

Kinetic Modeling for Removal of Pb, Cd, Ni, and Cr Ions from Petrochemical Effluent using Termite Soil

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Abstract: Increase in concentration of heavy metals ions in our water bodies is of great concern. This work is aimed at providing an environmental and cost effective adsorbent for the removal of Pb, Ni, Cr and Cd from petrochemical effluent. Termite soil was pretreated and used for the sorption process and process parameters such as contact time and particle size of the adsorbent was varied. Optimum contact time of 60 minutes was obtained for Pb and Cd ions while 40 minutes was obtained for Ni and Cr ions for all particle sizes of adsorbent used. Initial reaction rate $H(\text{mg/g}\cdot\text{min})$ was of the order for the different particle sized adsorbent, 75mm: $\text{Pb} > \text{Cd} > \text{Cr} > \text{Ni}$, 212mm: $\text{Cd} > \text{Pb} > \text{Cr} > \text{Ni}$ and 300mm: $\text{Cd} > \text{Pb} > \text{Ni} > \text{Cr}$. Pseudo first order kinetics had less difference between experimental and theoretical adsorption capacity ($Q_a - Q_b$) with R^2 close to that obtained for Pseudo-second order kinetics. Hence it is considered as the kinetic order for the adsorption process. Percentage of the studied ions removed from the wastewater solution shows the suitability of the adsorbent sequestering of heavy metal ions from industrial wastewater.

Keywords: Batch adsorption, heavy metals, petrochemical effluents, termite hill

Introduction

Water is an indispensable natural resource that is vital for life. However, it is difficult to find it in pure form due to human activities. European Public Health Alliance (2009) reported that greater percentage of the world's populations cannot find clean water. Rain water and sewage water pollution, industrial discharged effluents are major sources of water pollution. Polluted water consists of industrial discharged effluents, sewage water and rain water pollution (Ashraf *et al.*, 2010). In Nigeria, today, it has been reported that wastewater from industrial effluents containing heavy metals most especially liquid in the form of wastewater or effluents into water ways or bodies (Ashraf *et al.*, 2010). The deterioration of aquatic animals has occurred due to improper discharge of industrial effluents containing heavy metals have been a global concern. Heavy metals can easily enter the food chain because of their high solubility in water. These non-biodegradable species have been proven hazardous and tend to cause a number of health problems, diseases and disorders (WHO, 2006).

Different convectional techniques have been adopted for sequestering of heavy metal ions in wastewater, such as chemical precipitation, coagulation, ion exchange, oxidation, electro dialysis, membrane separation, solvent extraction, photocatalytic reduction and adsorption methods (El-Ashtoukly *et al.*, 2008). Application of the above conventional methods can be expensive, prohibitive for developing economy and most times do not effectively remove polluting metals (Bassey *et al.*, 2014), thus it becomes imperative to search for cheap and alternative means and bio-sorbents lately have become of considerable interest. The use of indigenous biodegradable resources for treating hazardous waste would be less expensive and more effective (Okieimen and Wuana, 2007; Tarawouet *et al.*, 2007 and Dilek and Ozgur, 2008). Adsorption becomes a preferred choice than other physico-chemical techniques of heavy metal remediation due to its simplicity, cheap, easy to scale-up and most importantly able to remove low concentration substance even at part per million levels with high efficiency (Kurniawan *et al.*, 2006). Recently, different researcher such as Muhammad and Wahabi (2011), Ademiluyi and Ujile (2013), Dada *et al.*,

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(2013) and Agbozu and Emoruwa (2014) had applied adsorption as a technique for heavy metal removal. Hence this research is aimed at investigating the adsorption capacity of different particle sized termite hill biomass for the removal of toxic heavy metal ions: Pb, Fe, Ni, and Cr ions from a petroleum industry effluent.

Materials and Method

Termite moundsoil was sampled in Federal University of Petroleum Resources Effurun at Uvwie Local Government Area of Delta State, Nigeria. The soils samples were collected using soil auger 5.0cm deep into the surface soil. The sampled soil was then air-dried in the laboratory at room temperature for 5 days and crushed in a mortar. The milled mound was then sieved into different particle sizes (75mm 212mm and 300mm) and was used for subsequent experiments. This fraction was pretreated to remove non-clay material such as carbonate and quartz minerals in order to concentrate the active minerals and improve the sorption property of the adsorbent. The biomass was treated with 0.1M HCl for removal

of any trace concentration of the studied heavy metal ions.

Wastewater Sampling

Wastewater effluent was collected from Warri Refinery and Petrochemical Company (WRPC) and was stored in Five Liters (5L) polyethylene container and 0.1 M Trioxonitrate (V) acid was added to the mixture.

Batch adsorption technique as reported by Agbozu and Emoruwa (2014) was adopted and modified for all process parameters in this study. Batch adsorption process was carried out at room temperature. Process parameters such as particle size, contact time, and adsorbent dose were varied in order for optimization. 40ml of wastewater was introduced and allowed to remain in the packed column as shown in Figure 1 for the studied contact time (20, 40 and 60 minutes). Thereafter, the filtrate was collected for metal analysis determination.

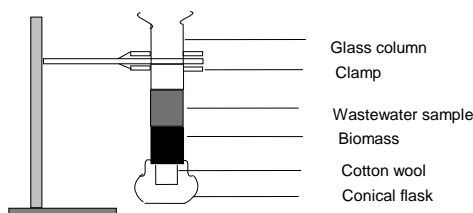


Figure 1: Batch Adsorption Process

The sorption capacity Q_e (mg/g) and removal efficiency Q were obtained according to equations 1 and 2 respectively.

$$Q_e = \frac{(C_0 - C_e)v}{m} \dots\dots\dots 1$$

$$Q = \frac{(C_0 - C_e) \times 100}{C_0} \dots\dots\dots 2$$

Where v (L) is the volume of the solution, m (g) is the amount of adsorbent; C_0 and C_e are the initial and final concentration of the metal ions in the solution before and after adsorption (Nassar, 1997).

Kinetics Modeling

These include; pseudo-first order and pseudo-second order models which considers that the rate of occupation of the biosorption sites is proportional to the unoccupied site (Ertugay and Bayhan, 2008).

The expression for the Lagergren pseudo-first order model

$$\text{Log} (Q_e - Q_t) = \text{log} Q_e - \frac{K_1 t}{2.303} \dots\dots\dots 3$$

Where, K_1 is the Lagergren rate constant for adsorption (min^{-1})

Q_t is equilibrium concentration of metal ion in solution at a particular time in (mg/g)

The Lagergren pseudo-second order kinetic model

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \dots\dots\dots 4$$

K_2 is equilibrium rate constant of second order kinetics model (g/mg/min).

Intra-particle diffusion model

$$Q_t = K \sqrt{t} + C \dots\dots\dots 5$$

Where C is the boundary layer or thickness of the adsorbent

Results and Discussion

Figures 2, 3 and 4 gives plot for various percentages of metal ions sequestered. Initial increase in metal ion removal is due to the availability of adsorption sites at the start of the reaction. Optimum percentage removal of Ni and Cr ions occurred for all the particle size used at 40 minutes contact time while for Pb and Cd ions occurred at 60minutes. This is not surprising as in adsorption process, metal ions from the bulk solution travels to the thin film surrounding the adsorbent, during the process; the thin film in the liquid generates an impermeable membrane for the metal ion to pass through (Kannan and Sundaram,

2001). This in turn increases the time profile of the metal ion uptake by the adsorbent. Ni and Cr ions which have reduced atomic size compared to Pb and Cd ions travels faster to the surface of the adsorbent. Reduction in percentage sequestering of Ni and Cr ions occurred due to desorption of the ions into the solution. Also difference in ionic sizes causing competition among them on the adsorption sites affected percentage removal of Ni and Cr ions compared to Pb and Cd ions as seen from Appendix 2,3 and 4. Similar results were reported by Abia and Igwe (2005).

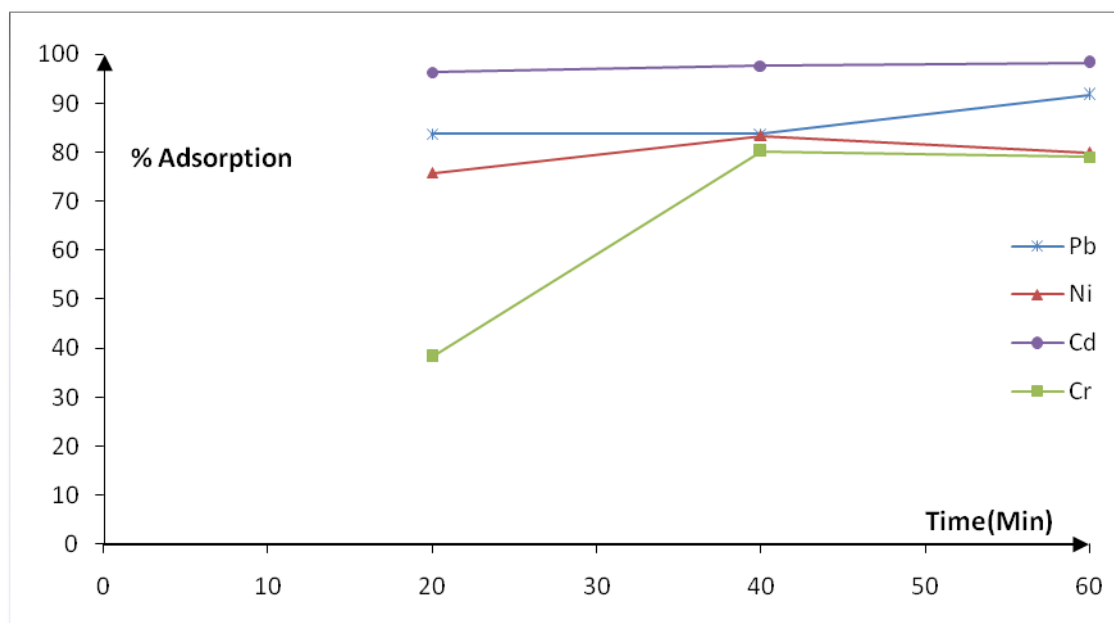


Figure 2: Percentage removal of Cu, Pb, Fe, Ni, Zn and Cr ions using 75mm particle mesh size adsorbent

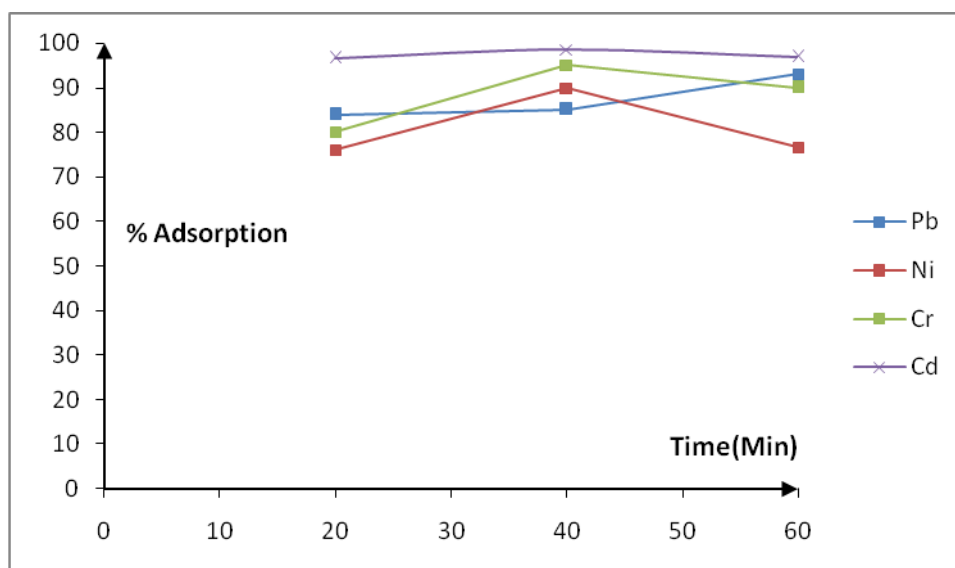
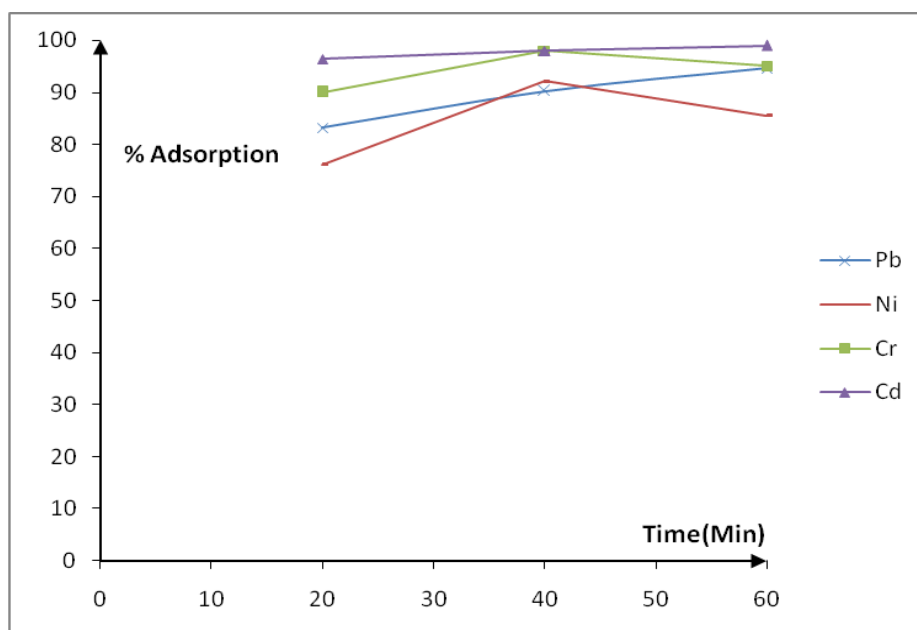


Figure 3: Percentage removal of Cu, Pb, Fe, Ni, Zn and Cr ions using 212mm particle mesh adsorbent**Figure 4: Percentage removal of Cu, Pb, Fe, Ni, Zn and Cr ions using 300mm particle mesh adsorbent**

Tables 1 and 2 give parameters for pseudo-first and pseudo-second order kinetics of Pb, Ni, Cr and Cd adsorption. The slopes and intercepts of plots of $\log(Q_e - Q_t)$ versus t were used to determine the first-order rate constant K_1 and equilibrium adsorption capacity (theoretical adsorption capacity) Q_b . $Q_a - Q_b(E_{ABS})$ values obtained showed the closeness of experimental adsorption capacity using 300mm particle mesh size adsorbent. This probably occurred due to better surface area of the adsorbent. Intercept from the plot of t/Q_t versus t was used in estimating the value of h (initial reaction rate). The results revealed that Pb and Cd tend to have higher initial

reaction rate compared to other ions. Although this process tends to be high initially, but gradually became slower with passage of time as the reaction proceeded. This can be seen from their various rate constant k (s^{-1}) for Pb and Cd: (0.230×10^{-3} and 0×10^{-3} for 75mm particle size), (9.212×10^{-3} and 0×10^{-3} for 212mm particle size) and (4.606×10^{-3} and 0×10^{-3} for 300mm particle size). Rate constant k (s^{-1}) for Ni and Cr is appreciable higher for particle size studied causing positive change of their initial concentration, depicting increase in their movement to the surface of the adsorbent.

Table 1: Pseudo-first order parameters

Parameters	75 mm				212mm				300mm			
	Pb	Ni	Cr	Cd	Pb	Ni	Cr	Cd	Pb	Ni	Cr	Cd
R^2	0.850	0.960	0.996	0.911	0.789	0.938	0.545	0.809	0.988	0.692	N/R	0.952
$Q_a \times 10^2$	1.029	0.308	0.06	1.067	0.949	0.263	0.06	1.085	0.984	0.316	0.06	1.08
$Q_b \times 10^3$	0.654	0.149	0.7413	1.01	1.361	0.721	0.047	10.06	6.36	0.545	0.062	10.0
$K_1 \times 10^3$	0.230	9.212	9.212	0	9.212	2.303	4.414	0	4.606	5.527	5.228	0
$Q_a - Q_b(E_{ABS}) \times 10^2$	0.964	0.293	0.189	0.966	0.813	0.191	0.055	0.079	0.348	0.262	0.054	0.080

Q_a and Q_b are experimental and theoretical adsorption capacity in mg/g

Table 2:Pseudo-second order parameters

Parameters	75 mm				212mm				300mm			
	Pb	Ni	Cr	Cd	Pb	Ni	Cr	Cd	Pb	Ni	Cr	Cd
R ²	0.983	0.984	1.000	0.970	0.744	0.876	0.992	0.891	0.942	0.939	N/A	0.942
Q _a x10 ²	1.029	0.308	0.06	1.067	0.949	0.263	0.06	1.085	0.984	0.316	0.06	1.08
Q _b x10 ³	0.034	0.069	0.019	0.015	1.06	0.272	1.67	0.125	0.235	0.202	0	0.090
H x10 ⁴	2.52	1.19	1.6	2.3	1.99	1.54	1.62	7.2	2.35	1.12	0	4.98
Q _a -Q _b (E _{ABS}) x 10 ²	1.03	0.301	0.0581	1.0655	0.843	0.2358	0.433	1.073	0.605	0.296	0.060	1.0791

H: initial reaction rate in (mg/g.min)

Q_a and Q_b are experimental and theoretical adsorption capacity in mg/g

N/A: not applicable

Table 3 give parameters for intra-particle diffusion of metal ions. Intra-particle kinetics gives an idea of the penetrating capacity and movement of ions into the micropores structure of the adsorbent. It is observed that for all the metal ions studied boundary layer C is negligible. These greatly influence the uptake of the metal ions through the boundary layer of the adsorbent as shown in figures 2, 3 and 4

above. According to Itodo et al., (2009), non deviation of plot of Q_t against √t from the origin signifies superiority of intra-particle process over film adsorption. Since the value of C is insignificant it shows there was intra-particle transport of the metal ions and movement occurred through the particle-sample interface. Similar result was reported by Badmus et al. (2007).

Table 3: Intra-particle diffusion order parameter

Parameters	75 mm				212mm				300mm			
	Pb	Ni	Cr	Cd	Pb	Ni	Cr	Cd	Pb	Ni	Cr	Cd
C	0.000	0.000	0.000005	0.000005	0.001	0.001	0.000	0.000	0.003	0.002	0.000	0.000
R ²	0.933	0.994	0.812	0.443	0.005	0.715	0.391	0.797	0.972	0.999	0.002	0.998

Conclusion

Petrochemical effluents are a major source of heavy metals into the environment. Process parameters such as contact time and mesh size of adsorbent was varied. At various contact time, the following order of percentage removal was obtained at 20,40 and 60 minutes respectively for 75 mm: Cd>Pb>Ni>Cr; for 212mm: Cd>Pb>Cr>Ni, Cd>Cr>Ni>Pb and Cd>Pb>Cr>Ni, for 300mm: Cd>Cr>Pb>Ni, Cd>Pb>Ni>Cr and Cd>Pb>Cr>Ni. Percentage removal of the studied metal ions at various optimum time is of the order Cd>Pb>Ni>Cr for 75mm particle size, Cd>Pb>Cr>Ni for 212mm particle size and Cd>Cr>Pb>Ni for 300mm particle size. Particle size of 300mm used showed better removal of the ions due to large surface area. Percentages of various metal ions sequestered from the natural wastewater solution shows a great potential for its use in industrial fixed beds reactor for treatment of their wastewater.

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APPENDIX

Appendix1. Initial concentration (mg/l) of metal ions in wastewater before treatment process

Pb	Ni	Cr	Cd
1.04	0.343	0.006	1.101

Appendix2. Percentage (%) removal of metal ion from petrochemical wastewater by varying contact time using 75 mm particle size adsorbent

Time	Pb	Ni	Cr	Cd
20	83.8	75.8	38.3	96.3
40	83.4	83.4	80.2	97.6
60	91.7	80.0	79.0	98.3

Appendix3: Percentage (%) removal of metal ion from petrochemical wastewater by varying contact time using 212 mm particle size adsorbent

Time	Pb	Ni	Cr	Cd
20	83.94	76.09	80.00	96.64
40	85.09	89.80	95.00	98.50
60	93.10	76.67	90.00	96.90

Appendix4: Percentage (%) removal of metal ion from petrochemical wastewater by varying contact time using 300 mm particle size adsorbent

Time	Pb	Ni	Cr	Cd
20	83.14	76.00	80.00	96.40
40	90.19	92.12	95.00	98.00
60	95.00	85.54	90.00	98.91