Clay-Rice Husk Ash based Geopolymers for Remediation of Pb (II) and Cd (II) from Wastewater

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Received	Reviewed	Accepted	Published
26th June 2019	30th July 2019	17th Sept 2019	31st October, 2019

Abstract

Industrialization and technological advancements have led to the generation of numerous pollutants such as heavy metals into the aquatic ecosystem. These toxic compounds are extremely dangerous to human health and the environment due to their non-biodegradability, severe toxicity, ability to accumulate and contaminate ground and surface waters. Subsequently, pursuance of sustainable materials and technologies for better attainment of environmental sustainability is critical. This study reports the synthesis of geopolymers GP-1, GP-2 and GP-3 from different clays. Geopolymers were hydrothermally synthesized using clay and rice husks waste as an alumina and silica source respectively. The geopolymers were characterized using Fourier transform-infra red, energy dispersive spectrometry, X-ray diffraction and scanning electron microscope. Batch and gravitational column experiments using Pb (II) and Cd (II) ions were carried out. Increased metal ion uptake was recorded with raised Si/Al ratio of the adsorbents. The mean percentage uptake of 90.23 ± 0.4 and 89.63 ± 0.18 of Pb (II) and Cd (II) were achieved at pH of 4.0 and 5.0 respectively using GP-3. Langmuir, Freundlich and modified Langmuir Freundlich isotherms were used in equilibrium studies. Data for adsorption of Pb (II) and Cd (II) fitted best in the modified Langmuir Freundlich model. The highest adsorption capacities of Pb (II) and Cd (II) were 209.9 and 136.2 mg/g respectively, attained using GP-3. Based on the results obtained, geopolymers produced from common clay and rice husk waste displayed promising potentials in the removal of heavy metal ions from the aqueous phase. Considering the availability of raw materials for geopolymerization and the high metal ions uptake capacities of geopolymers, they can also be used as adsorbents for removal of heavy metals in industrial wastewater.

Keywords: Adsorption; Characterized; Geopolymers; Isotherm; Wastewater.

Introduction

Water is an essential resource for life which greatly influences our public and environmental health as well as providing the pedestal for most of our economic activities. Unsustainable use of fresh water resources, population increase, and the trend in industrial revolution have led to environmental degradation especially by the release of partially treated or untreated wastewater containing heavy metals such as Pb, Hg, Cd among others into aquatic systems (UNESCO, 2009). Some health effects of these heavy metals when ingested includes diarrhea, stomatitis, tremor, hemoglobinuria, rust– red colour to stool, paralysis, vomiting and convulsion, depression, renal dysfunction, cancer and Alzheimer's diseases (Verma and Dwivedi, 2013). Several conventional treatment strategies such as chemical precipitation, ion exchange, filtration and electrochemical treatments have been applied for removing these heavy metals, but most of them are only suitable for large scale treatments and are costly to operate (Aeisyah *et al*., 2014). The adsorption process is regarded as a captivating alternative for the removal of heavy metals ions from effluents due to its effectiveness and easily attainable nature (Pamukoglu and Kargi, 2008). Consequently, there is need for further investigation into geopolymer materials. Readily-available rice husks and common clay have been proposed to meet this demand of geosynthesis. The synthesis of geopolymers takes place using reactive precursors such as metakaolin or many other natural and artificial silico-aluminates, which are mixed with alkali metal (Na or K) hydroxide and/or silicate solutions (Barbosa *et al*., 2000). Applications of geopolymer-based materials in the fields of new ceramics, binders, matrices for hazardous waste stabilization, fire-resistant, asbestos-free, and high-tech materials have been documented (Van Jaarsveld *et al*., 1997). In order to improve environmental sustainability and enhance economic viability of geopolymers, this study reports synthesis of geopolymers from common clays and rice husk ash for adsorption applications.

Materials and Methods

Chemicals and Reagents

NaOH was used as a dissolution agent and as a catalyst in the course of geosynthesis. Analytical grade $Pb(NO_3)_2$, $Cd(NO_3)_2$ and HNO_3 from Sigma Aldrich were utilized in adsorption experiments.

Preparation of Geopolymers

Geopolymers were prepared using the procedure given by López *et al*. (2014). 20g of rice husk ash containing 71.54% of SiO_2 was blended with 100 cm^3 of 8 M NaOH solution and agitated with the aid of a magnetic stirrer for 15 minutes. 50g of calcined clay powder from Molo, Kuresoi and Kakamega containing 37.17,

36.16 and 40.94% SiO_2 respectively and 30.03, 32.54 and 36.25% Al_2O_3 respectively was added to the mixture and thoroughly mixed using a ball mill method for 5 hours. The ensuing pastes were vibrated for 5 minutes in pestles. Curing of the resulting pastes was carried out at 80 $^{\circ}$C for 12 hours. The pastes were removed from the molds, placed in an oven at 200 $^{\circ}$C for 12 hours in order to complete polycondensation process (López *et al*., 2014). Geopolymers were coded as GP-1, GP-2 and GP-3.

Adsorption Experiments

Effects of PH on Sorption of Pb (II) and Cd (II) Ions

Batch experiments were administered by adjusting the pH of Pb (II) and Cd (II) ions solution from 2 to 6. Monocomponent solution of metal ions containing 50 mL of 100 mg/L pH established was placed in 100 mL stoppered plastic bottles. 0.1g of geopolymer materials was put into each of the five stoppered bottles and placed in an electric shaker at 120 rpm, maintained at 25°C and shaken continuously for one hour. The reagent bottles were successively withdrawn after shaking for one hour and the supernatant solutions separated by filtration and the residual metal ions analyzed using the procedure of Ryan *et al*. (2001).

Column Studies for Pb (II) and Cd (II) Ions using Geopolymers

Column procedure used was adopted from Biswas and Mishra (2015). A glass column made of Pyrex tube with an internal diameter of 1 cm and height of 60 cm was fitted with cotton wool and held firmly in a vertical position. 5.0g of the prepared geopolymer was packed in the column, and then 0.5g of cotton wool placed on top of the bed and firmly secured in place by a layer of glass beads in order to provide a uniform flow of the solution through the column. Distilled water was poured to wet the column and ensure that all air was expelled between and within the geopolymer particles before the experiment was started. Adsorption experiments were done using 50 mL of 100 mg/L of synthetic wastewater containing monocomponent system of Pb (II) and Cd (II) ions at a pH of 4.0 and 5.0 respectively. Atmospheric pressure helped to push the sample through the geopolymer materials. The eluents were then analysed for residual metal ions concentration using AAS in accordance with the method reported in literature (Agbozu and Emoruwa, 2014).

Equilibrium Isotherm Study on Sorption of Pb (II) and Cd (II) Ions

The adsorption of metal ions from synthetic wastewater by geopolymer were explored by varying their initial concentrations from 20 to 500 mg/L, while upholding the pH of metal ion solution at 4.0 and 5.0 for Pb (II) and Cd (II) respectively and. 50 mL of concentrations 20, 50, 100, 200, and 500 mg/L of metal ions were put in plastic bottles and an exact amount of 0.10 g of

geopolymer material placed in each of the bottles. They were then placed in an electric shaker at 120 rpm for one hour. The data obtained was fitted in Langmuir, Freundlich and Langmuir Freundlich models.

Langmuir Isotherm

The Langmuir isotherm is based on the assumption that the adsorbent surface is homogeneous (Bakkory *et al*., 2016) is presented as shown in equation 1

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

Where, C_e is the concentration of metal ions at equilibrium (mg/dm^3); q_e is the amount of Pb (II) and Cd (II) ions adsorbed (mg/g); q_m is the adsorption capacities (mg/g); K_L is the isotherm constant (dm^3/mg).

Freundlich Isotherm

Freundlich isotherm is an empirical model which applies to multilayer adsorption (Foo and Hameed, 2010) and can be expressed by equation 2.

$$\text{Ln } q_e = \text{Ln } K_F + 1/n \text{ Ln } C_e \quad \text{.....(2)}$$

K_F is the Freundlich constant; $1/n$ is related to the adsorption intensity.

Modified Langmuir Freundlich Isotherm

The Langmuir Freundlich isotherm is a versatile isotherm expression used to simulate Langmuir and Freundlich behaviour (Nahm *et al*., 1977; Sips, 1948). Its expression is shown in equation 3 (Turiel *et al*., 2003).

$$qe = \frac{Q_{max}(KC_e)^b}{(KC_e)^b + 1} \quad \text{.....(3)}$$

where,

Q_{max} is the monolayer coverage (mg/ g), q_e is the adsorption capacity at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K is the affinity constant (L/mg) and b represents heterogeneity index.

Results and Discussion

Chemical Composition of Geopolymer

The principal components as analyzed by XRF (S1 titan) are shown in Table 1. The mean percentage of Al_2O_3 obtained was 16.05, 15.83 and 8.93 % and that of SiO_2 was 66.84, 66.21 and 73.99 % for GP-1, GP-2 and GP-3 respectively. Other elements and oxides found included Fe at 6.42, 5.65 and 9.05 %, K_2O at 4.43, 6.08 and 2.89 %, CaO at 1.88, 1.43 and 0.92 % and Ti at 1.38, 1.12 and 1.85 % for GP-1, GP-2 and GP-3, respectively. All the other elements and oxides were below 1 %. The results on composition of geopolymers are in agreement with results obtained by Lopez *et al*. (2014).

Table 1: Chemical Composition of Geopolymer

(%) Composition	GP-1		GP-2		GP-3	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**
SiO_2	66.84	0.44	66.21	0.49	73.99	0.45
Al_2O_3	16.05	0.39	15.83	0.43	8.93	0.32
Fe	6.42	0.03	5.65	0.03	9.05	0.04
CaO	1.88	0.02	1.43	0.02	0.92	0.02
K_2O	4.43	0.03	6.08	0.04	2.89	0.02
Ti	1.38	0.01	1.12	0.01	1.85	0.01
SiO_2/Al_2O_3	4.16		4.18		8.28	

GP-1= Geopolymer from Kakamega clay, GP- 2= Geopolymer from Kuresoi clay, GP- 3= Geopolymer from Molo clay and SD = Standard deviation.

Functional Group Analysis on Geopolymers

Fourier transform infra-red analysis was used to identify functional groups in the polymers. Absorption spectra in terms of transmittance were recorded in the 4000–400 cm^{-1} range using IRTracer model Shimadzu, equipped with deuterated, L-alanine doped triglycine sulfate with potassium bromide windows detector. Broad bands were observed in all geopolymers at ~3450 cm^{-1} attributed to –OH stretching mode as shown in Figure 1.

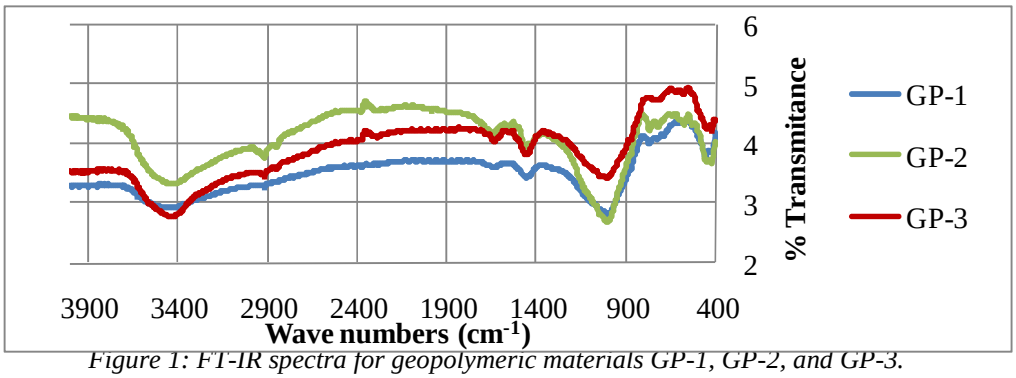


Figure 1: FT-IR spectra for geopolymeric materials GP-1, GP-2, and GP-3.

Another spectral band at around 1400 cm^{-1} appeared in all the geopolymer samples characteristic of the asymmetric O-C-O bonds of CO_3^{2-} stretching mode. The band indicates the presence of atmospheric carbonation of a high alkaline NaOH aqueous phase forming sodium carbonate, which is diffused onto the geopolymeric materials surface (Akpomie *et al*., 2015; Lee and Van Deventer, 2002b). The peaks at~979 cm^{-1} is associated with Al-O and Si-O asymmetric stretching vibrations, the fingerprint of geopolymerization region (Akpomie *et al*., 2015).

XRD Characterization of Geopolymers

Analysis was done using XRD and Cu Kα radiation at 40 kV with a graphite monochromator (λ=1.5418 À). The samples were ground using a micronizing mill (Glen Creston Company). XRD diffraction patterns obtained with different SiO_2/Al_2O_3 ratios are shown in Figure 2.

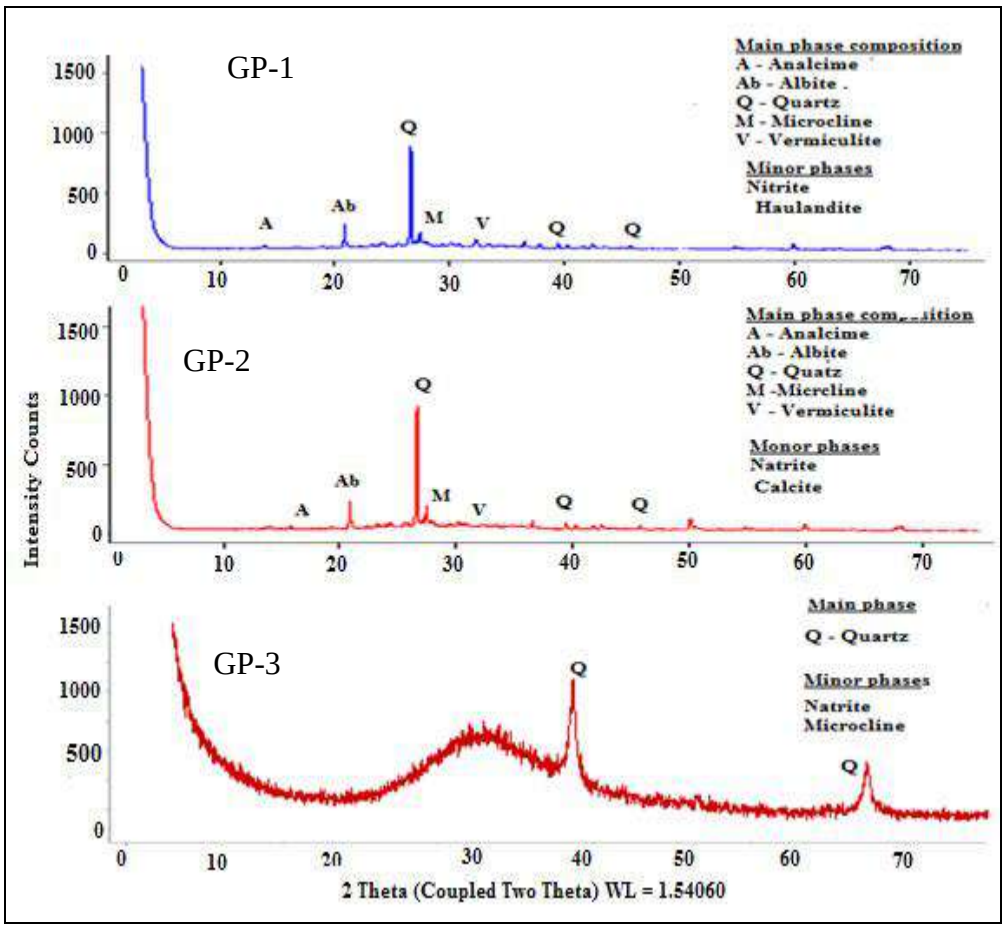


Figure 2: XRD diffraction patterns of materials GP-1, GP-2 and GP-3.

Crystalline phases identified in GP-1 and GP-2 included quartz (SiO_2), albite ($NaAlSi_3O_8$), vermiculite, microcline ($KAlSi_3O_8$), analcime ($NaAlSi_2O_6 \cdot H_2O$) and natrite (Na_2CO_3) among others. The main crystalline phase in GP-3 was quartz (SiO_2). The formation of carbonates was attributed to reaction of sodium-rich pores with atmospheric CO_2 on the surface of geopolymer (Hajimohammadi *et al*., 2011). Quartz is contained in all geopolymer materials. Absence of alumina phase in geopolymers is an indication that Al_2O_3 in raw materials existed in reactive amorphous form and hence took part in geopolymerization. An amorphous hump between 18-36° (2θ) was identified in all geopolymeric materials a characteristic reflection of amorphous geopolymers.

SEM Microstructure Analysis of Geopolymers

SEM images shown in Figure 3 revealed that the particles of the geopolymers were irregularly shaped but very compact. According to Mu *et al*. (2012), aperture surroundings in figure GP-2 could be consisting of tubular vitreous network. Energy dispersive X ray fluorescence analysis of gel showed that the phases contained Na-Si-Al in the bulk region (Lloyd *et al*., 2009). The main elements (Na, Al, Si, and O) make up geopolymers (Duxson *et al*., 2007). The remnants (Fe, Ca, K, and Mg) represent the calcined clay and rice husk ash phases which did not dissolve during alkali activation (Mu *et al*., 2012). Lee and Van Deventer (2002) suggested that during alkaline activation these remnants may be dispersed through the gel. This correlates with the published works of Lee and van Deventer (2002).

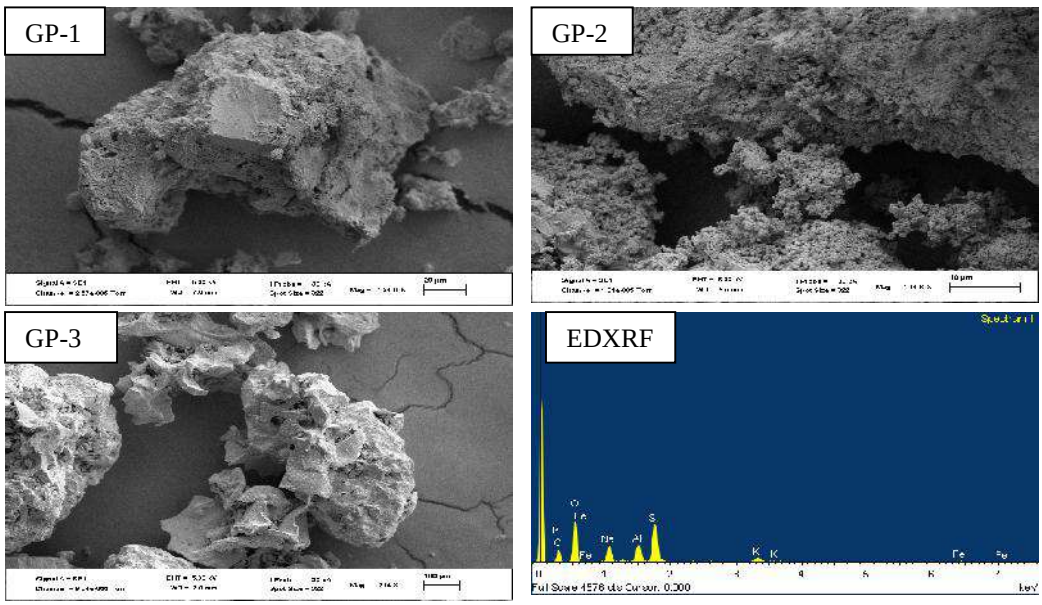


Figure 3: SEM micrographs for GP-1, GP-2 and GP-3 and EDXRF spectrum

Effect of PH on Adsorption of Pb (II) and Cd (II) Ions

The pH affects for both the surface charge of adsorbent and degree of ionization of the heavy metal ions in solution was explored. The adsorption of Pb (II) and Cd (II) ions was found to be strongly dependent on the pH of the solution as shown in Figure 4. Adsorption of Pb (II) ions on geopolymer material 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. The mean percentage removal of Cd (II) ions also increased from 82.85% ± 0.20, 82.93% ± 0.13 and 85.41% ± 0.11 to 86.16% ± 0.31, 86.71% ± 0.26 and 89.63 % ± 0.18 when pH was varied from (pH 2 – 5), for geopolymeric materials GP-1, GP-2 and GP-3 respectively. GP-3 gave higher adsorption of the metal ions than GP-1 and GP-2 and this could have been linked to high SiO_2: Al_2O_3 ratio present in the material. This led to increased negatively charged groups of O-Si-O- in the geopolymers (Aranberri and Bismarck, 2007). The low adsorption at lower pH could be attributed to electrostatic repulsion between H^+ and the metal ions on the available exchange sites of the adsorbents (Sari *et al*., 2007). Similar trend on effect of pH on adsorption was reported by Amer *et al*., (2010).

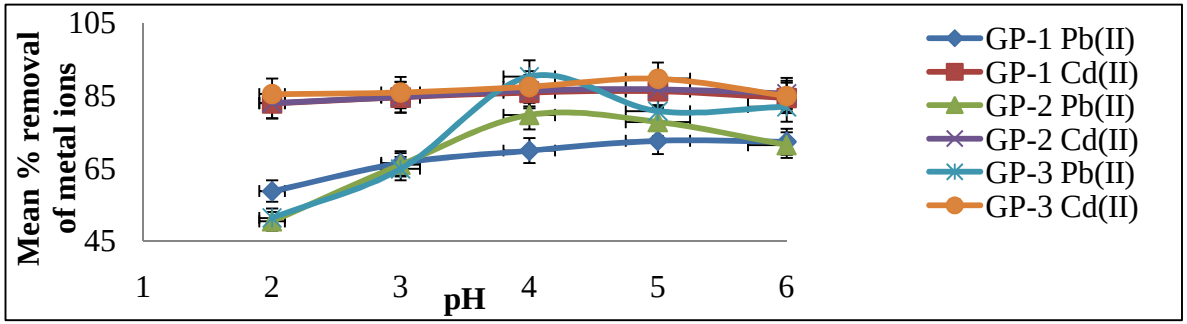


Figure 4: Effect of pH on Pb (II) and Cd (II) ions removal onto geopolymer materials

Column Adsorption Studies of Pb (II) and Cd (II) Ions

In order to improve the adsorption processes with conditions closer to real life water treatment systems, continuous processes were adopted. Percentage removal of Pb (II) ions increased from 80.54 ± 0.94% to 84.31 ± 0.74% while that of Cd (II) increased from 70.14 ±0.49% to 79.00 ± 0.64% with change of adsorbent from GP-1 to GP-3 as shown in Figure 5.

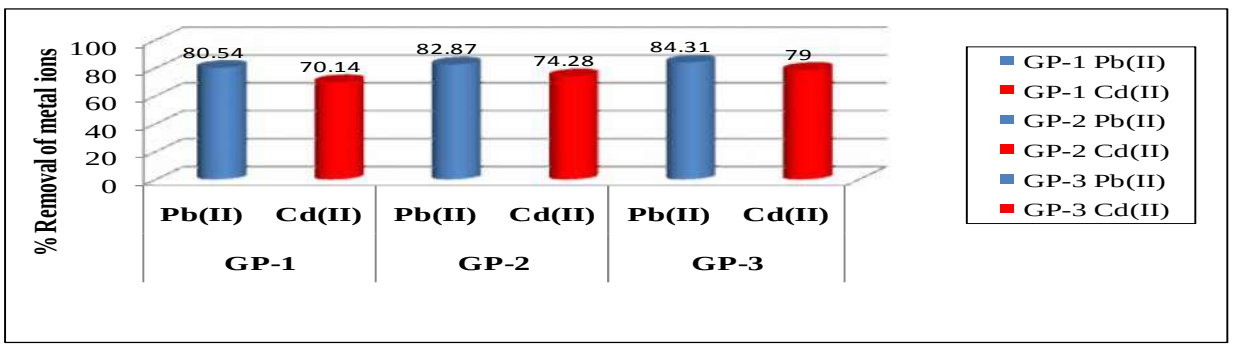


Figure 5: Effect of gravitational column adsorption of Pb (II) and Cd (II) ions onto geopolymer

The sorption uptake of Pb (II) and Cd (II) ions obtained using the batch mode at optimum pH differed from those obtained when using gravitational column studies. This phenomenal observation could be attributed to the fact that equilibrium between the solution metal phase and adsorbed metal phase had not been reached in the column study (Sounthararajah *et al*., 2015). However, the column study is closer to the operational conditions in the real full-scale treatment system and consequently the results from this study are more applicable to actual practical conditions.

Equilibrium Studies using Adsorption Isotherms

The adsorption data for Pb (II) and Cd (II) ions on the adsorbents were fitted onto Langmuir, Freundlich and modified Langmuir Freundlich and their equilibrium constants presented in Table 2.

Table 2: Isotherm model constants and correlation coefficients for adsorption of Pb (II) and Cd (II) ions

		Freundlich			Langmuir			Langmuir Freundlich			
Sorbent	Ion	1/n	K_f mg/g	R^2	K_L L/mg	Q_{max}	R^2	Q_{max}	K_{LF}	1/n	R^2
	Pb	1.33	0.76	0.995	-1.00	0.006	0.423	27.0	$1.0x10^{1}$	0.72	0.996
GP-1	Cd	1.25	0.14	0.982	-3.80	0.003	0.927	6.04	0.63	0.79	0.984
	Pb	1.33	0.75	0.983	-0.99	0.007	0.522	58.0	$1.5x10^{-4}$	0.68	0.999
GP-2	Cd	1.15	0.34	0.728	-22.02	0.017	0.108	45.2	0.111	0.67	0.939
	Pb	1.44	0.41	0.962	-2.68	0.006	0.610	209.9	5.85	0.62	0.982
GP-3	Cd	1.29	0.14	0.939	-3.52	0.004	0.776	136.2	$2.1x10^{-2}$	0.96	0.989

1/n = heterogeneity index, K_F =Freundlich constant, R^2= correlation coefficient, Q_{max}= adsorption capacity, K_L = Langmuir constant and K_{LF}= Modified Langmuir Freundlich constant.

The data obtained for all the adsorbents best fitted into the modified Langmuir Freundlich isotherm. R^2 values of 0.996, 0.999 and 0.982 for GP-1, GP-2 and GP-3 were obtained respectively for Pb (II) ions while those of Cd (II) ions were 0.984, 0.939 and 0.989 for adsorbents GP-1, GP-2 and GP-3 respectively. Increase in adsorption capacities of Pb (II) and Cd (II) as shown in Table 2 are as a result of increase in SiO_2/Al_2O_3 ratio caused by use of different clays which possibly increased the negative charges in the geopolymer lattice. The negative charges are balanced by Na^+ which is exchangeable with heavy metal ions during adsorption increasing adsorption capacities (Erdem *et al.*, 2004). Table 3 and 4 shows comparison between adsorption capacities of Pb (II) and Cd (II) respectively obtained in this study to that reported in literature for some commercial adsorbents.

Table 3: Comparison of adsorption capacities, Q max of Pb (II) ion by various adsorbents

Adsorbent	Q_{max} (mgg^{-1})	Reference
Commercial activated carbon	47.2	Largitte *et al.*, 2014
Commercial granular activated carbon	43.1	Largitte & Laminie , 2015
Commercial granular activated carbon (GAC)	10.8	Machida *et al.*, 2005
GP-1	27.0	This study
GP-2	58.0	This study
GP-3	209.9	This study

Table 4: Comparison of adsorption capacities, Qmax of Cd (II) ion by various adsorbents

Adsorbent	Q_{max} (mgg^{-1})	Reference
Commercial activated carbon (AC)	10.3	Hydari *et al.*, 2012
Commercial activated carbon pellets	16.2	Bian *et al.*, 2015
Granular commercial activated carbon (GAC)	11.7	Wasewar *et al.*, 2010
GP-1	6.0	This study
GP-2	45.2	This study
GP-3	136.2	This study

Conclusion

Molo clay produced geopolymers with higher SiO_2/Al_2O_3 ratio with increased ability to adsorb Pb (II) and Cd (II) ions from synthetic wastewater. Equilibrium studies have shown that the adsorption data fitted best in modified Langmuir Freundlich model. Higher adsorption capacities of 209.9 and 136.2 mg/g for Pb (II) and Cd (II) respectively using GP-3 were obtained. This study has shown that Kenyan common clays that are of very few economic endeavours may be good raw materials for synthesis of geopolymers for sorption application of metal ions from wastewater.

Acknowledgements

The authors would like to express gratitude to Kenyatta University where the study was carried and National Research Fund for funding this study.

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