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Adsorption of Lead from Aqueous Solution by Pulverized Local Clay

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Abstract

Removal of heavy metals from water presents a lingering challenge. Inorganic pollutants are persistent and non-biodegradable, hence are retained in polluted sites for a very long time. Due to their poisoning nature, it becomes imperative to develop cost-effective methods for their removal. In this study, a local clay mineral was collected and mildly treated for the adsorption of lead from an aqueous solution. The applicability of the pulverized clay from the Akoko region of Ondo state Nigeria, for removal of lead from aqueous solution, was evaluated using the batch sorption process. The role of pH, initial lead concentration, agitation time, and temperature were analyzed to get optimum conditions for maximum removal of lead. Experimental data were best fitted to Freundlich adsorption isotherm with a maximum adsorption capacity of 0.49 mg/g at correlation coefficient > 0.99. It was found that 80 minutes of contact, basic pH, and ambient temperature were optimum conditions for the removal of lead using pulverized clay. These findings further buttress that readily available geochemical substance can be harnessed for the decontamination of metal pollution in water/wastewater.

Keywords: Adsorption, Clay, Heavy metal pollution, Water treatment, Lead.

1.0.INTRODUCTION

Lead is regarded as one of the heavy metals and it belongs to the carbon group in the periodic with an atomic number of 82[1]. Lead (Pb) has been reported to cause several toxic effects on exposure and highly persistent in the environment [2, 3]. Lead poisoning is a threat to public health especially in developing countries, causing hematopoietic, renal, reproductive, and central nervous system damage on chronic exposures to lead [2, 4]. Lead can get into man by inhalation or through his diets. The absorption of lead salt from the gastro-intestinal tract of mammals is about 1.5% over a dosage of a range of 2-108Mg Pb per day. In man, the process of absorption increases to 7% with increase of lead intake within that same range [5]. Lead can be inhaled as tetraethyl lead (TEL) which is readily absorbed from digestive and respiratory tract and through the skin, owing to solubility of TEL in lipids and to its diffusibility. The accumulation of lead in the body often led to high level toxicity. Exposures affecting the blood lead concentrations in the general population include house paint containing lead[6], drinking water distributed through lead pipes[7-9], and lead-glazed household ceramics[10, 11].

Lead inhibits the biosynthesis of heam (the iron porphyrin component of hemoglobin) resulting in anemia. Other health effects where lead has been implicated are cot death (sudden infant death syndrome) and stillbirths [12-14].

Modern day technologies available for managing or controlling heavy metals in the environment include adsorption, chemical precipitation, reverse osmosis, solvent extraction, and ion exchange [15]. The adsorption process is a suitable remediation approach for the removal of several metallic pollutants (heavy and trace metals) from water without chemical transformation. Different conventional and nonconventional adsorbents have been cited in the open literature for this purpose such as red mud [16], coconut coirpith [17], sewage sludge [18], silica [19], tree fern [20] bone char [21] polymetallic sea nodule [22] and modified zeolites [23].

Geosorbents have been reported to be effective for the removal of heavy metals; however, most of the adsorbents have disadvantages such as reusability of

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spent adsorbent, cost of synthesis, availability of raw materials, etc [4, 24-26].

It is a known fact that pH, temperature and initial concentration of sorbate in solution affect the sorption process. Therefore in this study, the effect of temperature, initial concentration of lead (II) and pH of solution on the adsorption of lead (II) from aqueous solution by readily available geosorbent (clay) was investigated.

2.0. MATERIALS AND METHODS

2.1. Materials

Kaolinite clay was collected from Erusu Akoko in Akoko Northwest, Ondo state, Nigeria. After the collection, stones, debris, dirt, and other particles were removed from the sample. The clay was crushed, soaked, and sieved through a 63 µm mesh-sized sieve as previously reported in my earlier work [27]. Polytetrafluoroethylene (PTFE) membrane syringe filters were purchased from Sigma-Aldrich (USA). Lead nitrate ($Pb(NO_3)_2$), HCl) and sodium hydroxide (NaOH) were supplied from Merck. All the solutions were prepared using de-ionize water from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2. Adsorption procedures

50ml of different concentrations of Pb (II) was shaken with 1g of the adsorbents on a thermostat shaker bath for a contact time of 6 hours. The mixtures were then allowed to stand for at least 1 hour after which the suspensions were filtered. The filtrates were analyzed for their Pb(II) contents using the literature procedure [28]. Blank solutions were also shaken without adsorbent and the concentrations of the Pb (II) were determined and this was taken as the initial concentration. The concentrations of the Pb (II) ions were determined using Atomic Absorption Spectrophotometer (SP-9 Unicam model). The difference between the initial and final concentrations of the respective ions was calculated to be the amount adsorbed by the clay. The procedure was extended to determine the effect of contact time, temperature, and pH on the adsorption capacities of the adsorbent.

$$q_e = \frac{(C_0 - C_e)V_0}{S_m} \qquad (1)$$

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 10 \qquad (2)$$

Where Co is the initial heavy metal concentration, Ce is the final concentration remaining in solution after adsorption (mg/L), m is the clay mass (g), and V is the volume of solution (L).

3.0. RESULTS AND DISCUSSION

3.1. Characterization of adsorbent

The chemical compositions and morphology of pulverized clay from ErusuAkoko were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM), and BET surface area analyzer. Clay sample was pre-treated before analysis. The pulverized clay exhibited loss in moisture content (13.23 and 13.14%) in air and argon respectively at 1000℃. The Brunner-Emmett-Teller (BET) analysis revealed mineral is mainly mesoporous, displaying a type IV sorption-desorption isotherm. The micropore surface area obtained from the t-plot is 9.06 m^2/g indicating that the materials also contain micropore with size and volume of 15.611 Å and 0.265cc/g respectively. The XRD, FTIR, and TEM analysis confirmed the presence of Kaolin and Quartzas constituents. The absorption band at 1120 cm^{-1} is assigned to Si-O normal the plane stretching. The bands placed at 1028 - 910.78 cm^{-1} region corresponds to Si-O planar stretching which agrees closely with 1027 - 1009 cm−1 reported. The frequency vibration 910 cm^{-1} assigned to OH deformation linked to Fe^{3+} and Al^{3+} [29,30]. The FTIR spectra clearly showed a predominance of kaolin in the studied sample and did not exhibit any peak for impurity such as smectite. Pure kaolinite exhibits two peaks 797 and 750 cm^{-1} in this region and well-crystallized kaolinite exhibits two sharp peaks at 3690 and 3620 cm^{-1}[27]. TEM image revealed an irregular and heterogeneous morphology with an estimated diameter of approximately 20 microns and a pHpzc of 6.8.

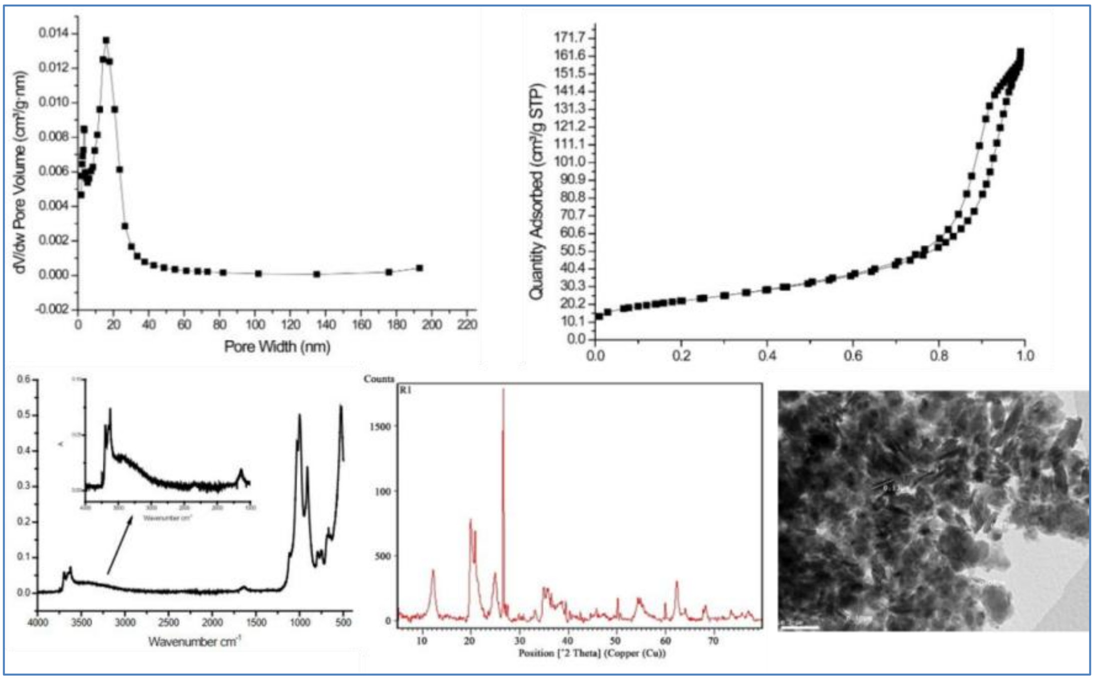

Fig-1: Characterization of pulverized clay

3.2. Adsorption isotherm

Adsorption isotherm study elucidates the interaction between adsorbates and adsorbents, especially the amount of contaminant adsorbed, and the amount left in solution after equilibrium is reached [31, 32]. Linear regression models such as Freundlich and Langmuir models were used to fit adsorption experimental data. The linearized form of the Freundlich isotherm model is given by;

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3)$$

Where K_f (L/g) and n are Freundlich isotherm constants, depicting saturation capacity. It was established that "n' values between 1 and 10 indicate favourable adsorption [33]. The values of "n" obtained in this study for the lead adsorption greater than one which implies favourable adsorption between lead and clay. The linearized form of the Langmuir model is given by;

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}} \qquad (4)$$

Where q_{max} (μg/g) is the saturation capacity or adsorption maxima, K_L is the Langmuir adsorption constant related to the solute-sorbent interaction energy (L/μg). In this study, the Freundlich model best fit isotherm data ($R^2 > 0.99$), as a result of site saturation leading to multilayer adsorption mechanism. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and the sorbent using the separation factor or dimensionless equilibrium parameter 'R_L', expressed as in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (5)$$

Where: K_L is the Langmuir constant and C_0 is the initial concentration of the PAHs. The value of the separation factor R_L provides important information about the nature of adsorption. The value of R_L is between 0 and 1 for favourable adsorption, while $R_L > 1$ represents unfavourable adsorption and $R_L = 1$ represents linear adsorption. The adsorption process is irreversible if $R_L = 0$ [34]. Table 1 and Figure 2 revealed that favourable adsorption took place between clay adsorbent and lead adsorbate, and the nature of adsorption is characterized by a heterogeneous, multilayer adsorption mechanism, given the correlation coefficient value, heterogeneity index (n), and separation factor (R_L) values. The maximum adsorption capacity was 0.49 mg/g and the adsorption intensity is close to unity.

Table-1: Adsorption isotherm models for clay-lead interactions

Isotherm models	Parameters	Values
	K_f	1.8239
Freundlich	N	1.8650
	R^2	0.9969
	q_{max}(mg/g)	0.4870
Langmuir	R_L	0.099
	K_L	0.9091
	R^2	0.9531

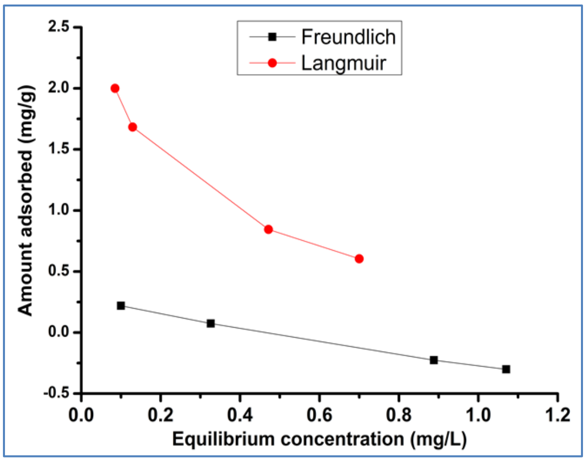

Fig-2: Isotherm model plots for the adsorption of lead by pulverized local clay

3.3. Effect of contact time

Figure 3 shows the effect of contact time on the rate of adsorption of Pb (II) unto pulverized local clay. The adsorption rate increased from 0 to 94.7% for Pb (II) with an increase in contact time from 0 to 80 minutes. After this range, there was no significant increase in the % adsorption suggesting that the first 2 hours was sufficient for optimum adsorption/lead removal. This trend could be attributed to the existence of a large number of vacant sites on the adsorbent and site saturation took place after the first 80 mins [34].

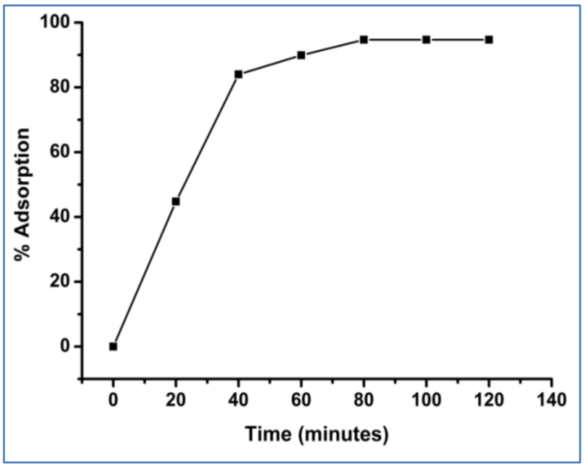

Fig-3: Effect of contact time on the adsorption of lead ions by pulverized clay

3.4. Effect of pH and temperature on adsorption

The effect of pH on the removal of lead (II) from aqueous solution by local clay is shown in Figure 4. The pH of the aqueous solution is a major or significant controlling factor in the adsorption mechanism [35, 36]. It is important to determine the optimum pH for the removal of lead because the pH of the solution affects the surface charge of the adsorbent, metal speciation, and the degree of ionization. It was observed that increasing the solution pH increases the percentage lead uptake on the clay adsorbate. Figure 4 revealed that adsorption of lead is favoured at alkaline pH. The surface of clay becomes significantly negatively charged in basic pH, thus promoting electrostatic attraction between cationic lead in solution at pH > PZC [25, 37]. Figure 4, further suggest that adsorption of lead was more favorable at ambient temperature and increase in temperature had a detrimental effect on lead removal, suggesting an exothermic interaction between sorbate and sorbent; and similar to the result obtained for lead adsorption by mesoporous silica [28].

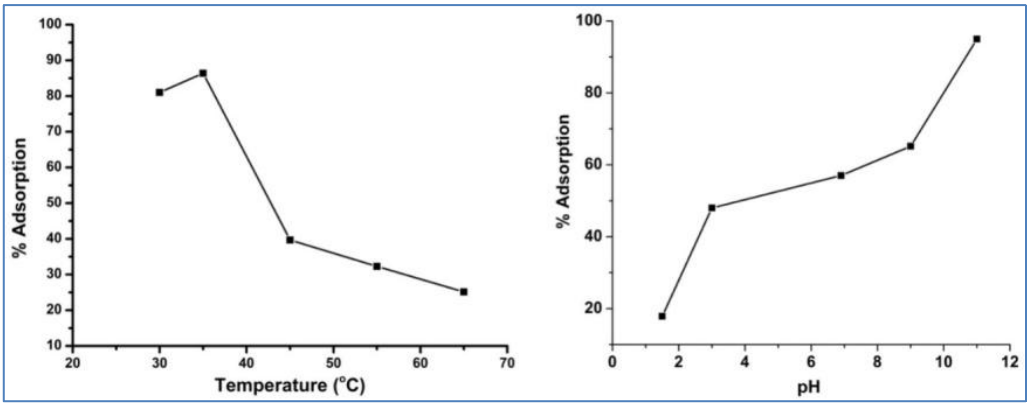

Fig-4: Effect of pH and temperature on the adsorption of lead onto pulverized clay

4.0. CONCLUSION

Pulverized clay samples from the Erusu Akoko area of Nigeria can be used for remediation of lead pollution in water. The optimal experimental conditions for maximum lead removal include basic pH medium, ambient temperature, and 2 hours contact time. Therefore, the adsorption of lead using pulverized clay can be regarded as a spontaneous and exothermic process that does not require an additional supply of heat energy. The Langmuir adsorption model revealed a maximum adsorption capacity of 0.49 mg/g while the Freundlich multilayer adsorption mechanism best fit sorption data with a strong correlation coefficient (R^2).

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