

Kinetic Studies of Periwinkle Shell Hydroxyapatite (PSHAP) for the Removal of Metal Ions in Steel Rolling Mill Wastewater

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Abstract

Heavy metals are one of the major contaminants in industrial wastewater. However, hydroxyapatite from biogenic wastes possesses the ability to chelate heavy metals in water. In this study, hydroxyapatite was produced from periwinkle shell (PSHAP) at different calcination temperatures 400, 500 and 600 °C to remediate heavy metals contaminated steel rolling mill wastewater. Kinetic studies of the sorption performance of PSHAP₄₀₀, 500 and 600 for the removal of Fe, Pb, Zn, Cd, Cu, Cr and Mn from steel rolling mill wastewater were investigated. The result shows the presence of metal ions concentration in the order: Fe > Zn > Mn > Cr > Cu > Pb > Cd. Only Cu and Zn are below USEPA (1999), the Standard Organization of Nigeria (SON) 2007, NESREA (2009), and World Health Organization (WHO) 2011 maximum permissible level of metal ions in wastewater. The sorption behaviour followed a pseudo-second-order model. PSHAP especially calcination at 500 °C with relatively highest values of R², lowest values of X² and Δqt (%) is a promising adsorbent for the remediation of heavy metals from wastewaters.

Keywords: Adsorption, Heavy metals, Contaminants, Periwinkle shell, Hydroxyapatite, Kinetics studies

1. Introduction

The great concern of heavy metals is due to their contrasting toxicity, long-term mobility, bio-availability and non-degradable nature in the environment. They enter the environment through a variety of anthropogenic and industrial activities, poor waste disposal mechanism; and pose serious threats to plants and human health (Kanamadi *et al.*, 2003; Jude and Augustin, 2007). Heavy metals like copper, zinc, nickel, chromium, cadmium and iron have been found in concentrations above acceptable and permissible levels in most industrial wastewaters (Eniola *et al.*, 2010).

The sorption properties of hydroxyapatite (HAP) are of great importance for both environmental and industrial purposes. Hydroxyapatite is an ideal material for long-term containment of contaminants because of its high sorption capacity for actinides and heavy metals, low water

solubility, high stability under reducing and oxidizing conditions, availability and cost-effectiveness (Krestou *et al.*, 2004). HAP has been utilized in the stabilization of a wide variety of metals e.g. Cr, Co, Cu, Cd, Zn, Ni, Pu, Pb, As, Sb, U, and V (Leyva *et al.*, 2001; Fuller *et al.*, 2002; Czerniczyniec *et al.*, 2003). Adsorption in HAP takes place through ionic exchange reaction, surface complexation with phosphate, calcium and hydroxyl groups and/or co-precipitation of new partially soluble phases (McGrellis *et al.*, 2001).

Synthetic hydroxyapatite is an attractive material which has received considerable attention over the past two decades for metal removal. Synthetic hydroxyapatite (HAP) has been extensively studied for its kinetics and chemical reaction with a wide variety of metals e.g. Cr, Cu, Cd, Zn, Sb and U (Mobasherpour *et al.*, 2012; Baba *et al.*, 2013; Bich *et al.*, 2016; Mousa *et al.*, 2016).

This study presents the kinetic, uptake performance and sorption capacity evaluation of periwinkle shell hydroxyapatite (PSHAP) for heavy metal ions in industrial steel rolling mill wastewater.

2. Materials and Methods

2.1. Materials

Fresh periwinkle shells were obtained from Ebute Meta market, Lagos. The periwinkle shells were washed thoroughly with distilled-deionized water to remove the bulk flesh, sun dried for 24 h and crushed into pellets. Then, it was soaked in 50 % hydrogen peroxide for 24 h to oxidize all residual organic matter, washed thoroughly with distilled-deionized water and placed in an oven at 105 °C for 24 h to remove the moisture content (Amuda *et al.*, 2017). The oven-dried sample was kept in the desiccators to prevent absorption of moisture from the atmosphere.

2.2. Production of Hydroxyapatite from periwinkle shell.

The oven-dried Samples were calcined at different temperatures (400, 500 and 600 °C) in the furnace (Muffle Furnace Model SM1008, Surgifield Medical England) for 2 h each, ground to powder and sieved to a particle size of 2 mm, soaked with 0.26 M Di-ammonium hydrogen phosphate solution for 24 h. The liquid part was decanted and the sediment was washed repeatedly with distilled-deionized water and drained using a Buchner funnel and suction bump, this was then oven-dried at 105°C for 24 h to remove the moisture content completely (Amuda *et al.*, 2017).

2.3. Sampling and analysis of heavy metals in steel rolling wastewater

Wastewater samples were collected and the composite sample was obtained. The pH and temperature of these water samples were determined using Jenway 3505 pH- portable meter. For quantification of heavy metals (Fe, Pb, Zn, Cd, Cu, Cr and Mn) content level in the steel rolling wastewater, 20 ml of wastewater was digested in concentrated HNO₃ and HCl mixture (3:7 ratio), then heated on a hot plate at 70°C till brown turns to light yellow in colour. After digestion, the sample was filtered with Whatman No.1 filter paper and transferred to 25 ml polythene tubes, then made up to 20 ml with distilled-deionized water (Azeez *et al.*, 2019). A metal analysis of the digested sample was determined using Agilent 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES). Detection limit was estimated from digested blank (distilled-deionized water) which was run during

the analysis. Triplicate digestion analyses were run and average values were reported. Same procedure was repeated after the samples had been treated with hydroxyapatite.

2.4. Adsorption studies

Effect of contact time (5–85 min) on the adsorption of metal on PSHAP was studied in batches. The pH of the metal solution was adjusted with 0.1 M HCl or 0.1 M NaOH. 1 g of PSHAP was weighed and added to 100 ml of 50 mg/l metal solution in a 250-ml conical flask. The flask was shaken in a Uniscope water bath shaker at 30 °C, agitated at 150 rpm for 30 min. The solution was centrifuged at 1500 rpm. The concentration of unadsorbed metal was determined using Microwave Plasma Atomic Emission Spectroscopy (MP-AES). Percentage removal and quantity adsorbed at a given time *t* were calculated using the following equations:

$$\% \text{ Removal} = \left(\frac{C_o - C_f}{C_i} \right) \times 10 \dots \dots \dots (1)$$

$$q_t = \frac{(C_o - C_t)V}{M} \dots \dots \dots (2)$$

where q_t is the amount of metal adsorbed per unit mass of adsorbent (mg/g), C_o is the initial metal concentration (mg/l), C_f is the final metal concentration (mg/l), C_i is the residual concentration at time t , V is the volume of metal solution (l) and M mass of adsorbent (g).

2.5. Adsorption kinetics

The pseudo- first order, pseudo-second order, elovich and intra-particle diffusion kinetic models were employed to determine the rate constant and the controlling mechanism of the sorption process. These were done to further confirm the best fit kinetic model (s) for the sorption process. The pseudo-first-order and intra-particle diffusion equations were generally acclaimed to be applicable over the initial stage of the adsorption process (Mohan *et al.*, 2006; Pan *et al.*, 2009). The linear forms of pseudo- first order, pseudo- second order, elovich and intra-particle diffusion equations are as expressed in Equations 3, 4, 5 and 6 respectively (Kamari, 2011; Ho and McKay, 2000).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \dots \dots \dots (3)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \dots \dots \dots (4)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln \dots \dots \dots (5)$$

$$q_t = K_{diff} t^{1/2} + C \dots \dots \dots (6)$$

Where q_e and q_t are the amount of metal ions sorbed (mg/g) at equilibrium and at time t (min) respectively while k_1 (mg/g/min), k_2 (mg/g/min) and k_{diff} (mg/g/min^{1/2}) are the rate constants of the pseudo-first order, pseudo-second order and intra-particle diffusion equations for the bio-sorption processes respectively, α and β are constants depicting chemisorption rate and the extent of surface coverage respectively (Kamari *et al.*, 2011).

3. Results and Discussion

The results of Metal Concentration in Steel Rolling Wastewater (mg/L) is presented in table 3.1

Table 3.1: Metal Concentration in Steel Rolling Wastewater (mg/L)

Metal	Fe	Pb	Zn	Cd	Cu	Cr	Mn
Concentration (mg/L)	28.373	0.1487	1.1199	0.0712	0.1656	0.2500	0.6778
USEPA Limit (1999)	0.3000	0.0030	0.1200	0.002	0.0090	NS	0.0050
SON Limit (2007)	0.3000	0.0100	3.0000	0.003	1.0000	0.0500	0.0200
NESREA limit(2009)	0.1000	0.0500	2.0000	1.000	1.0000	0.0100	0.2000
WHO Limit (2011)	0.3000	0.0100	3-5	0.0030	2.0000	0.0100	-

3.2a: Adsorption kinetics parameters for the uptake of metals on PSHAP₄₀₀

PSHAP ₄₀₀	Kinetics	Constants	Fe	Pb	Zn	Cd	Cu	Cr	Mn
Pseudo-first order		q _e exp (mg/g)	1.3813	0.0068	0.0525	0.0033	0.0077	0.0115	0.0318
		q _e cal (mg/g)	0.2781	0.0012	0.0097	0.0006	0.0014	0.0020	0.0058
		K ₁ (mg/g/min)	0.0318	0.0409	0.0409	0.0418	0.0409	0.0406	0.0409
		R ²	0.9536	0.9175	0.9175	0.9240	0.9175	0.9175	0.9175
		X ²	4.3759	0.0275	0.1899	0.0114	0.0289	0.0458	0.1162
		Δqt (%)	23.055	23.958	23.556	23.352	23.691	23.905	23.595
Pseudo-second order		q _e exp (mg/g)	1.3812	0.0068	0.0525	0.0033	0.0077	0.0116	0.0318
		q _e cal (mg/g)	1.4165	0.0070	0.0536	0.0034	0.0078	0.0117	0.0325
		K ₂ (mg/g/min)	0.2511	77.952	9.2197	141.66	64.744	45.078	15.355
		R ²	0.9988	0.9996	0.9995	0.9996	0.9996	0.9996	0.9996
		X ²	0.0009	2.E-06	2.E-05	1.E-06	3.E-06	4.E-06	1.E-05
		Δqt (%)	0.7371	0.5420	0.5924	0.6141	0.5754	0.5512	0.5875
Elovich		B(mg/g/min)	11.367	2899.9	346.42	5337.9	2424.3	1715.9	576.36
		A (g/g)	6324.1	1498.4	2835.6	129.75	650.31	2613.9	1951.0
		R ² (J/mol)	0.9619	0.9578	0.9578	0.9623	0.9578	0.9632	0.9578
Intraparticle diffusion		K _{diff} (mg/gmin ^{1/2})	0.0336	0.0058	0.0011	6.E-05	0.0002	0.0096	0.0006
		C (mg/g)	1.0842	0.0057	0.0433	0.0027	0.0064	0.0096	0.0263
		R ²	0.9751	0.9126	0.9126	0.9198	0.9126	0.9269	0.9126

Table 3.2b: Adsorption kinetics parameters for the uptake of metals on PSHAP₅₀₀

PSHAP ₅₀₀	Kinetics	Constants	Fe	Pb	Zn	Cd	Cu	Cr	Mn
Pseudo-first order		q _e exp(mg/g)	1.2694	0.0071	0.0554	0.0035	0.0081	0.0121	0.0333
		q _e cal (mg/g)	0.3028	0.0016	0.0119	0.0007	0.0018	0.0028	0.0075
		K ₁ (mg/g/min)	0.0397	0.0395	0.0513	0.0462	0.0425	0.0394	0.0422
		R ²	0.9159	0.9149	0.9185	0.9279	0.9209	0.9143	0.9196
		X ²	3.0849	0.0185	0.1590	0.0100	0.0219	0.0308	0.0881
		Δqt (%)	21.981	22.278	22.666	22.680	22.409	22.183	22.336
Pseudo-second order		q _e exp(mg/g)	1.2694	0.0071	0.0554	0.0035	0.0081	0.0121	0.0333
		q _e cal (mg/g)	1.3054	0.0073	0.0567	0.0036	0.0083	0.0124	0.0343
		K ₂ (mg/g/min)	0.2725	50.855	9.0596	127.90	48.121	29.271	11.455
		R ²	0.9991	0.9991	0.9997	0.9996	0.9993	0.9991	0.9993
		X ²	0.0010	5E-06	3E-05	2.E-06	6.E-06	99E06	3E-05
		Δqt (%)	0.8177	0.7803	0.6950	0.7637	0.8032	0.7957	0.8199
Elovic		B(mg/g/min)	11.589	2181.9	316.62	4677.2	1932.5	1269.6	469.27
		A (g/g)	2499.1	29.206	1823.0	35.043	42.043	42.82	163.05
		R ² (J/mol)	0.9705	0.9700	0.9784	0.9755	0.9746	0.9694	0.9737
Intraparticle diffusion		K _{diff} (mg/gmin ^{1/2})	0.0325	0.0001	0.0012	7.E-05	0.0002	0.0003	0.0008
		C (mg/g)	0.9875	0.0056	0.0457	0.0028	0.0063	0.0095	0.0265
		R ²	0.9609	0.9679	0.9343	0.9383	0.9490	0.9712	0.9656

Table 3.2c: Adsorption kinetics parameters for the uptake of metals on PSHAP₆₀₀

PSHAP ₆₀₀	Kinetics	Constants	Fe	Pb	Zn	Cd	Cu	Cr	Mn
Pseudo-first order		q _e exp (mg/g)	1.2479	0.0070	0.0554	0.0035	0.0081	0.0120	0.0333
		q _e cal (mg/g)	0.3044	0.0016	0.0127	0.0009	0.0020	0.0028	0.0073
		K ₁ (mg/g/min)	0.0398	0.0394	0.0361	0.0395	0.0400	0.0395	0.0365
		R ²	0.9163	0.9143	0.9364	0.9149	0.9169	0.9149	0.9475
		X ²	2.9237	0.0178	0.1437	0.0083	0.0188	0.0300	0.0926
		Δqt (%)	21.825	22.183	22.254	21.866	21.777	22.100	22.538
Pseudo-second order		q _e exp (mg/g)	1.2479	0.0070	0.0554	0.0035	0.0081	0.0120	0.0333
		q _e cal (mg/g)	1.2841	0.0072	0.0570	0.0036	0.0083	0.0124	0.0343
		K ₂ (mg/g/min)	0.2710	50.803	5.9935	95.850	41.643	29.166	10.442
		R ²	0.99902	0.9991	0.9989	0.9990	0.9991	0.9991	0.9991
		X ²	0.0010	5.E-06	4.E-05	2.E-06	6.E-06	9.E-06	2.E-05
		Δqt (%)	0.8377	0.7957	0.8190	0.8383	0.8408	0.8050	0.8283
Elovic		B(mg/g/min)	11.477	2203.6	260.51	4156.8	1738.1	1257.1	441.78
		A (g/g)	1720.6	24.670	82.248	6.1378	9.1983	33.749	66.318
		R ² (J/mol)	0.9701	0.9694	0.9699	0.9700	0.9693	0.9700	0.9736
Intraparticle diffusion		K _{diff} (mg/gmin ^{1/2})	0.0328	0.0002	0.0015	9.E-05	0.0002	0.0003	0.0009
		C (mg/g)	0.9641	0.0055	0.0428	0.0027	0.0063	0.0094	0.0259
		R ²	0.9571	0.9712	0.9646	0.9679	0.9490	0.9679	0.9652

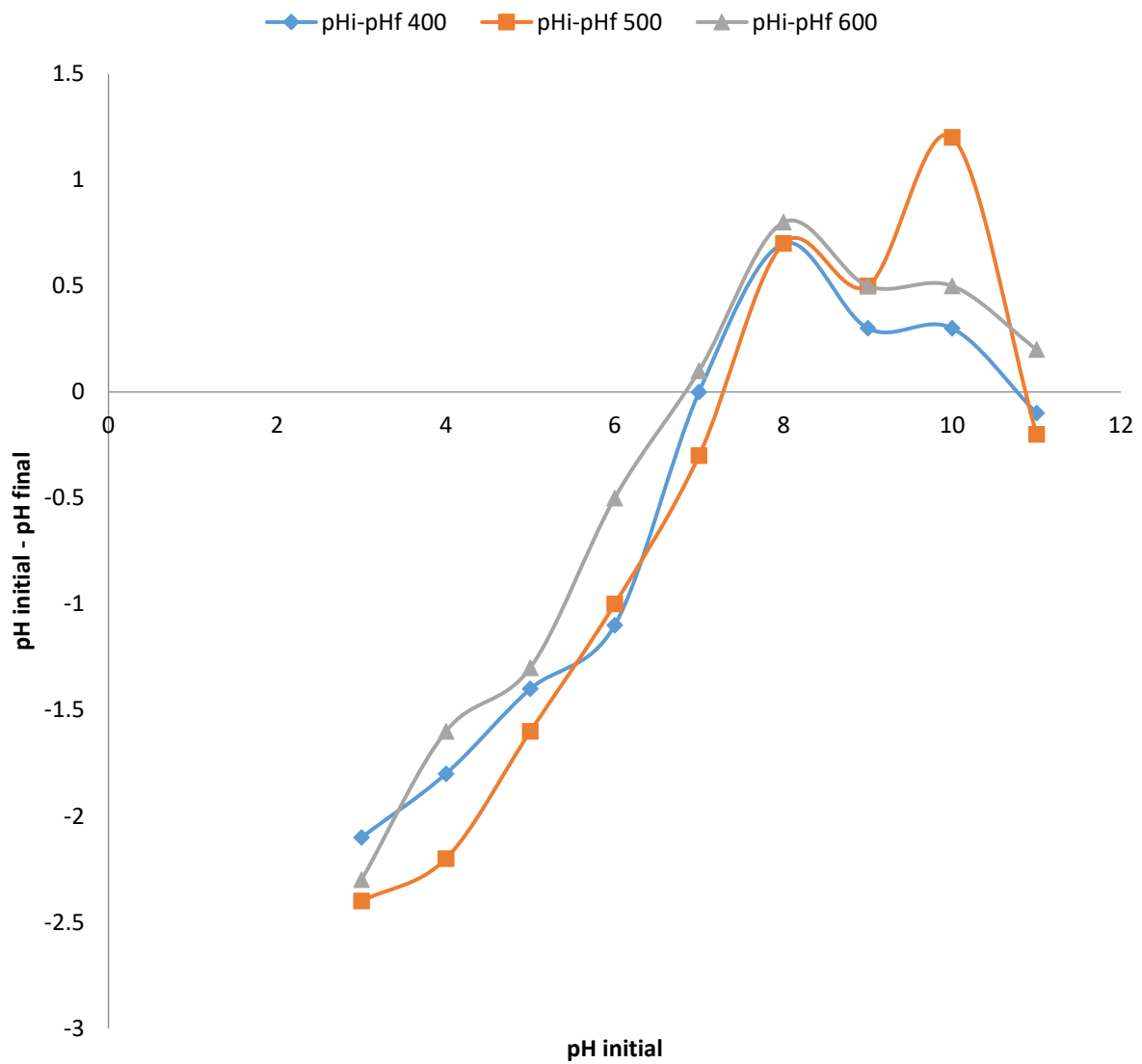


Fig. 3.1: pH point of zero charge (pHpzc) of PSHAP₄₀₀, ₅₀₀ and ₆₀₀

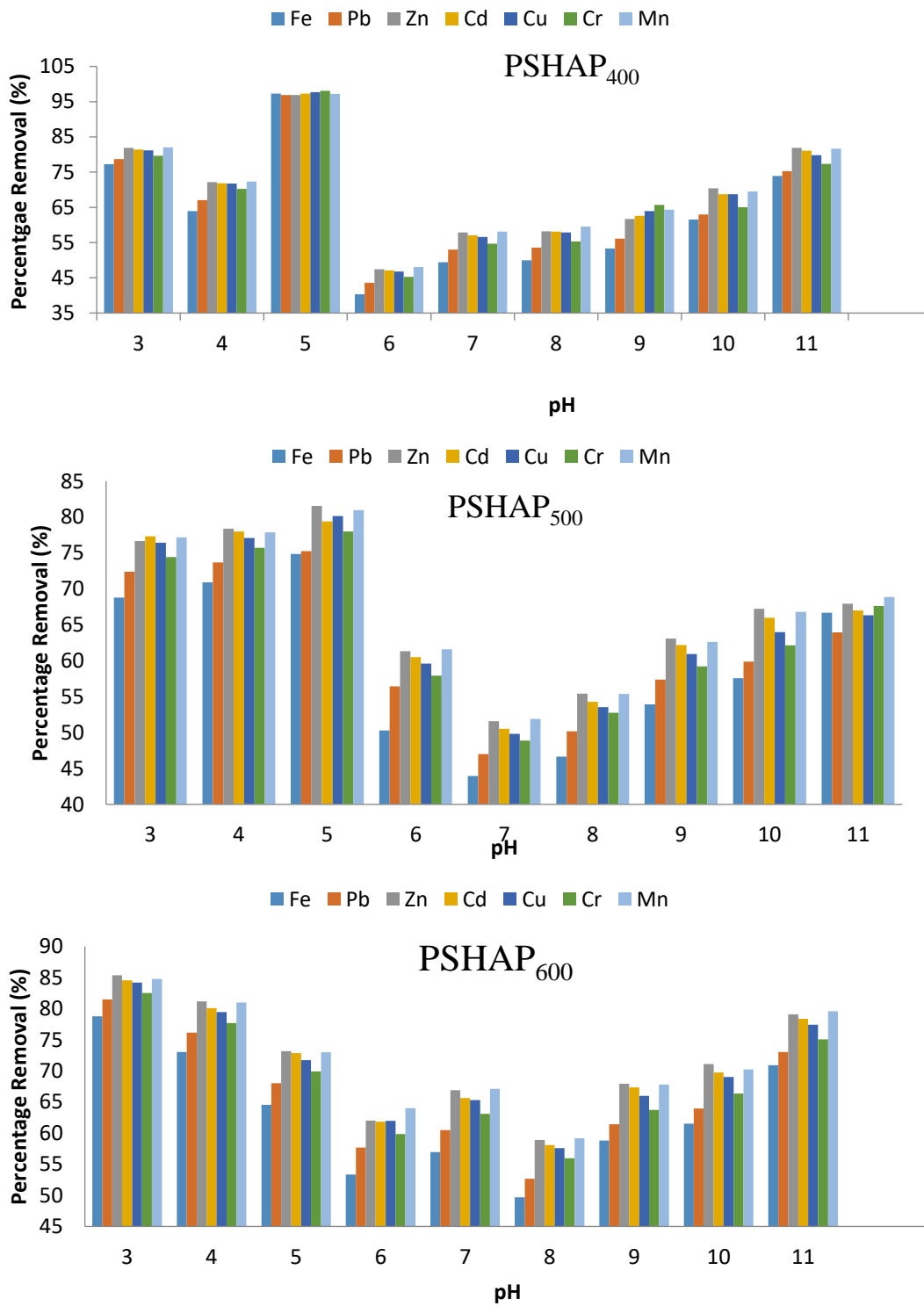


Fig. 3.2: Effect of pH on the percentage removal of metals using PSHAP₄₀₀, 500 and 600

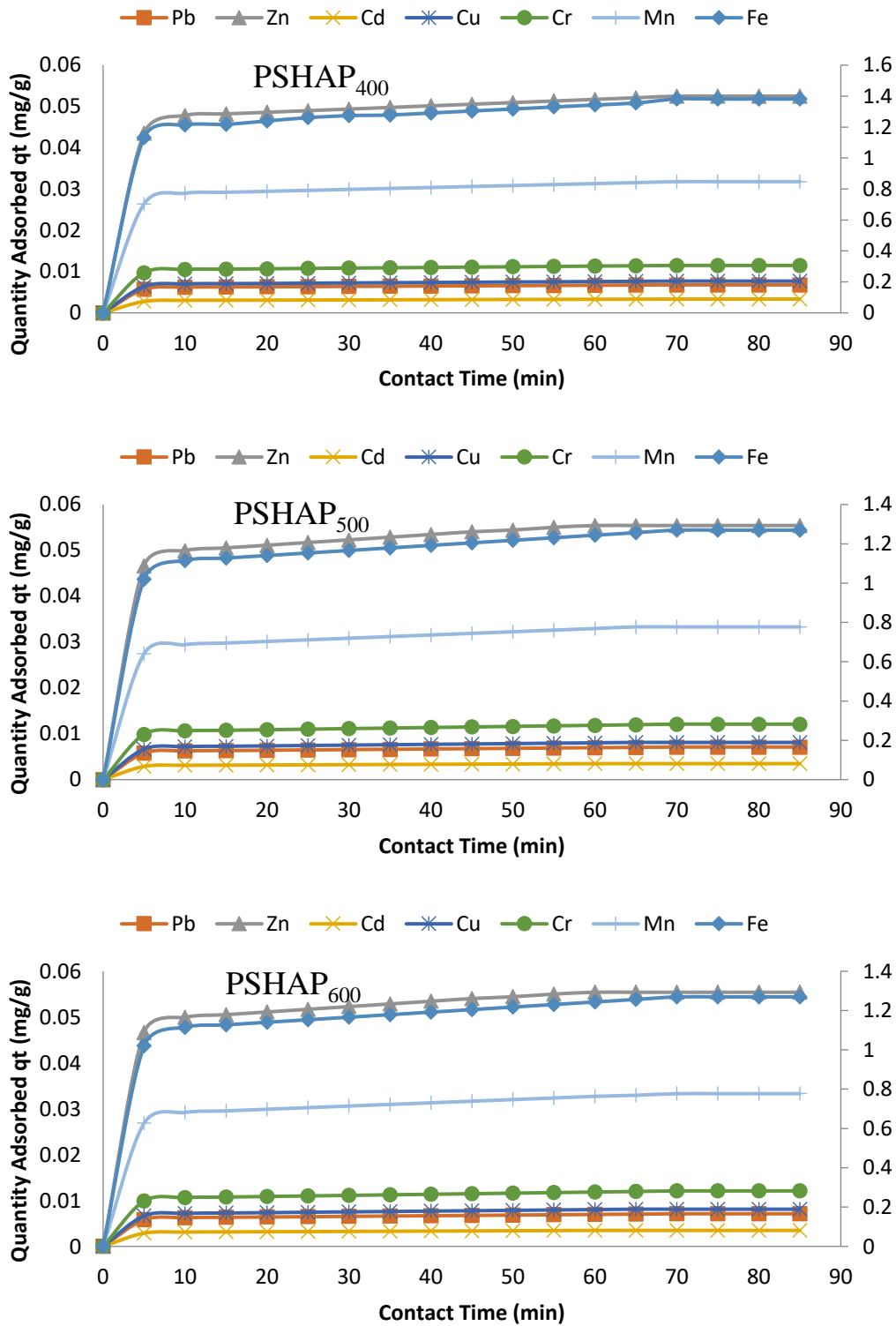


Fig. 3.3: Effect of contact time t on the quantity q_t of metals adsorbed using PSHAP₄₀₀, 500 and 600

3.1. Evaluation of heavy metals in the steel rolling mill wastewater

The concentration of heavy metals in the steel rolling mill waste water as reported in Table 3.1 indicated the prevalence of seven heavy metals (Fe, Pb, Zn, Cd, Cu, Cr and Mn) follow the order: Fe > Zn > Mn > Cr > Cu > Pb > Cd. Only Cu and Zn are below USEPA (1999), the Standard Organization of Nigeria (SON) 2007, NESREA (2009), and World Health Organization (WHO) 2011, maximum permissible level of metal ions in wastewater.

3.2. Biosynthesized PSHAP₄₀₀, PSHAP₅₀₀ and PSHAP₆₀₀

pH_{pzc} for PSHAP₄₀₀, PSHAP₅₀₀ and PSHAP₆₀₀ occurred at 6.7, 6.85 and 6.0 respectively (Fig. 3.1) suggesting maximum adsorption of heavy metals would be effective above these pH values. pH facilitates and influences the mobility of adsorbate on adsorbent. This is due to the fact that surfaces of adsorbents were cationic below pH_{pzc} and adsorbates were also cationic, hence, there would be repulsion. The surface of adsorbent is cationic at $pH < pH_{pzc}$ whereas it is anionic at $pH > pH_{pzc}$. pH_{pzc} plays an effective role in determining the electrostatic surface charge on adsorbent needed for optimum adsorption of the adsorbate. It influences adsorbent surface charge and dissociation of functional groups responsible for adsorption (Huang *et al.*, 2017; Ojedokun and Bello, 2017; Azeez *et al.*, 2018).

Maximum adsorption pH of PSHAP₄₀₀, PSHAP₅₀₀ and PSHAP₆₀₀ were 5, 5 and 3 respectively (Fig. 3.2). Maximum adsorption results at $pH > pH_{pzc}$ for all adsorbents in this study are consistent with the cationic nature of adsorbate and anionic surface charges of adsorbents. Sorption of adsorbate is hinged on adsorbent surface charges/chemistry and influence of pH on the mobility of adsorbate (Torres *et al.*, 2007; Chen *et al.*, 2015; Giwa *et al.*, 2015). Consequently, all batch adsorption experiments were therefore carried out at pH 5, 5 and 3 respectively.

3.3. Adsorption Kinetics

Kinetic parameters are important for adsorption studies because they predict the rate at which adsorbate can be removed from aqueous solutions and provide valuable data for understanding the mechanism of sorption reactions. Calculated parameters of the various kinetic models and validated results are reported in Tables 3.2a-c. Pseudo first order, pseudo second order, Elovich and intra-particle diffusion model were employed to describe metals uptake onto the adsorbents. The goodness of fit between experimental and calculated data was determined by the correlation coefficient (R^2) validated by normalized standard deviation ($\% \Delta qt$) and calculated data expressed using non-linear Chi-square test (X^2). R^2 of the best fit model must be the closest to 1, $\% \Delta qt$ and X^2 must be relatively low.

Comparison of R^2 of pseudo first order, pseudo second order and Elovich kinetic models shows that pseudo-second order best described the mechanism and the rate of uptake of all the metals (Fe, Pb, Zn, Cd, Cu, Cr and Mn) onto PSHAP₄₀₀, PSHAP₅₀₀ and PSHAP₆₀₀. Relatively low values of $\% \Delta qt$ and X^2 (less than 1 in all cases) are also in consonance with R^2 values (0.999) describing the rate of uptake of metals onto these adsorbents. A relatively low (X^2) values indicate the model successfully describes the equilibrium kinetics (Al-Mraeshgi *et al.*, 2008; Boulinguez *et al.*, 2008) and validates pseudo-second order as the kinetics model describing the rate of adsorption.

Many factors controlled the rate of adsorption, one of which was intra-particle diffusion. The possibility of involvement of intra-particle diffusion affecting the adsorption process was

studied and is presented in Tables 3.2a-c. K_{diff} , C and R^2 are the slope, intercept and correlation respectively. A single linear plot obtained for intra-particle diffusion of metal-PSHAP did not pass through the origin and has high correlation coefficient R^2 indicating that intra-particle diffusion was involved in the adsorption. The value of C (intercept) gives the idea about the thickness of the boundary, the larger the value of C , the greater the boundary layer diffusion effect (*Konicki et al.*, 2013).

3.4. Effect of contact time and adsorption capacity of PSHAP

The time profiles of metal ions sorption by PSHAP₄₀₀, ₅₀₀ and ₆₀₀ carried out on the steel rolling mill wastewater at 30 °C are presented in Fig. 3.3. The amount of metal ions sorbed increased with contact time before plateauing, beyond which no more ions were removed from the samples. At this point, equilibrium has been reached between the amount of the heavy metal ions desorbed from the PSHAP and heavy metal ions sorbed onto it.

4. Conclusion

Kinetic studies of the sorption perforce of PSHAP₄₀₀, ₅₀₀ and ₆₀₀ for the removal of Fe, Pb, Zn, Cd, Cu, Cr and Mn from steel rolling mill wastewater were investigated. Maximum adsorption Ph of PSHAP₄₀₀, ₅₀₀ and ₆₀₀ were 5, 5 and 3 respectively. The amount of metal ions sorbed increased with contact time before plateauing and pseudo-second order best described the mechanism and the rate of uptake of all the metals. This study has shown that PSHAP especially calcination at 500 °C with relatively highest values of R^2 , lowest values of X^2 and Δqt (%) is a promising adsorbent for the remediation of heavy metals from wastewaters. Equally, the trend of potential adsorbent capacity of low-cost and eco-friendly biogenic PSHAP at different calcination temperatures for metal removal from industrial steel rolling mill wastewater varies with the factors that affect adsorption process.

REFERENCES

- Al-Meshragi, M., Ibrahim, H.G. and Aboabboud, M.M. (2008). Equilibrium and Kinetics of Chromium Adsorption on Cement Kiln Dust. In: *Proceedings of the World Congress on Engineering and Computer Science*. WCECS, October 22–24, San Francisco, USA.
- Amuda, O.S., Olayiwola, A.O. and Farombi A. G. (2017). Production and Characterization of Hydroxyapatite Prepared from Periwinkle shell. *International journal of Chemical, Gas and Material Science (IJCGM)*, 1(1): 23-26.
- Azeez, L., Lateef, A., Adebisi, S.A. and Oyedeji, A.O. (2018). Novel Biosynthesized Silver Nanoparticles from Cobweb as Adsorbent for Rhodamine B: Equilibrium Isotherm, Kinetic and Thermodynamic Studies. *Applied Water Science*, **8**: 32. DOI: 10.1007/s13201-018-0676-z.
- Azeez, L., Adejumo A. L., Agabje L., Adebisi S. A., Adetoro R. O., Adewuyi S., Tijani K. O. and Olaoye S. (2019). Zero-valent silver nanoparticles attenuate Cd and Pb toxicities on *Moringa oleifera* via immobilization and induction of phytochemicals. *Plant Physiology and Biochemistry*. 139, 283-292.
- Baba, A.A., Oduwole, I.T., Salami, F.O., Adekola, F.A. and Adeboye, S.E. (2013). Synthesis of Hydroxyapatite from Waste Egg-Shell by Precipitation Method. *Ife Journal of Science*, 15(3): 435-440.
- Bich, T. N. Phan, Hanh T. Nguyen, Huong Q. Dao, Lam V. Pham, Trang T. T. Quan, Duong B. Nguyen, Huong T. L. Nguyen and Thuan T. Vu. (2016). Synthesis and Characterization of Nano-Hydroxyapatite in Maltodextrin Matrix. *Appl. Nanoscience*, DOI 10.1007/s13204-016-0541-z.
- Boulinguez, B., LeCloirec, P. and Wolbert, D. (2008). Revisiting the Determination of Langmuir Parameters Application to Tetrahydrothiophene Adsorption onto Activated Carbon. *Langmuir* **24**: 6420–6424.
- Chen, R.P., Zhang, Y.L., Shen, L.F., Wang, X.Y., Chen, J.Q., Ma, A.J. and Jiang, W.M. (2015). Lead (II) and Methylene Blue Removal using a fully Biodegradable Hydrogel based on Starch Immobilized Humic Acid. *Chemical Engineering Journal*, doi: <http://dx.doi.org/10.1016/j.cej.2015.01.081>
- Czerniczyniec, M., Farias, S., Magallanes, J. and Cicerone, D. (2003). Arsenic Adsorption on Biogenic HAP: Solution Composition Effects in: 11th *International Conference on Surface and Colloid Science*, Foz do Iguazu, Brazil, 269.
- Eniola, E.B; Chuckwu, L.O; Olaide, B.S. (2010). Hydro Chemistry, Nacro Invertebrate Fauna and Fish Production of Acids Fishing Sites in a Tropical Lagoon Ecosystem, *J. Am. Sci.*, 6(1), 22-28.
- Fuller, C., Bargar, J., Davis, J. and Piana, M. (2002). Mechanisms of Uranium Interactions with Hydroxyapatite: Implications for Ground-Water Remediation. *Environmental Science Technology*, 36: 158–165.
- Giwa, A.A., Oladipo, M.A. and Abdulsalam, K.A. (2015). Adsorption of Rhodamine B from Single, Binary and Ternary Dye Systems using Sawdust of *Parkia biglobosa* as Adsorbent: Isotherm, Kinetics and Thermodynamics Studies. *J. Chem. Pharm. Res.*, 7(2): 454–475.

- Ho, Y.S. and McKay, G. (2000). The Kinetics of Sorption of Divalent Metal Ions onto Sphagnum Moss Peat. *Water Res.* 34:735-742. [http://dx.doi.org/10.1016/S0043-1354\(99\)00232-8](http://dx.doi.org/10.1016/S0043-1354(99)00232-8)
- Huang, R., Liu, Q., Huo, J. and Yang, B. (2017). Adsorption of Methyl Orange onto Protonated Cross-linked Chitosan. *Arabian Journal of Chemistry*, **10**: 24–32.
- Jude, C.I. and Augustin, A.A. (2007). Equilibrium Sorption Isotherm Studies of Cd (II), Pb (II) and Zn (II) Ions Detoxification from Waste Water using Unmodified and EDTA-Modified Maize Husk. *Elect. J. Biotech.* 10(4): ISSN: 0717-3458. DOI: 10.2225/vol10-issue4-fulltext-15. <http://dx.doi.org/10.2225/vol10-issue4-fulltext-15>
- Kamari, A., Pulford, I.D. and Hargreaves, J.S.J. (2011). Binding of Heavy Metal Contaminants onto Chitosan: An Evaluation for Remediation of Metal Contaminated Soil and Water. *Journal of Environmental Management*, 92:2675-2682. <http://dx.doi.org/10.1016/j.jenvman.2011.06.005>
- Kanamadi, R.D., Ahalya, N. and Ramachandra, T.V. (2003). Review Paper: Biosorption of Heavy Metals. *Res. J. Chem. Environ.* 7(4):71-79.
- Konicki, W., Sibera, D., Mijowska, E., Lendzion-Bielun, Z. and Narkiewicz, U. (2013). Equilibrium and Kinetic Studies on Acid Dye Acid Red 88 Adsorption by Magnetic ZnFe₂O₄ Spinel Ferrite Nanoparticles. *J. Colloid Interf. Sci.* **398**:152–160.
- Krestou, A., Xenidis, A. and Panias, D. (2004). Mechanism of Aqueous Uranium (VI) Uptake by a Natural Zeolitic Tuff. *Mineral Engineering*, 16:1363–1370.
- Leyva, A., Marrero, J., Smichowski, P. and Cicerone, D. (2001). Sorption of Antimony onto Hydroxyapatite. *Environmental Science Technology*, 35: 3669–3675.
- McGrellis, S., Serafini, J., Jean, J., Pastol, J. and Fedoroff, M. (2001). Influence of the Sorption Protocol on the Uptake of Cd Ions in Calcium Hydroxyapatite. *Separation and Purification Technology*, 24: 129–138.
- Mobasherpoura, I., Salahia, E. and Pazouki Arabian, M. (2012). Comparative of the Removal of Pb²⁺, Cd²⁺ and Ni²⁺ by Nano Crystallite Hydroxyapatite from Aqueous Solutions: Adsorption Isotherm Study. *Journal of Chemistry*, 5: 439–446.
- Mohan, D. and Pitman Jr., C.U. (2006). Activated Carbon and Low Cost Absorbents for Remediation of Tri- and Hexavalent Chromium from Water. *Journal of Hazardous Materials*, **137**: 762-811.
- Mousa, S.M., Ammar, N.S. and Ibrahim, H.A. (2016). Removal of Lead Ions Using Hydroxyapatite Nano-Material Prepared from Phosphogypsum Waste. *Journal of Saudi Chemical Society*, 20: 357–365.
- Ojedokun, A.T. and Bello, O.S. (2017). Liquid Phase Adsorption of Congo Red Dye on Functionalized Corn Cobs. *Journal of Dispersion Science and Technology*, **38**(9), 1285-1294.
- Pan, X., Wang, J. and Zhang, D. (2009). Sorption of Cobalt to Bone Char: Kinetics, Competitive Sorption and Mechanism. *Desal.* 249:609-614. <http://dx.doi.org/10.1016/j.desal.2009.01.027>
- Shyamsundar, A.C. (2009). Use of Hydroxyapatite Derived from Cat Fish Bones for Remediating Uranium Contaminated Ground Water. M.Sc. Dissertation Auburn University, Alaba, 16-17.

Standard Organization of Nigeria (2007). Nigerian Standard for Drinking Water Quality. 1-30.
Torres, M.A., Beppu, M.M. and Santana, C.C. (2007). Characterization of Chemically Modified Chitosan Microspheres as Adsorbents using Standard Proteins (Bovine Serum Albumin and Lysozyme). Braz. J. Chem. Eng. 24:325–336

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