

Thermodynamic, Kinetic and Equilibrium Studies of Pb (II) Ions Adsorption Using Ordinary Clay/Rice Husk Ash Based Geopolymers

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Abstract: One key global challenge is the existing disparity in water distribution resulting to millions of people lacking access to safe clean water. It is currently assessed that 1.1 billion individuals on the planet lacks access to improved quality water supplies. This is aggravated by the looming climate change and increased pollution threats posed by industrialization and population growth. Use of adsorbents for water treatment is preferable due to simplicity of the technique and cheap materials involved. Geopolymers can be easily synthesized hydrothermally using alumina and silica and possess amorphous surface for use as adsorbents. Clay minerals have been reported to contain alumina and silica and previous research show that rice husk ash as well contain substantial amounts of silica. Geopolymers can be easily synthesized hydrothermally using alumina and silica and possess amorphous surface that is useful for adsorption. Hence this work reports information on adsorption of Pb (II) using geopolymers GP-1, GP-2 and GP-3 synthesized with SiO₂/Al₂O₃ ratios of 4.16, 4.18 and 8.29 respectively. Adsorption of metal ions was found to increase from 70.54% ± 0.43 to 90.23% ± 0.04 with increase in Si/Al ratio from 4.16 to 8.29 in geopolymers. Equilibrium studies unveiled that experimental data for adsorption of Pb (II) ions best fitted in modified Langmuir Freundlich model. The adsorption capacities of 27.0, 79.58 and 209.9mg/g were obtained for GP-1, GP-2 and GP-3 respectively. Adsorption thermodynamics showed the process corresponded on spontaneous physisorption activated by increase in temperature. Kinetic study on adsorption of Pb (II) ions onto clay based geopolymers was a Pseudo second order. This information may facilitate the development of optimized procedures for wastewater treatment, thus providing an alternative solution to environmental menace caused by heavy metal pollutants.

Key words: Thermodynamics, Kinetics, Equilibrium, Geopolymers, Adsorption.

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I. Introduction

The discharge of toxic heavy metals in water bodies is a serious pollution problem affecting water quality especially in wetlands and other water masses due to their toxicity and bio accumulative effect, creating a direct hazard to human health^[1]. There are known techniques for heavy metal wastewater treatments like; chemical precipitation, ion exchange, adsorption, membrane filtration among others^[2]. Chemical precipitation is not economical and produces large amounts of sludge, treatable with great difficulties. Ion exchange is expensive, especially when treating a large amount of wastewater containing heavy metals in low concentrations, so it cannot be used on a large scale while membrane filtration requires filter replacement that is expensive in terms of cost^[2]. The adsorption techniques present excellent approaches for treating industrial wastewaters containing metal ions, where solid adsorbents are employed for recovery of metal ions such as lead, copper, cadmium, nickel and zinc^[3]. In search for more adsorbents, geopolymers has proved effective in removal of metal ions from wastewater. Geopolymers are composed of silica and alumina similar to zeolite materials^{[4], [5]}. Several researchers used metakaolin as ideal raw material for manufacture of geopolymers^{[6], [7]} because of its high reactivity and purity compared to other clays^{[8], [9], [10]}. This work focuses on a new and green developing field that utilizes local Kenyan resources such as common clay that has not been used and rice husk waste for hydrothermal synthesis of geopolymers for wastewater management.

II. Experimental sections

2.1 Chemicals and reagents

Sodium hydroxide was used as a dissolution agent during geopolymer synthesis. Pb (NO₃)₂ and HNO₃ used in the adsorption experiments were of analytical grade and supplied by Sigma Aldrich. Preparation procedures and characterization of geopolymers are discussed in our earlier published work^[11].

2.2 Synthetic effluent preparation

An accurate weight of 1.6 g Pb (NO₃)₂ was dissolved in 1 L of distilled water to make the stock solution. The stock solution was then diluted into the required concentrations using distilled water where necessary. Every time the stock and standard solution was prepared, it was shaken for about 1 hour using temperature controlled water bath electric shaker at 25 °C and 120 rpm to ensure homogeneity.

2.3. Adsorption study

2.3.1 Effect of pH on adsorption process

Batch adsorption experiments were conducted by varying pH from 2 to 6 with initial Pb (II) concentrations of 100 mg/L, shaking speed of 120 rpm and room temperature of 25 °C ± 1. The experiments were carried out in 100 mL plastic bottles and the total volume of the reaction mixture kept at 50 mL. The pH of solution was adjusted to desired values using the procedure adopted from Moreno-piraján and Giraldo^[12]. The mixtures were shaken for a period of one hour in an electric shaker. The mixture was then filtered using whatman no 41 and residual metal ion concentration analysed using the procedure adopted from Ryan *et al.*^[13].

2.3.2 Effect of contact time on adsorption process

The impact of residence time was investigated by varying time from 20 to 100 minutes. 0.10 g of geopolymer material was added in 50 mL of 100 mg/L metal ion solutions in each of a series of adsorption bottles. The bottles were placed in a thermostatic electric shaker at 120 rpm, maintained at 25 °C ± 1. After 20 minutes of adsorption time was completed, the adsorbents were removed from the solution by filtration and the concentration of residual metal ion in each solution determined using AAS. Subsequently, the same procedure was repeated by adjusting time to, 40, 60, 80 and 100 minutes respectively.

2.3.3 Effect of temperature on adsorption process

The temperature range of 293 K to 328 K was used for Pb (II) ions adsorption to determine the equilibrium temperature. For each experimental run, 50 mL aqueous solution of the known concentration at optimum pH of 4.0 was put in a 100 mL stoppered plastic bottles containing 0.10 g of the adsorbent. The bottles were placed in a thermostatic electric shaker at constant shaking speed of 120 rpm at specified temperature and withdrawn after shaking for one hour. Filtration was done and residual metal ions present analyzed.

2.3.4 Isotherm studies of adsorption process

Adsorption quantitative data of metal ions studied were treated using Freundlich; Langmuir, and modified Langmuir Freundlich. The models were used to determine adsorption capacities of the geopolymers synthesized using different clays and rice husk ash (RHA). A 100 mL stoppered bottles were used where metal ion solutions with initial concentrations of 100 mg/L were placed. 0.10 g of each of the prepared adsorbents was added to each bottle and kept in an electric shaker at 25 °C ± 1 for 1 hour in the laboratory to equilibrate^[14]. AAS (AA 6300 Shimadzu) was used to determine both the initial metal ions concentration before adsorption (C₀) and the residual metal ion concentration (C_e) obtained after the adsorption process. The amount of adsorption at equilibrium, q_e(mg/g), was calculated by equation 1.

$$q_e = \left[\frac{C_0 - C_e}{W} \right] V \dots\dots\dots 1$$

Where; C₀ and C_e (mg/L) are concentrations of respective metal ions at initial and equilibrium conditions respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g) ^[15]. For the Freundlich isotherm, the plot of log q_e against log C_e will give a straight line with a slope of 1/n and intercept of log K_F. For Langmuir isotherm, the plot of C₀/q_e against C_e gives a straight line with a slope of 1/Q_{max} and intercepts 1/Q_{max} K_L. For modified Langmuir Freundlich isotherm C_e was plotted against q_e and the model fitting was accomplished using the generalized reduced gradient algorithm available in Microsoft Excel solver.

2.3.5 Thermodynamic study of adsorption process

The sorption studies were carried out at different temperatures (293, 298, 308 318 and 328 K). This was used to determine the effect of temperature on the thermodynamic parameters. The thermodynamic studies were performed using batch experiments. In each of the stoppered bottle contained 0.10 g of geopolymers and 50 mL of aqueous solutions. The experiments were carried out with initial concentration of 100 mg/L for all metal solutions at $25^{\circ}\text{C} \pm 1$ and pH 4 for Pb (II) ions. The residue was filtered after the 1- hour time of adsorption had been completed. The final concentration of metal ions left in the filtrate was analyzed using AAS. Adsorption standard free energy changes (ΔG°), the standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) were obtained from experiments at various temperatures using equations 2 and 3^[16].

$$\Delta G^{\circ} = -RT \ln K \dots\dots\dots 2$$

$$\ln K = \Delta S^{\circ}/R - \Delta H^{\circ}/RT \dots\dots\dots 3$$

where R (8.3145 J mol⁻¹ K⁻¹) is the gas constant, K(L g⁻¹) is the Langmuir constant and T (K) is the absolute temperature^[16].

2.3.6 Kinetics study

To perform the kinetics experiment, 0.10 g of the geopolymer adsorbents was placed in 100 mL stoppered bottles. 50 mL of 100 mg/L of the metal ions of monocomponent was added and the mixture put in a water bath electric shaker at residence time ranging from 20 to 80 minutes. The mixtures were kept at a constant shaking speed of 120 rpm at $25^{\circ}\text{C} \pm 1$ and then filtered and residual metal ions concentration contained in the filtrate measured using a spectrophotometer. This provides C_t data, and equation (4) was used to calculate q_t.

$$qt = (C_0 - C_t) \frac{V}{W} \dots\dots\dots 4$$

Where V is the volume of adsorbate solution in (L), and W is the mass of the adsorbent in (g). The data obtained was used to plot graphs of log (q_e - q_t) against t for Pseudo- first order and t/qt against t for Pseudo-second order and determine kinetic parameters as per equations 5 and 6 respectively.

$$\text{Log} (q_e - q_t) = \text{Log} q_e - \frac{K t}{2.303} \dots\dots\dots 5$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_t} t \dots\dots\dots 6$$

Where q_e is amount adsorbed at equilibrium, q_t is amount adsorbed at a given time, t is residence time in minutes, K is Lagergren rate constant and K₂ is rate constant for Pseudo -second order.

III. Results and Discussion

3.1 Adsorption studies of geopolymers

3.1.1. Effect of pH

The adsorption of Pb (II) ions was found to be strongly dependent on the pH of the solution. Figure 1 demonstrates that the optimum pH for the adsorption of Pb (II) ions was about 4.0 on geopolymers which were rather acidic. Adsorption increased from over 50 % at pH of 2 to higher mean percentages of 70.54± 0.43, 79.65 ± 0.27 and 90.23 ± 0.04 for GP-1, GP-2 and GP-3 respectively. GP-3 gave higher adsorption of Pb (II) than GP-1 and GP-2 and this could be associated with the high SiO₂/ Al₂O₃ ratio in it^[11] that led to increase in the silica content in the framework causing increased negatively charged groups of O-Si-O- in the geopolymers^[17].

The low adsorption percentage of the metal ion at lower pH values could be explained by the competition between H⁺ and Pb (II) ions on the available exchange sites of the adsorbents^[18]. At moderate pH values (4-5), linked H⁺ ions are released from the active sites leading to an increase of metal ions. However, the experiments on adsorption of Pb (II) ions could not be performed beyond pH of 6.0 due to the low solubility of

Pb (II) hydroxide in water which forms as white precipitation at that pH^[19]. Similar trend of effect of pH on adsorption of Pb (II) ions was reported by Amer *et al.* ^[20] on adsorption of Pb (II), Zn (II) and Cd (II) ions onto polyphosphate-modified kaolinite clay.

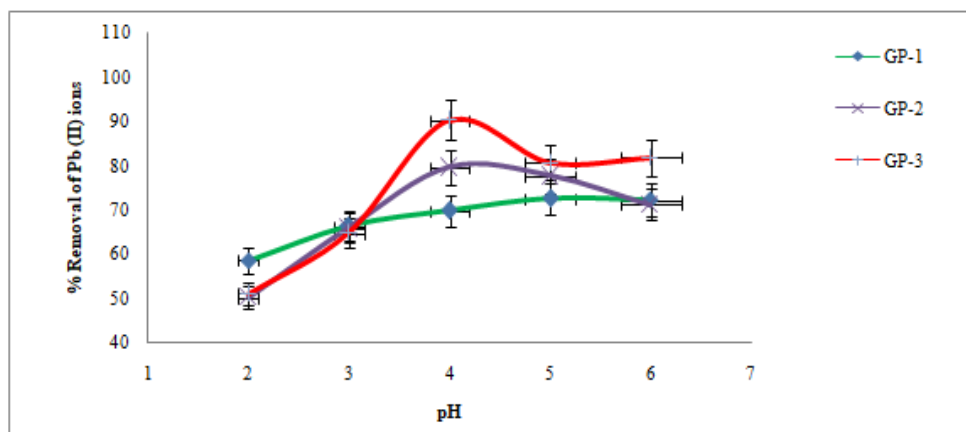


Figure 1: Effect of pH on Pb (II) ions removal onto geopolymer materials (Pb (II) ions concentration = 100 mg/L, adsorbent dose = 0.1 g/50 mL, shaking speed = 120 rpm, temperature = 25 °C ± 1 and error bars indicate the average deviation from the mean).

3.1.2 Effect of residence time on adsorption process

The importance of contact time comes from the need for characterization of the feasible rapidness of binding and removal processes of the heavy metal ions by the new geopolymers and obtaining the optimum time for complete removal of the target metal ions^[21]. The result from figure 2 showed that adsorption efficiency increased with increase in contact time. This may be due to the fact that the number of active adsorption sites on the surface of adsorbent was more initially^[22]. The fast adsorbate adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the adsorbent surface. Adsorption rate slowed down after 80 minutes and this could have been due to the electrostatic hindrance caused by already sorbed positively charged adsorbate species and the slow pore diffusion of the ions. The slow rate could also be due to lesser number of available active sites and slow rate of conveying adsorbates from the outer surface to the inner surface of the adsorbent^[22]. Similar results have been reported in literature^{[23], [24]}.

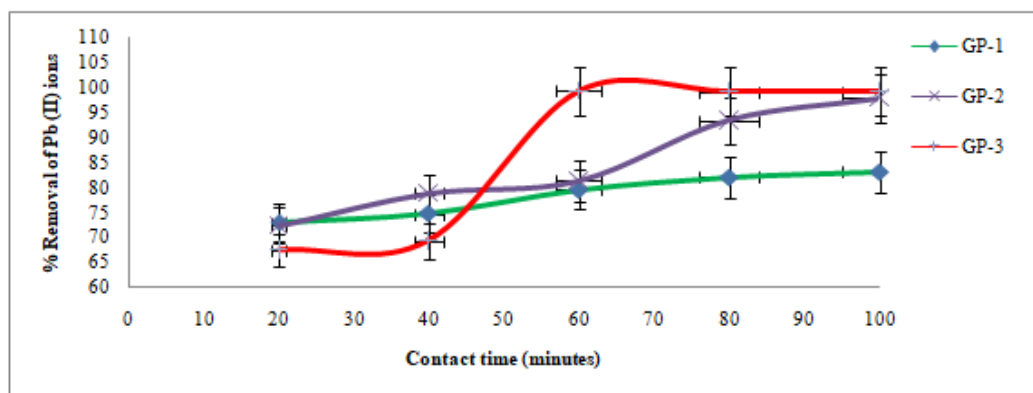


Figure.2: Effect of contact time on Pb (II) ions removal onto geopolymer materials (Pb (II) ions concentration = 100 mg/L, adsorbent dose = 0.1 g/50 mL, shaking speed = 120 rpm, pH = 4.0 temperature = 25 °C and error bars indicate the average deviation from the mean).

3.1.3 Effect of temperatures on adsorption process

Temperature is a crucial parameter in adsorption reactions. Higher temperature increases adsorbate motion allowing the uptake of metal ions into the pores more easily, causing adsorption to increase. Figure 3 shows the effect of percentage removal of Pb (II) against temperature. The percentage removal increased from

87.65 ± 0.30 to 90.15 ± 0.11 when temperature was varied from 293 to 328 K for adsorbents GP-1. The mean percentage removal increased from 89.77 ± 0.11 and 92.55 ± 0.08 to 91.5 ± 0.02 and 93.94 ± 0.05 when temperature was adjusted from 293 to 318 K and then dropped to 91.35 and 93.72% for adsorbents GP-2 and GP-3 respectively. According to Nassar and Magdy^[25], increase in adsorption at equilibrium with increase in temperature is due to the acceleration of some originally slow adsorption steps or to the creation of some active sites on the adsorbent surface. Adsorption with ion exchange is an endothermic reaction, whereas adsorption with nonionic exchange is an exothermic reaction^[26]. Therefore, increasing temperature increased the sorption rate suggesting that Pb (II) ions and Na ions underwent an ionic exchange to achieve heavy metal removal by the geopolymer. At temperature above 328 K, the thickness of the boundary layer decreased due to the increased tendency of the metal ions to escape from the geopolymer surface to the bulk of solution and this lead to decrease in adsorption as temperature increases^[27]. Al-Zboon *et al.*^[28] studied the effects of temperature on the adsorption of Pb (II) ions from aqueous solution by fly ash-based geopolymer, which showed a similar pattern.

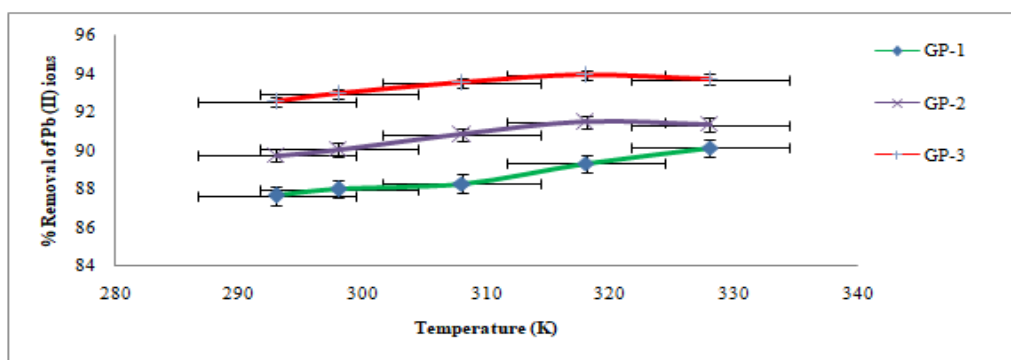


Figure 3: Effect of temperature on Pb (II) ions removal onto geopolymer materials (Contact time = 60 minutes, shaking speed of 120 rpm, pH = 4.0 and adsorbent dose = 0.1g/50mL).

3.1.4 Effect of the initial concentration

Initial concentration of metal ions is an important factor for practical application^[29]. Results of the study on the influence of initial Pb (II) ions concentration on the removal efficiency of the geopolymers are depicted in figure 4 and the results obtained indicated that the adsorption efficiency decreased with increase in initial Pb (II) ions concentration. Mean percentage removal decreased from 89.33 ± 1.12, 95.82 ± 0.05 and 88.15 ± 2.44 to 69.31 ± 0.04, 65.09 ± 0.03 and 67.04 ± 0.21 when concentration was varied from (20 – 500 mg/L) for GP-1 GP-2 and GP-3 respectively. In this study, adsorption decreased with increase of initial concentration and any increase of metal ion led to increase of the residual ion in solution. It is probable that along with increase of surface load (adsorbed substances) on the adsorbent, upper surface adsorption sites are saturated and the efficiency of removal decreased rapidly^[30]. At lower concentrations, the number of moles of Pb (II) ions is small relative to the available adsorption sites on the adsorbent hence high rate of adsorption^[31]. However, at higher concentrations, most of the adsorption sites are occupied by Pb (II) ions and the available sites of adsorption become fewer^[32]. Rezaei^[33] reported that with increase of metal ion concentration, adsorption decreases. This behaviour is connected with the competitive diffusion process of the metal ions through the micro- channel and pores in geopolymers^[23]. This competition locks the inlet of channel on the surface and prevents the metal ions from passing deeply inside the geopolymer; hence adsorption occurs only on the surface^[23]. A similar trend of decrease in adsorption of Pb (II) ions with increase in metal ion concentration was reported by Senthil Kumar and Gayathri^[34].

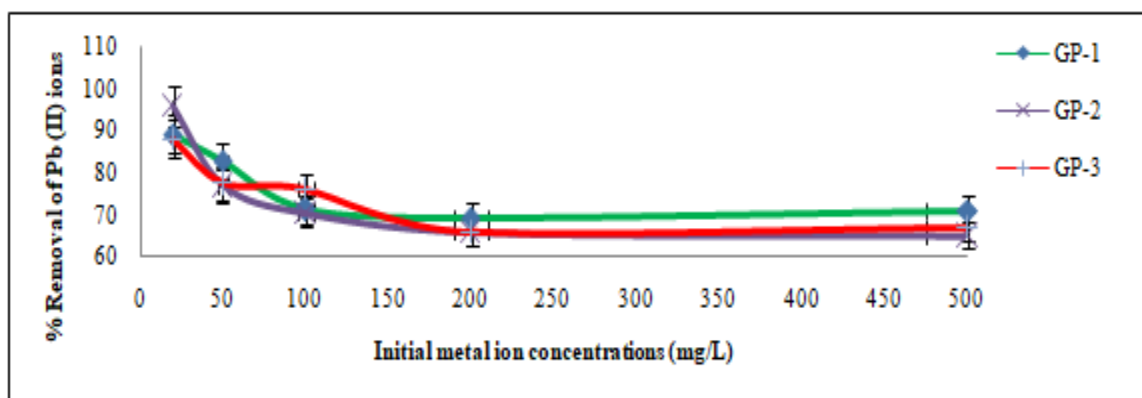


Figure 4: Effect of metal ion concentration on Pb (II) ions removal onto geopolymer materials (Contact time = 60 minutes, adsorbent dose = 0.1 g/50 mL, shaking speed = 120 rpm, pH = 4.0, temperature = 25 °C and error bars indicate the average deviation from the mean).

3.2 Adsorption isotherms

The adsorption data for Pb (II) ions on the adsorbents were fitted onto Langmuir, Freundlich, the Langmuir Freundlich mathematical models and their equilibrium constants are presented in table 1. The adsorption data for all the adsorbents best fitted into the modified Langmuir Freundlich isotherm. The variables estimation was done using the Microsoft excel solver with a non-negativity constraint restriction for K_{LF} values. The R^2 values of the fitting were 0.996, 0.999 and 0.982 for GP-1, GP-2 and GP-3 respectively. The values of R^2 showed good fit for the experimental data. The results indicate that the L F isotherm is the best suited to describe metal ion dependent Pb (II) ions adsorption effects. Adsorption capacities obtained using L F isotherms are as recorded in table 1.

Table 1: Equilibrium constants for Pb (II) ions sorbed onto geopolymers

adsorbents	Freundlich			Langmuir			Langmuir-Freundlich			
	1/n	K_f (mg/g)	R^2	b (dm ³ /g)	Q_{max}	R^2	Q_{max}	K_{LF}	b	R^2
GP-1	1.33	0.76	0.995	-1.00	0.006	0.423	27.0	1.0×10^1	0.72	0.996
GP-2	1.33	0.75	0.983	-0.99	0.007	0.522	79.58	1.5×10^{-4}	0.68	0.999
GP-3	1.44	0.41	0.962	-2.68	0.006	0.610	209.9	5.85	0.62	0.982

The equations of these models are: Langmuir: $q_e = Q_m K_L C_e / (1 + K_L C_e)$; Freundlich: $q_e = K_f C_e^{1/n}$; Langmuir Freundlich: $q_e = Q_m (K_{LF} C_e)^b / [1 + (K_{LF} C_e)^b]$.

These results show that the modified Langmuir Freundlich isotherm was best suited to describe metal ion dependent adsorption effects. Consequently, it implies that cooperative adsorption occurred between heterogeneous surface and homogenous surface of adsorbent. The indexes of heterogeneity, b values were 0.72, 0.68 and 0.62 for GP-1, GP-2 and GP-3 respectively. According to Rushton *et al.*^[35], approach of heterogeneity index to unity, indicates change of adsorbent surface to homogenous and whereas decrease approaching zero indicates change of surface to heterogeneous. The values obtained in this study shows increase in SiO_2/Al_2O_3 ratio as reported by Maingi *et al.*^[11] on geopolymers GP-1, GP-2 and GP-3 favoured change of adsorption surface to heterogeneous. Increase in Si/Al ratio caused by use of different clays increased the isomorphous replacement of Si^{4+} by Al^{3+} hence producing more negative charges in the geopolymer lattice^[36]. The negative charges are balanced by Na^+ which is exchangeable with heavy metal ions increasing adsorption capacities^[37]. Adsorption capacities obtained using Langmuir Freundlich isotherms are recorded in table 1. Günay *et al.*^[38] also stated that three-parameter isotherm models resulted in better performance than two-parameter models.

3.3 Adsorption thermodynamic studies

The ΔH° and ΔS° values obtained are presented in table 2. The decrease in the value of ΔG° with an increase in temperature shows that the reaction was more spontaneous, which indicates that adsorption was favoured by increase in temperature^[39]. All ΔG° values calculated were between 0 and -20 kJ/mole corresponding to spontaneous physisorption^[40]. The positive values of ΔH° obtained indicated the endothermic

nature of adsorption and governs the possibility of physical adsorption^[41]. The low ΔH° values also depict that the metal ion was physisorbed onto the adsorbent^{[42], [43]}. The negative values of ΔG° (Table 2) stipulated that the adsorption was highly favorable for Pb (II) ions. Additionally, the positive values of ΔS° confirmed the increased randomness at the solid- solute interface during the adsorption process which shows the solution systems tends towards stability when the adsorption of Pb (II) ions on the surface of adsorbent occurred according to the second law of thermodynamics^[44]. More heat was required to bind the metal ions on the surface of adsorbent.

Table 2: Thermodynamic parameters for adsorption of Pb (II) ions onto geopolymers

Geopolymer	ΔH° (KJ/Mol)	ΔS° (J/Mol/K)	ΔG° (KJ/Mol)				
			293K	298K	308K	318K	328K
GP-1	2.49	15.51	-4.78	-4.93	-5.17	-5.62	-6.04
GP-2	2.08	14.99	-5.29	-5.46	-5.88	-6.28	-6.43
GP-3	1.99	15.99	-6.14	-6.40	-6.85	-7.25	-7.37

ΔH° = Enthalpy change, ΔS° = Change in entropy, ΔG° = Change in Gibbs free energy

3.4 Kinetic studies

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 density q_e . However, the experimental data deviated considerably from the calculated data as shown in table 3. A comparison of the results with the correlation coefficients is shown in table 3. The correlation coefficients for the Pseudo- first order obtained at the studied concentration were low compared to those of Pseudo- second order. In addition, the theoretical q_e values found from the Pseudo-first order did not give reasonable values. This suggests that adsorption system of Pb (II) ions was not a first order reaction. The correlation coefficients for the second order kinetic obtained were greater than 0.95. The equilibrium adsorption capacities obtained with this model were more reasonable than those of the Pseudo-first order when comparing predicted results with experimental data. Moreover, the values of R^2 also indicated that this model produced better results. These indicate that the adsorption system studied belongs to the second order kinetic model that presupposes that Pb (II) ions adsorption on geopolymer adsorbents may have occurred through a chemical process involving the valence forces or exchanged electrons^[45]. Similar phenomena were also observed in adsorption of Cu (II) ions and Pb (II) ions on tea waste^[46].

Table 3: Descriptive data on rate constants of Pb (II) adsorption on geopolymers as estimated from Pseudo-first and second order kinetic models

Pseudo-first order							Pseudo-second order			
GP	q_e (exp)	SD	q_e (cal)	SD	K_L	R^2	q_e (cal)	SD	K_2	R^2
1	36.34	0.05	15.91	1.34	0.034	0.939	39.95	0.09	2.5×10^{-3}	0.996
2	39.82	0.04	21.82	0.65	0.033	0.887	43.54	0.11	2.0×10^{-3}	0.991
3	45.12	0.01	62.78	0.51	0.054	0.773	57.47	0.00	7.05×10^{-4}	0.968

GP= Geopolymer adsorbents, SD = standard deviation, q_e (exp) (mg/g) = q_e obtained from adsorption experiment, q_e (cal) (mg/g) = q_e calculated from the Pseudo graphs, K_L (min^{-1}) = rate constant for Pseudo –first order reaction, K_2 (g/mg.min) = rate constant for Pseudo –second order reaction and R^2 = correlation coefficients, initial metal ion concentration = 100mg/L and residence time varied (20 - 100 minutes).

IV. Conclusions

Based on adsorption data obtained, GP-3 proved better in adsorption of Pb (II) ions than GP-1 and GP-2 as a result of its higher $\text{SiO}_2/\text{Al}_2\text{O}_3$. Geopolymers GP-3 recorded a high adsorption capacity of 209.9mg/g which makes it a potential good adsorbent. The experimental data was found to fit modified Langmuir Freundlich adsorption model better than the other models and hence was used for analyzing the efficiency of adsorption of the lead ions onto the geopolymers. The correlation coefficients for the second-order kinetic model obtained were greater than those of Pseudo- first order and therefore indicating that adsorption system studied belonged to the pseudo-second order. The positive values of ΔH° obtained in this study indicate the endothermic nature of adsorption and governs the possibility of physical adsorption. Additionally, the positive value of ΔS° confirmed the increased randomness at the solid- solute interface during the adsorption process which shows the solution systems tended towards stability when the adsorption of Pb (II) on the surface of adsorbent occurred according to the second law of thermodynamics. This study has shown that Kenyan common

clays which have few economic endeavors are good raw material for synthesis of geopolymers for adsorption application of Pb (II) ions.

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References

- [1]. Ogoyi, D. O., Mwita, C. J., Nguu, E. K., and Shiundu, P. M. Determination of Heavy Metal Content in Water, Sediment and Microalgae from Lake Victoria, East Africa. *The Open Environmental Engineering Journal*, 2011; 4: 156–161.
- [2]. Fu, F., and Wang, Q. Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, 2011; 92: 407–418.
- [3]. López, F. A., Martín, M. I., Pérez, C., López-Delgado, A., and Alguacil, F. J. Adsorción de metal espes adossobre cascarilla de laminación. *Revista de Metalurgia*. <https://doi.org/10.3989/revmetalim.2003.v.39.i3.332>
- [4]. Buchwald, A., Zellmann, H. D., and Kaps, C. Condensation of aluminosilicate gels-model system for geopolymer binders. *Journal of Non-Crystalline Solids*, 2011; 357: 1376–1382.
- [5]. Barbosa, V. F. F., and MacKenzie, J. D. Synthesis and thermal behaviour of potassium sialate geopolymers. *Materials Letters*, 2003; 57: 1477–1482.
- [6]. Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G. C., Palomo, A., and Van Deventer, J. S. J. Geopolymer technology: The current state of the art. *Journal of Materials Science*, 2007; 42: 2917–2933.
- [7]. Goretta, K. C., Gutierrez-Mora, F., Singh, D., Routbort, J. L., Lukey, G. C., and Van Deventer, J. S. J. Erosion of geopolymers made from industrial waste. *Journal of Materials Science*, 2007; 42: 3066–3072.
- [8]. Yip, C. K., Lukey, G. C., and Van Deventer, J. S. J. Effect of blast furnace slag addition on microstructure and properties of metakaolinite geopolymeric materials. *Advances in Ceramic Matrix Composites IX*, 2003; 153: 187–209 347.
- [9]. Kong, D. L. Y., Sanjayan, J. G., and Sagoe-Crentsil, K. Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures. *Cement and Concrete Research*, 2007; 37: 1583–1589.
- [10]. Cheng, T. W., Lee, M. L., Ko, M. S., Ueng, T. H., and Yang, S. F. The heavy metal adsorption characteristics on metakaolin-based geopolymer. *Applied Clay Science*, 2012; 56: 90–96.
- [11]. Maingi, F. M., Mbuvi, H. M., Ng'ang'a, M. M. and Mwangi, H. Adsorption Kinetics and Isotherms of Methylene Blue by Geopolymers Derived from Common Clay and Rice Husk Ash. *Journal of Physical Chemistry*, 2017; 7(4): 87-97.
- [12]. Moreno-piraján, J. C., and Giraldo, L. Heavy Metal Ions Adsorption from Wastewater Using Activated Carbon from Orange Peel, *European Journal of Chemistry*, 2012; 9: 926–937.
- [13]. Ryan, J., Estefan, G., and Rashid, A. Soil and Plant analysis Laboratory Manual, (2 nd ed.), International Center for Agricultural Research in the Dry Areas, Aleppo, Syria, 2001; pp. 5–141.
- [14]. Okewale, A., Babayemi, K., and Olalekan, A. Adsorption Isotherms and Kinetics Models of Starchy Adsorbents on Uptake of Water from Ethanol – Water Systems. *International Journal of Applied Science and Technology*, 2013; 3:35–42.
- [15]. Vijayakumar, G., Tamilarasan, R., and Dharmendrakumar, M. Adsorption, kinetic, equilibrium and thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite. *Journal of Materials and Environmental Science*, 2012; 3:157–170.
- [16]. Yao, Y., Xu, F., Chen, M., Xu, Z., and Zhu, Z. Adsorption behavior of methylene blue on carbon nanotubes. *Bioresource Technology*, 2010; 101: 3040–3046.
- [17]. Aranberri, I., and Bismarck, A. Caracterización Superficial de Minerales Arcillosos Presentes en los Depósitos de Crudo. *Anales de Química*, 2007; 103: 23–27.
- [18]. Sari, A., Tuzen, M., Citak, D., and Soylak, M. Adsorption characteristics of Cu(II) and Pb(II) onto expanded perlite from aqueous solution. *Journal of Hazardous Materials*, 2007a; 148: 387–394.
- [19]. Sen Gupta, S., and Bhattacharyya, K. G. Immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium. *Journal of Environmental Management*, 2008; 87: 46–58.
- [20]. Amer, M. W., Khalili, F. I., and Awwad, A. M. Adsorption of lead, zinc and cadmium ions on polyphosphate-modified kaolinite clay. *Environmental Chemistry*, 2010; 2: 001–008.
- [21]. Arshadi, M., Amiri, M. J., and Mousavi, S. Kinetic, equilibrium and thermodynamic investigations of Ni(II), Cd(II), Cu(II) and Co(II) adsorption on barley straw ash. *Water Resources and Industry*, 2014; 6: 1–17.
- [22]. Dubey, A., and Shiwani, S. Adsorption of lead using a new green material obtained from Portulaca plant. *International Journal of Environmental Science and Technology*, 2012;9: 15–20.
- [23]. Al-Anber, Z. A., and Al-Anber, M. A. S. Thermodynamics and kinetic studies of iron(III) adsorption by olive cake in a batch system. *Journal of the Mexican Chemical Society*, 2008; 52: 108–115.
- [24]. El-Ashtouky, E. S. Z., Amin, N. K., and Abdelwahab, O. Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination*, 2008; 223: 162–173.
- [25]. Nassar, M. M., and Magdy, Y. H. Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles. *Chemical Engineering Journal*, 1997; 66: 223–226.
- [26]. Cheng, T. W., Lee, M. L., Ko, M. S., Ueng, T. H., and Yang, S. F. The heavy metal adsorption characteristics on metakaolin-based geopolymer. *Applied Clay Science*, 2012; 56: 90–96.
- [27]. Aksu, Z., and Kutsal, T. A bioseparation process for removing lead (II) ions from waste water by using *Chlorella vulgaris*. *Journal of Chemical Technology and Biotechnology*, 1991;52: 109–118.
- [28]. Al-Zboon, K., Al-Harashsheh, M. S., and Hani, F. B. Fly ash-based geopolymer for Pb removal from aqueous solution. *Journal of Hazardous Materials*, 2011;188P: 414–421.
- [29]. Sobhanardakani, S., Zandipak, R., and Javad, M. Removal of Ni (II) and Zn (II) from Aqueous Solutions Using Chitosan, *Archives of Hygiene Science*, 2016; 5: 47–55.
- [30]. Banat, F. A., Al-Bashir, B., Al-Asheh, S., and Hayajneh, O. Adsorption of phenol by bentonite. *Environmental Pollution*, 2000; 107: 391–398.

- [31]. Jnr, M. H., and Spiff, A. I. Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by *Caladium bicolor* (wild cocoyam). *African Journal of Biotechnology*, 2005; 4: 191–196
- [32]. Berhe, S., Ayele, D., Tadesse, A., and Mulu, A. Adsorption Efficiency of Coffee Husk for Removal of Lead (II) from Industrial Effluents : *Equilibrium*, 2015; 5: 1–8.
- [33]. Rezaei, H. Biosorption of chromium by using *Spirulina* sp. *Arabian Journal of Chemistry*, 2016; 9: 846–853.
- [34]. Senthil Kumar, P., Ramalingam, S., Senthamarai, C., Niranjanaa, M., Vijayalakshmi, P., and Sivanesan, S. Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination*, 2010; 261: 52–60.
- [35]. Rushton, G. T., Karns, C. L., and Shimizu, K. D. A critical examination of the use of the Freundlich isotherm in characterizing molecularly imprinted polymers (MIPs). *Analytica Chimica Acta*, 2005; 528: 107–113.
- [36]. Shaheen, S. M., Derbalah, A. S., and Moghanm, F. S. Removal of Heavy Metals from Aqueous Solution by Zeolite in Competitive Sorption System. *International Journal of Environmental Science and Development*, 2012; 3: 362–367.
- [37]. Erdem, E., Karapinar, N., and Donat, R. The removal of heavy metal cations by natural zeolites. *Journal of Colloid and Interface Science*, 2004; 280: 309–314.
- [38]. Günay, A., Arslankaya, E., and Tosun, I. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, 2007; 146: 362–371.
- [39]. Mustafa, S., Zaman, M. I., Gul, R., and Khan, S. Effect of Ni^{2+} loading on the mechanism of phosphate anion sorption by iron hydroxide. *Separation and Purification Technology*, 2008; 59: 108–114.
- [40]. Mahmoud, M., El-Latif, A., Ibrahim, A. M., Showman, M. S., and Hamide, R. R. A. Alumina/Iron Oxide Nano Composite for Cadmium Ions Removal from Aqueous Solutions. *International Journal of Nonferrous Metallurgy*, 2013; 2: 47–62.
- [41]. Ghosh, D., and Bhattacharyya, K. G. Adsorption of methylene blue on kaolinite. *Applied Clay Science*, 2002; 20: 295–300.
- [42]. Gong, R., Li, M., Yang, C., Sun, Y., and Chen, J. Removal of cationic dyes from aqueous solution by adsorption on peanut hull. *Journal of Hazardous Materials*, 2005; 121: 247–250.
- [43]. Bueno, B. Y. M., Torem, M. L., Molina, F., and de Mesquita, L. M. S. Biosorption of lead(II), chromium(III) and copper(II) by *R. opacus*: Equilibrium and kinetic studies. *Minerals Engineering*, 2008; 21: 65–75.
- [44]. Liu, L. E., Liu, J., Li, H., Zhang, H., Liu, J., and Zhang, H. Equilibrium, kinetic, and thermodynamic studies of lead (II) biosorption on sesame leaf. *BioResources*, 2012; 7: 3555–3572.
- [45]. Al-Ghouti, M., Khraisheh, M. A. M., Ahmad, M. N. M., and Allen, S. Thermodynamic behavior and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: A kinetic study. *Section Title: Surface Chemistry and Colloids*, 2005; 287: 6–13.
- [46]. Amarasinghe, B. M. W. P. K., and Williams, R. A. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal*, 2007; 132: 299–309.