerus) were collected from Amassoma, Nigeria. The bones were thoroughly washed with distilled water and sun-dried for a week. They were oven-dried for 48 hours at 200°C. They were then crushed and ground into powder and sieved into particle size of 335 µm. Bone powder was activated with 25% concentrated solution of zinc chloride by soaking it in the solution for 20 – 24 hours. It was allowed to drain for 1 hour and rinsed repeatedly in distilled water. The rinsed sample was thereafter dried in the oven.

Equilibrium Studies

Adsorbate working solutions of Pb (II) and Ni (II) ions were prepared from stock solutions of 1000 ppm of lead nitrate and nickel nitrate respectively. Batch adsorption experiments were carried out by shaking 1.00g of activated cow bone ash with 10 mL of metal ion solutions of 20, 30 40 and 60 ppm at 150 rpm for minutes. The mixture was filtered and the residual concentrations of Pb (II) and Ni (II) ions were determined with an atomic absorption spectrophotometer (AAS).

Time Dependent Studies

1.00g of activated cow bone ash was added to 10 mL of 60 ppm of metal ion solutions in five pre-cleaned glass vials. The mixtures were shaken at 150 rpm for different time intervals of 10, 20,30,40,50 and 60 minutes respectively. The mixtures were filtered and the residual concentrations of Pb (II) and Ni (II) ions were determined with an atomic absorption spectrophotometer (AAS).

3. Results and Discussion

Effect of initial metal ion concentration

The effect of initial metal ion concentration on the adsorption capacity of cattle bone ash is shown in fig. 1. The data plot shows that sorption capacity increased with increase in initial metal ion concentration, an indication of available binding sites as the concentration gradient is increased (Altaher and ElQada, 2011). This observation is in line with the reports of other investigators adsorption of plant materials. The results also show that the adsorption of Ni (II) was greater than Pb (II) on the same adsorbent at higher concentrations of the metal ions. Ionic radius, nature of anions and affinity for active groups on biomass are ascribed as some of the factors that enhance differential sorption (Ho et al; 1995). According to Horsfall and Spiff,(2005), the element with smaller ionic radius will compete faster for exchange sites than those of larger ionic radius. Ni²⁺ has a radius of 0.69Å, while that of Pb²⁺ is 1.20Å: thus the smaller Ni²⁺ is expected to preferentially

take more exchange sites than Pb^{2+} . However, the percent sorption places Pb^{2+} above Ni^{2+} at a maximum of 99.25% against 31.85%. This observation follows from the reason of higher tendency of the smaller ion to persist in solution as the larger ion then has more access to sorbent sites. The effect of the nature of the anion of the metal for a differential adsorption will be the same because both metals have the same anion, NO_3^- .

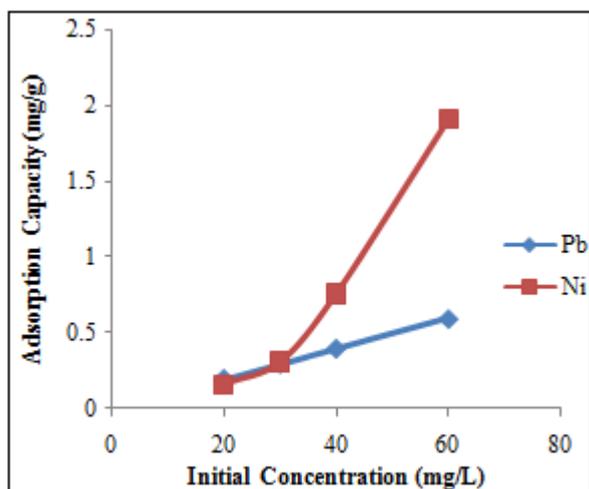


Figure 1: Effect of initial concentration on the adsorption of Ni (II) and Pb (II) on bone ash.

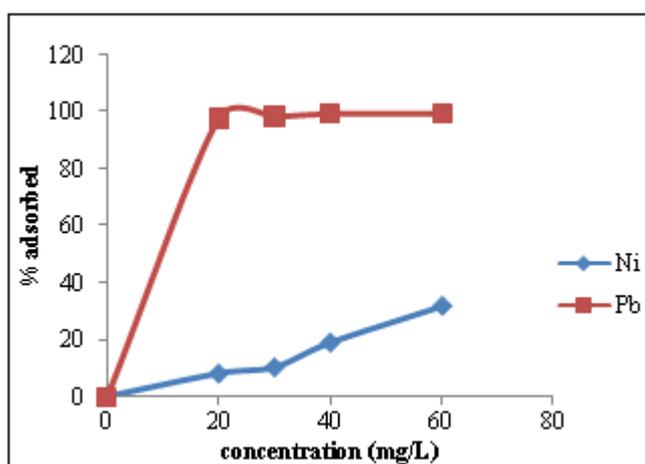


Figure 2: Effect of contact time on the % Removal of Ni (II) and Pb (II) by cow bone ash

Sorption capacity

The extent of adsorption was estimated using some equilibrium isotherms, namely: Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Harkins-Jura. These are shown in figure 1 and 2 for the two metal ions studied. With the exception of the Temkin, all other four isotherms used to fit the experimental data gave correlation values above 0.9 for Ni (II) ions. The high correlation values indicate the validity of the sorption operations for which the isotherms represent. The best fitting and the most applicable of the isotherms is the Langmuir isotherm for Ni (II) with a linear regression (R^2) value of 0.985. The Langmuir isotherm assumes a sorption on a homogenous surface at monolayer coverage without interaction with sorbed molecules. Monolayer sorption is classified as chemisorption; hence the uptake of Ni (II) ions on cattle bone ash is dominated by chemisorption. The linearized form of the Langmuir

equation used to estimate the sorption of Ni (II) ions is the type II, expressed in (1) as:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (1)$$

where,

K_L = Langmuir isotherm constant (L/g);

q_m = Langmuir monolayer sorption capacity (mg/g).

A plot of $1/q_e$ against $1/C_e$ was made to confirm the Langmuir isotherm.

To further establish the favourability of the Langmuir isotherm, the dimensionless separation factor, S_F was used for the data. The equation is given as (2)

$$S_F = \frac{1}{1 + K_L C_0} \quad (2)$$

where :

C_0 is the initial concentration of dye solution (mg/L) and

K_L is the Langmuir constant (L/g).

The favourability of the sorption is guided by the following: unfavourable if $RL > 1$, linear if $RL = 1$, irreversible if $RL = 0$, and favourable if $0 < RL < 1$. The plot of S_F values for Ni(II) and Pb(II) sorption is shown in figure 4. From the plot, it could be seen that the isotherm was favourable for Ni (II) and unfavourable for Pb(II) which was negative.

The isotherms are plotted with the experimental data to show the fit of the isotherm models at varying levels of initial metal ion concentration. As shown in figures 2 and 3, the linearity of the data fit in the models are better for Ni(II) than for Pb(II) which has a linear fit for only the experimental data. The rest of the isotherms are poorly fitted in the Pb(II) plot.

Freundlich isotherm assumes a sorption on a heterogeneous surface with sites having different energy of adsorption (Weber and DiGiano, 1996; Walker, 1995, in Altaher and ElQada, 2011). The linear form of the equation applied to data is as in (3):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where:

K_F = Freundlich constant (mg/g) and

n = adsorption affinity or heterogeneity factor.

The K_F value is related to the adsorption capacity; while $1/n$ value is related to the adsorption intensity. The value of n indicates the affinity of the sorbent for the sorbate and hence the favourability of the sorption. According to Kadirvelu and Namassivayan (2000), n values between 1 and 10 indicate a beneficial adsorption. From the data, the affinity factor of 0.3247 and - 0.6365 for Ni (II) and Pb (II) respectively, are low values: favourability in terms of this isotherm is therefore very low.

The correlation value for the D-R isotherm was fair for Ni(II) and poor for Pb(II), but the apparent energy, E , of adsorption below 40 kJ/mol is indicative of a dominant physisorption process (Horsfall et al., 2004).

The Temkin model was tested to confirm the fall in the heat of adsorption as the initial concentration increased. The respective correlation values for Ni (II) and Pb (II) at 0.768

and 0.346 indicate a low conformation of the data with the sorption model.

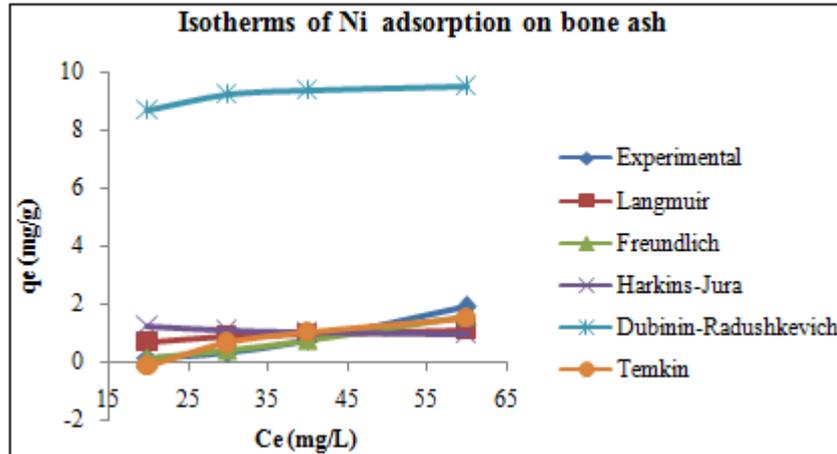


Figure 3: Isotherm plots for the adsorption of Ni(II) ions on bone ash

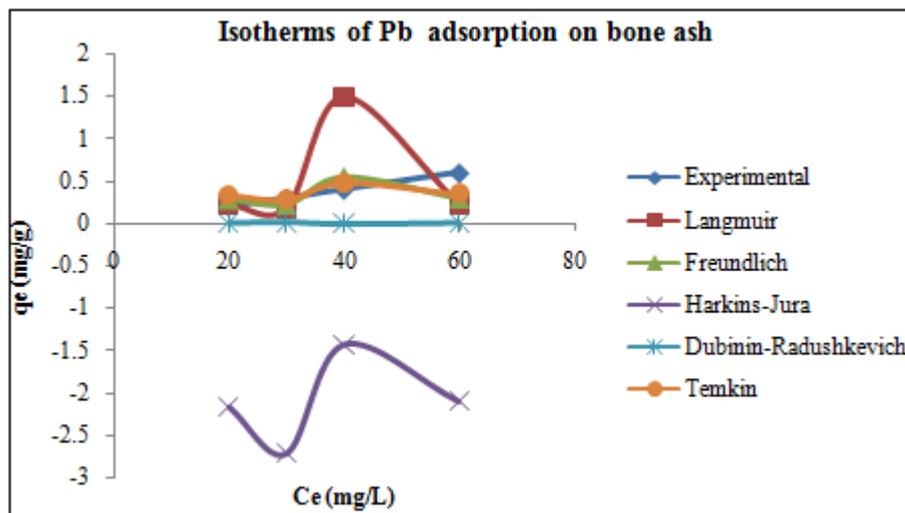


Figure 4: Isotherm plots for the adsorption of Pb(II) ions on bone ash

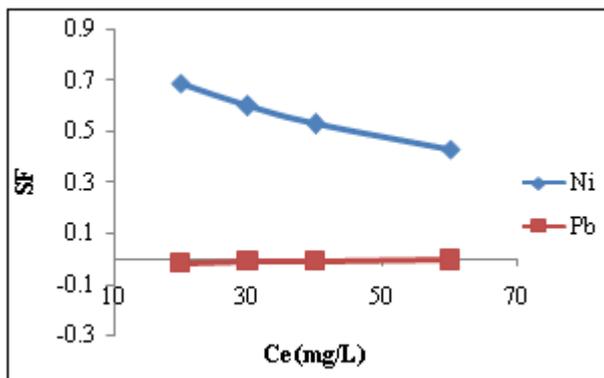


Figure 5: Separation factor profile for the adsorption of Ni (II) and Pb (II) on bone ash as a function of metal ion concentration

Table 1: Isotherm parameters of adsorption of Ni (II) and Pb (II) on bone ash

Isotherms/Parameters	Ni (II)	Pb (II)
Langmuir		
q_{max} (mg/g)	- 0.2355	0.0791
K_L or b	0.02216	- 3.462
R^2	0.986	0.532
Freundlich		
K_F (mg/g)	1.74×10^{-5}	0.0837
n	0.3247	- 0.6365
R^2	0.945	0.573
Temkin		
A (L/g)	0.05157	0.8407
B (mg/L)	2.051	- 0.349
b_T (J/mol)	1228.25	- 7218.17
R^2	0.768	0.346
Dubinin-Radushkevich		
q_D (mg/g)	9.7279	0.01972
B_D (mol ² /kJ ²)	0.016	- 0.00045
E (kJ/mol)	5.5902	- 33.33
R^2	0.884	0.5402
Harkins-Jura		
A	0.00896	0.03135
B	1.5654	0.7373
R^2	0.903	0.102

Table 2: Kinetic parameters of adsorption of Ni (II) and Pb (II) on bone ash

Type	Parameters	Metal ions	
		Ni(II)	Pb(II)
Pseudo-first order	q_e (mg/g)		0.8871
	K_1	N/A	- 0.03224
	R^2		0.980
Pseudo-second order	q_e (mg/g)	0.4098	
	K_2	30.85	N/A
	R^2	0.999	
Intraparticle diffusion (external film)	X_i		- 2.738
	K_1	N/A	1.084
	R^2		0.980

Key: N/A = Not applicable

Effect of contact time

The quantity of Pb(II) ions adsorbed increased with time within the limit used to a maximum of 99.50%, while that of Ni(II) ions was at maximum of 33.33%. Smaller sized ions are more hydrolyzed in aqueous solution than heavier ones (Horsefall,2005), hence Ni(II) ions may persist longer in solution as the larger Pb(II) ions has greater accessibility to the surface of the sorbent. Figures 5 and 6 show the result for the effects of contact time on the adsorption of Ni (II) and Pb (II) on bone ash

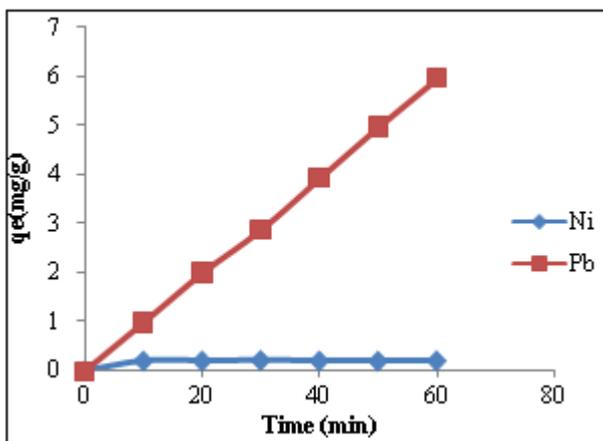


Figure 6: Effect of contact time on the quantity of Ni (II) and Pb (II) adsorbed on cow bone ash

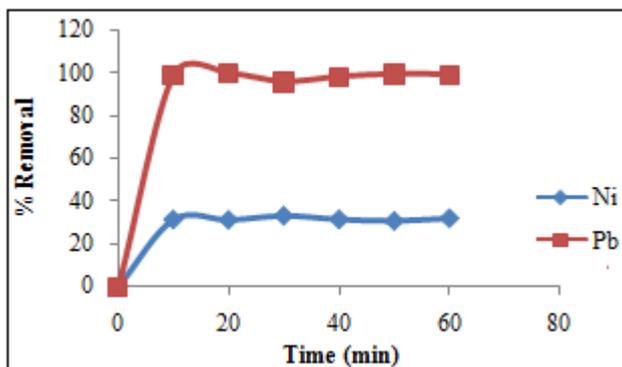


Figure 7: Effect of contact time on the % Removal of Ni (II) and Pb (II) by cow bone ash

Sorption kinetics

The kinetic behaviour of the metal ions towards the adsorbent was studied using two rate models: pseudo-first order and pseudo-second order. The pseudo-first order model as given by Lagergren takes the form 4:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{4}$$

The pseudo-second order equation as given by Ho *et al.*, (1995) is expressed as 5:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where q_e and q_t are the amounts of metal ion on the adsorbent at equilibrium and at time "t" respectively. k_1 and k_2 are the rate constants (g/mg-min) of pseudo-first order and pseudo-second order adsorption respectively. While the pseudo-first order model applied to Pb (II) data correlated at $R^2=0.945$, the pseudo-second order correlated the Ni (II) sorption data very well at $R^2=0.999$. This could only mean that they were the controlling kinetics of the respective metal ions adsorption on the sorbent. The intraparticle diffusion by external film mechanism was tested using equation 6. This equation is given as:

$$q_t = X_i + k_1 t^{0.5} \tag{6}$$

Where, X_i is the boundary layer diffusion effects and K_1 is the rate constant for intraparticle diffusion.

The diffusion model was only correlated to the data of Pb(II) sorption; there was no correlation for the Ni(II) sorption data. The indication of this correlation at $R^2 = 0.980$ could mean that the controlling diffusion of the Pb(II) sorption was the external film diffusion. This result is shown in figure 9.

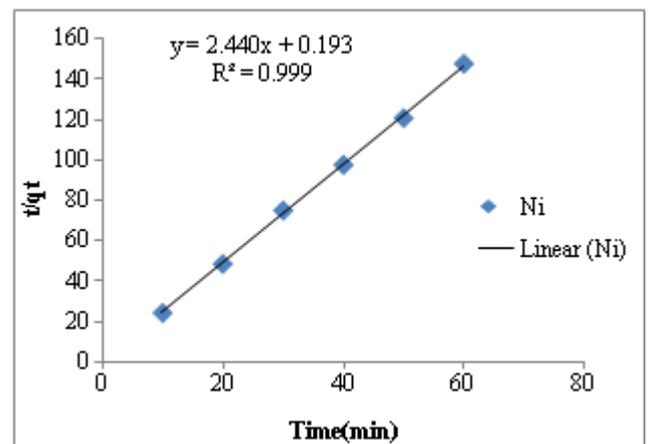


Figure 8: Pseudo-second order plot of adsorption of Ni (II) ions on bone ash

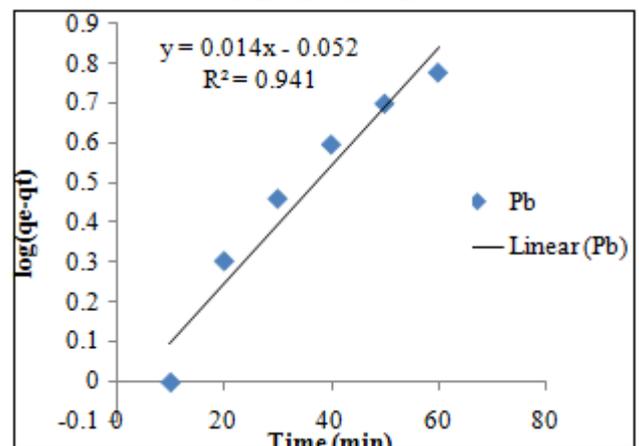


Figure 9: Pseudo-first order plot of adsorption of Pb (II) ions on bone ash

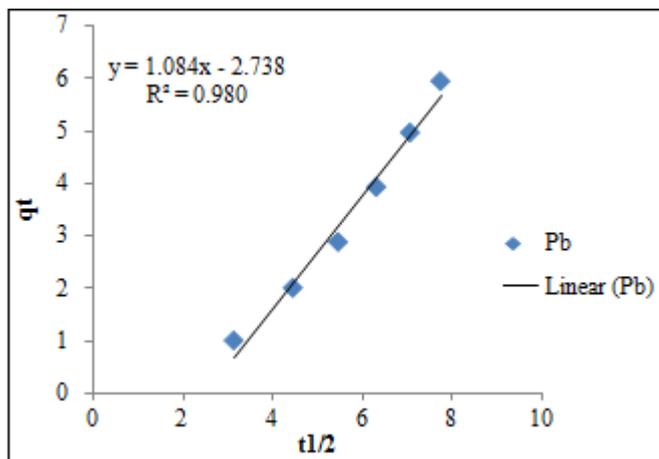


Figure 10: Plot of intraparticle diffusion for the Pb(II) ions adsorption on cow bone ash

4. Conclusion

The equilibrium sorption study showed a high percent removal efficiency of Pb(II) ions by cow bone ash at a maximum of 99.26%: the kinetic equivalent also put the percent removal efficiency of Pb(II) ions at a maximum of 99.50 at 50 minutes. The equilibrium isotherms applied to the experimental data fitted in the order: Langmuir > Freundlich Dubinin-Raduskevich > Temkin for Ni(II) ions: correlation of data was poor on these isotherms for Pb(II) ions. Adsorption kinetics followed pseudo-second order kinetic model for Ni (II) ions and pseudo-first order kinetic model for Pb(II) ions. Kinetic results also showed that intraparticle diffusion (external film) was the controlling adsorption mechanism.

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