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Evaluation of the Application of *Carica papaya* Seed Modified Feldspar Clay for Adsorption of Pb^{+2} and Cu^{+2} in Aqueous Media: Equilibrium and Thermodynamic studies

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Abstract

Feldspar clay sample obtained from Federal Institute of Industrial Research Oshodi (FIIRO), Lagos, Nigeria was modified with *Carica papaya* seed to obtain CPS-modified feldspar clay Composite. The SEM of modified and unmodified samples showed irregular crystal structures. FTIR results proved the surface modification of the Feldspar at –Al–O and –Si–O centers. The CPS-modified adsorbent presented with broader peaks of inner –OH. Modification of feldspar clay sample with papaya seed decreased its PZC from pH 4.34 to 3.50 while its Specific Surface Area (SSA) was increased from 12.58 m^2g^{-1} to 18.64 m^2g^{-1}.

Modification with *Carica papaya* seed increased the adsorption capacity of feldspar clay from 18.26 mg/g to 45.81 mg/g for Pb (II) and 12.57 mg/g to 46.18 mg/g for Cu (II) at 308°K. Increasing temperature and initial metal ions concentration was found to increase the adsorption of both metals onto both adsorbents suggesting an endothermic adsorption reaction.

The simultaneous presence of electrolyte in aqueous solution with Pb and Cu (II) was found to decrease the adsorption capacity of CPS-modified adsorbent for Pb and Cu (II). The thermodynamic calculations for the modified feldspar clay sample indicated an endothermic nature of adsorption (ΔH_{mean} +4.38 kJ mol^{-1} for Pb (II) and +3.81 kJ mol^{-1} for Cu (II)) and an increase in entropy as a result of adsorption of Pb (II) and Cu (II) (ΔS_{mean} −21.75 J mol^{-1} K for Pb (II) and −18.32 J mol^{-1} K for Cu (II)). The small positive values of free energy change (ΔG_{mean}) indicated that the adsorption of Pb (II) and Cu (II) onto the modified adsorbent may require some small amount of energy to make it more feasible.

Modeling equilibrium adsorption data obtained suggested that CPS-modified adsorbent sample has homogeneous adsorption sites and fit very well with Langmuir adsorption model. CPS-modified feldspar clay sample show some very good potentials as a low-cost adsorbent for the adsorption of Pb (II) and Cu (II) from aqueous solutions.

Keywords: Adsorbent; Feldspar; *Carica papaya*; Modification; Heavy metal; Thermodynamics; Adsorption capacity

Introduction

The presence of heavy metals in water sources has become a significant topic of concern for scientists in various fields associated with quality of life and health of the natural environment as well as concern of the general public. Heavy metals are one of the most worrisome pollutants in the natural environment due to their potential toxicity, persistence and bio-accumulation problems. Direct toxicity to man and other forms of life and indirect toxicity through the food chains are the focus of this concern. In order to combat the threat to the environment and thus human health, it is highly essential to reduce their concentration levels to a tolerable limit in municipal and industrial effluents prior to final repository in the ecosystem [1].

Two of the most potentially toxic heavy metal is lead and copper. Classified as soluble and strongly hydrating cations, both metals are particularly toxic to higher animals, producing kidney and blood diseases among other health disorders. Exposure to Lead (Pb) for instance, is widely recognized as a major risk factor for several human diseases, and the structure of industrial ecological systems have made exposure to Pb unavoidable for most people alive today. Copper which is one of the most important heavy metal used in electroplating industries causes serious toxicological effects at high doses; after uptake it is known to deposit in brain, skin, liver, pancreas and myocardium.

The extraction of these metal ions from water and wastewater has become a challenge for researchers. Over the years, various techniques have been employed to remove metal ions from aqueous solutions. Conventional methods that have been used include ion-exchange, reverse osmosis, electrochemical treatment, evaporative recovery, and adsorption. These conventional techniques can reduce metal ions, but they do not appear to be highly effective due to limitations in the pH range as well as the high material and operational costs [2]. However, adsorption has assumed a wide application because of its high efficiency and easy operation. Moreover, with adsorption process, there is no sludge formation that could add to the operational cost [3].

Biosorption, the removal of heavy metals using biological adsorbents, has gained importance in recent years because it eliminates most of the above techno-economic challenges. There have been in the past and recent times, series of investigations carried out by researchers on the use of agricultural wastes and by-products as biomaterials for heavy metal uptake from aqueous solution. These include moringa leaves, maize cob, coconut shell [4], hazelnut shell, cocoa pod husk [5], Manisonia wood sawdust [6], mango stone and cocoa pod waste [7]. However, the uses of biomaterials for metal adsorption have degeneration and spent life problems.

Among available natural materials, clay minerals have received considerable attention as alternative low-cost materials for removal of various pollutants such as organic and inorganic compounds, heavy metals from aqueous solution. Clays are regarded as good adsorbents because of their non-toxic, abundant, environmentally friendly and

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multifunctional group properties. A number of researchers have utilized wide variety of clays for adsorption experiments. Clays such as sepiolite, kaolinite, Feldspar, and bentonite have attracted great interest in environmental pollution management [8,9].

However, in many instances, inherent downsides of the natural clays such as high impurities, heterogeneous functional surfaces, fragile molecular structure, as well as low cation exchange capacity have limited their uses to adsorption applications. Such drawbacks could be minimized by adopting a physicochemical modification prior to utilization. Modification of clays could be done by a range of different surface treatment such as organo-clay, chemical/polymer grafting, mechanical grinding, thermal activation and acid-alkaline treatment. Modification of clays improves their adsorption capacity.

Feldspar clay has been used for removal of methylene blue dye from aqueous solution by Awala and El-Jamal. Though feldspar clay has small crystals, large surface area and high cation exchange capacity, there are rare literatures on its use for heavy metal adsorption studies in unmodified and/or modified form.

This study seeks to introduce new low-cost adsorbent, *Carica papaya* seed-Modified Feldspar Clay (MFC). Some of the characteristics of this adsorbent in the adsorption Pb (II) and Cu (II) are studied under various operating parameters such as contact time, solution pH, adsorbent dose, sorbate concentration, and temperature in this paper with the view of discovering its metal recovery potential from industrial effluents with high concentration of these metal ions.

Materials and Methods

Purification and characterization of feldspar clay

The Feldspar clay used in this study was obtained from Federal Institute of Industrial Research Oshodi (FIIRO), Lagos, Nigeria. On collection, it was purified by method described by the Adebowale et al. [8]. Once dried, it was sieved to +230 µm particle size to remove large non- clay fractions from the clay.

Preparation of CPS-Modified Feldspar Clay Adsorbent (CPSF) material

Equal weight of feldspar clay and papaya seeds (20 g each) were weighed into a 500 mL beaker. 200 mL of 0.1 M NaOH was added to the beaker, followed by stirring. The mixture was then transferred into an oven and heated at 105°C for 4 h. The mixture was then allowed to stand for 72 h and subsequently dried in an oven at 70°C. Samples of the dried mixture were weighed into crucibles and calcined at 300°C in a furnace for 12 h in air. The resulting dark powdery material was washed with deionized water to remove all carbon material on the surface of the composite and was subsequently dried to remove all moisture. The dried sample was stored in an airtight container and is subsequently referred to as Modified Feldspar Clay Adsorbent (CPSF).

Characterization of adsorbents

The Cation Exchange Capacity (CEC) of unmodified feldspar clay and CPS-modified feldspar clay sample was determined using the ammonium acetate method of Adebowale et al. [8]. The Specific Surface Area (SSA) of the unmodified and CPS-modified feldspar clay was determined using the Sear's method. 0.5 g of the sample was acidified with 0.1 M HCl to a pH 3-3.5. The volume was made up to 50 mL with distilled water after addition of 10.0 g of NaCl [10]. The titration was carried out with standard 0.1 M NaOH in a thermostatic bath at 298 ± 0.5 K to pH 4.0, and then to pH 9.0. The volume, V, required to raise the pH from 4.0 to 9.0 was noted and the surface area (S) was computed from the following equation:

$$S\left(\frac{m^2}{g}\right) = 32V - 25$$

The Infrared spectra of the adsorbents were obtained by method described by Unuabonah et al. [9]. The Point of Zero Charge (PZC) of both adsorbents was determined using the method described by Ofomaja [6]. A Philip XL30 Scanning Electron Microscope/EDAX was used to obtain micrograms cans of both Unmodified and CPS-modified feldspar clay samples. Fourier transform infrared spectrometer (Nexus 870 FT-IR) was used for the Infrared Spectroscopic analysis of the samples.

Adsorption equilibrium study

The synthetic metal ion (Pb^{2+} and Cu^{2+}) solutions were prepared from AnalaR grade of their salts ($Pb(NO_3)_2$ and $Cu(NO_3)_2$). A stock solution of 1000 mg/L was prepared by dissolving 2.0319 g and 3.0185 g of Pb^{2+} and Cu^{2+} salts respectively in 200 cm^3 distilled water and then made up to mark in a 1 L standard volumetric flask. Working solutions of various concentrations were prepared from this stock solution as required.

Replicate batch experiments were used to determine metal sorption capacity of both the CPS-modified and unmodified feldspar clay samplesin 60 mL polyethylene bottles by contacting approximately 1.0 g of the unmodified and CPS-modified feldspar clay with 20 mL of metal solution, except where otherwise stated, for determining effect of pH, time, and temperature and sorbate concentration. The sorbent-sorbate mixtures were shaken on a mechanical shaker during the course of the adsorption experiment and concentrations of metal in the filtrate solutions were determined using the Buck Scientific 205 Atomic Absorption Spectrometer (AAS) with air-acetylene flame on absorbance mode.

Effect of operating variables

Effect of pH: A 300 mg/L solution of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ were prepared from a stock solution of 1000 mg/L each of both salts using distilled-deionised water. Metal ion solution (20 mL of 300 mg/L) was added to 1 g of both modified and unmodified feldspar clay samples weighed into 120 mL polyethylene bottles. The solutions were adjusted to 2.0-8.0 using either 0.1M NaOH or HCl. The suspensions were agitated for 3 h. The supernatant obtained after centrifugations were analysed for the respective metal ions using an atomic absorption spectrometer, AAS while the amount adsorbed was calculated by difference.

Effect of time: Weights of 1 g of the samples were placed in 120 mL polyethylene bottles containing 20 mL of metal ions. The solutions were adjusted to pH 5.0 ± 0.2 with either 0.1M NaOH or HCl. These were agitated at 100 rpm at different times within the range of 15-300 min after which they were centrifuged and left for 24 hrs. The supernatant solution taken for metal ion analysis using AAS. The amounts of metal ions adsorbed by the clay samples were calculated by difference.

Effect of adsorbent dose: In 120 ml polyethylene bottles containing 300 mg/L of 20 ml of metal ion solution 0.5-3.0 g of the CPS-modified and unmodified kaolinite clay sample were introduced. The samples were agitated for 3 h. The pH of metal ion solutions was kept at 5 ± 0.2. After agitation, the suspensions were centrifuged at 1500 rpm for 15 min and supernatant kept for Pb (II) and Cu (II) analysis using AAS. The amounts of metal ion adsorbed by the adsorbents were calculated by difference [11,12].

Effect of initial metal ion concentration: Stock solutions of 1000 mg/L each of the standardized Pb^{2+} and Cu^{2+} were prepared from their nitrates using distilled-deionised water. The solutions were adjusted to pH 5 ± 0.2 with either 0.1M NaOH or HCl. Batch sorption experiments were performed at room temperature (28.0 ± 2°C) on a rotary shaker at 100 rpm using 120 ml capped polyethylene bottles containing 20 mL of 100-600 mg/L of metal ion solutions and 1 g of the adsorbent. After agitation, the suspensions were centrifuged at 1500 rpm for 30 min. The supernatants were then collected and analysed for the metal ions using AAS. The amounts of metal ion adsorbed by the sorbents were calculated by difference.

Effectof ionic strength of electrolyte: Twenty millilitres of the two electrolytes (NaCl and $CaCl_2$) in three concentrations (0.1, 0.01, and 0.001M) were separately added to 20 mL of each of the metal ion solutions of concentration range 100-600 mg/L [13]. These solutions were then added to 1 g of modified and unmodified feldspar clay adsorbents. The solutions were adjusted to pH 5.0 ± 0.2 with either 0.1M NaOH or HCl. These solutions were agitated in a rotary shaker and were subsequently centrifuged. The supernatants collected were analysed for Pb^{2+} and Cu^{2+} using AAS. The amounts of metal ions adsorbed were calculated by difference.

Effect of binary solutions of metal ions: For the binary solution of the metal ions, 20 mL each of the same concentration of Pb^{2+} and Cu^{2+} metal ion solutions were mixed together and added to 1 g of modified and unmodified feldspar clay adsorbents. The solutions were adjusted to pH 5.0 ± 0.2 with either 0.1M NaOH or HCl. All the suspensions were agitated for 3 h in a rotary shaker at 100 rpm and they were subsequently centrifuged at 1500 rpm for 30 min. The supernatants were collected and analysed for metal ions (Pb^{2+} and Cu^{2+}) using AAS. The amounts of metal ions adsorbed by the clay samples were calculated by difference.

All experiments were carried in duplicates and the data obtained were used for analysis. The batch experimental test method was used for all experiments and the temperature at which experiments were carried was 28 ± 2°C. Calculation of amount of metal ion adsorbed by both modified and unmodified adsorbents after AAS reading of equilibrium solution was obtained by calculating the difference using the following equation:

$$q_e = \frac{(C_o - C_e)\,V}{M} \qquad (1)$$

Where C_o and C_e are the initial and equilibrium sorbate concentrations in solutions; q_e, V and M are the amount of sorbet adsorbed (mg/g), volume of the solution (mL) used for incubation and mass (g) of sample, respectively.

To obtain insights into the surface properties and degree of affinity of CPS, sorption data were tested against the Langmuir and Freundlich equilibrium isotherms using the linear forms of these models in Eqs. (2) and (3).

$$\text{Langmuir:} \quad \frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad (2)$$

$$\text{Freundlich:} \quad \log q_e = \log K_f + n \log C_e \qquad (3)$$

Where Q_o is the maximum adsorption capacity per unit weight of sorbent, *b* is a solute–surface interaction energy-related parameter, while q_e and C_e are the amount of solute adsorbed per unit mass of the adsorbent (mg/g) and equilibrium metal concentrations in the solution (mg/L); where K_F and *n* are the Freundlich model capacity factor and the isotherm linearity parameter, respectively.

Thermodynamic study

The thermodynamics of the adsorption of Pb (II) and Cu (II) onto CPS-modified and unmodified feldspar clay adsorbent was studied when 1 g of CPS-modified adsorbent was added to 20 ml of various concentrations (100-400 mg/L) of metal ion solutions at pH 5.0 ± 0.2. These were agitated and samples were collected after 5 hrs. These samples were subsequently filtered and filtrate collected for metal ion analysis using AAS. The above procedure was carried out at 308°K, 318°K and 328°K [14-16].

Results and Discussion

Physicochemical properties

Some of the physicochemical characteristics of the unmodified feldspar clay adsorbent used in this study have been described in Awala and El-Jamal. The values of the PZC of modified and unmodified feldspar clay samples were measured to be at pH 3.50 and 4.34 respectively. This suggests that modification of feldspar clay with *Carica papaya* seed decreased the PZC of feldspar clay.

The PZC value obtained above for CPS-modified feldspar clay adsorbent indicates that it could be used to efficiently adsorb metal ions at pH values as low as 3.50 as the adsorbent becomes more negative at values above the PZC. The unmodified feldspar clay adsorbent gave Cation Exchange Capacity (CEC) of 9.51 meq/100 g of feldspar clay which is a bit higher than the value obtained for kaolinite by Adebowale et al. [2]. However, the Cation Exchange Capacity of CPS- modified adsorbent was determined to be 36.18 meq/100 g of CPS-modified feldspar clay.

The Fourier Transformed Infrared Spectrograph of both CPS-modified and Unmodified feldspar clay absorbents are similar to that described in previous work by Awala and El-Jamal. In the CPS-modified feldspar clay adsorbent the Si-O and Al-O peaks were found to shift from 1034.4 cm^{-1} and 918.7 cm^{-1} (Figures 1 and 2) to 1027.86 cm^{-1} and 912.90 cm^{-1} respectively. These peaks were also broader and more prominent when they were compared with those of the unmodified feldspar clay sample. However, because of the structure of *Carica papaya* seed, it is possible to say that the OH site may not be the only site available for the adsorption of Pb (II) and Cu (II) as lone pairs of electrons present on the seed surface layer could also have participated in the adsorption of the metal ions. Moreover there was the presence of the outer-OH peak which suggests the possibility for the adsorption of Pb (II) and Cu (II) onto this site on this adsorbent [17-19].

When viewed under a Scanning Electron Microscope (SEM), the shapes of CPS-modified adsorbent particles were quite similar to those of the unmodified adsorbent. CPS-modified and the unmodified feldspar clay adsorbents gave particles with irregular structures. The unmodified adsorbent showed some white particles on the surface of the mineral particles (Figures 3 and 4). These are likely to be non-clay minerals like Sodium, Potassium, Calcium, Iron and Magnesium [10].

The specific surface area for CPS-modified feldspar clay adsorbent was observed to be 18.64 m^2g^{-1} while that of the unmodified adsorbent was 12.58 m^2g^{-1}.

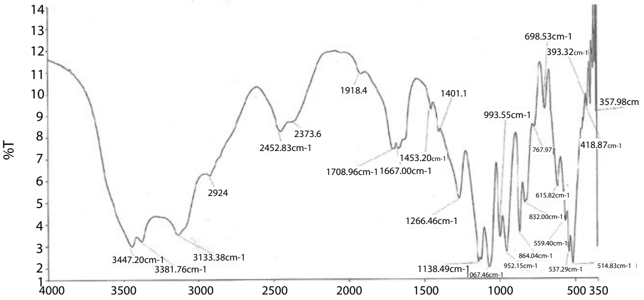

Figure 1: FT- IR Spectra of unmodified feldspar clay adsorbent.

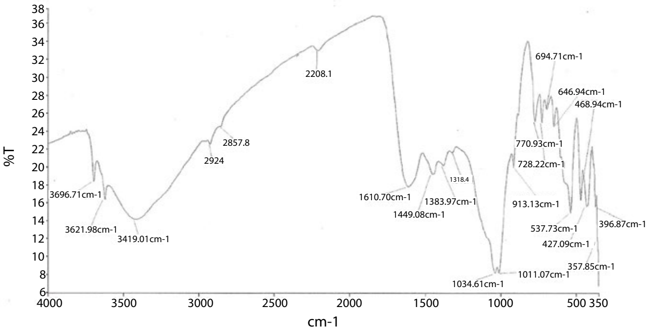

Figure 2: FT-IR Spectra of *Carica papaya* seed-modified feldspar clay adsorbent (CPS-Mod).

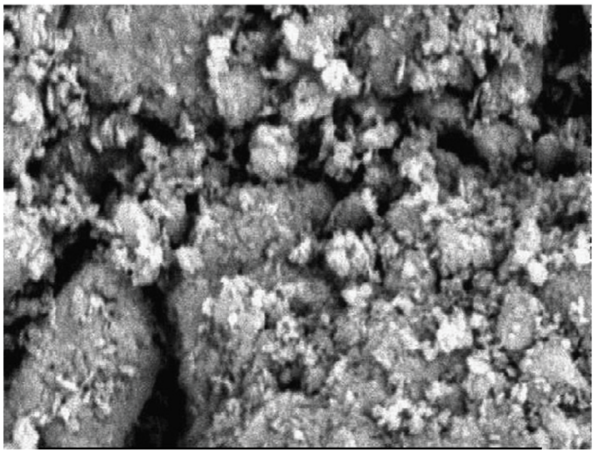

Figure 3: Scanning Electron Microscope scan for unmodified felspar clay.

Effect of pH on metal adsorption

The unmodified feldspar clay adsorbent showed an observed increase in the adsorption of both Pb (II) and Cu (II) as the pH of both metal ion solutions were increased (Figure 5). This enhanced metal ion uptake of the adsorbents has also been reported by Orumwense [11] and Adebowale et al. [2] for Pb (II) and Unuabonah et al. [10]. CPS-modified feldspar clay showed a reverse trend for the adsorption of both metal ions after pH 5.0 (Figure 5). This behavior shown by the CPS-modified feldspar clay sample may be connected with the surface modified by *Carica papaya* seed which perhaps has lone pairs of electrons on its surface layers.

The variation of the adsorption of the divalent cation with the change in pH at constant weight of adsorbent and metal ion concentration may be given by Sposito [12]

$$\mathrm{LnD} \;=\; a + b\,\left(\mathrm{pH}\right) \tag{4}$$

Where $D=f_{adsorb}/f_{sol}$; n and a and b are empirical constants. D, the distribution ratio, is defined as the ratio of the fraction of metal ion that is adsorbed to the fraction of the metal ion in solution. A plot of ln D vs pH is called a Kurbatov plot [10]. The pH at which D=1, where 50% of the added metal is adsorbed and 50% is in solution, is designated pH 50.

From Eq. (4) the pH 50 for the adsorption of Pb (II) and Cu (II) onto unmodified and CPS-modified samples were calculated. For Pb, the pH 50 was 4 and 6 for CPS-modified and unmodified samples respectively. For the adsorption of Cu (II), pH 50 was 3 and 7 for CPS-modified and unmodified kaolinite clay samples respectively [20].

Several reasons may be attributed to the increased adsorption of metal ions by unmodified adsorbent relative to adsorbate solution pH. The surface of the feldspar clay sample contains a large number of active sites and may become positively charged at very low pH, thus increasing the competition between H^+ and the metal ions for available adsorption sites. However, as pH increases, this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction [21-23].

It was observed during the adsorption of metal ions onto CPS-modified feldspar clay that increasing metal ion concentration increased the pH of equilibrium solution of the metal ions from 5.0 to 6.0 and 6.50 for Pb (II) and Cu (II) respectively [24]. This is similar to studies on the unmodified Kaolinite clay with an observed decrease in the initial pH value of metal ions from 6.0 to pH 4.08 and 4.45 for Pb (II) and Cd (II) adsorption onto the unmodified kaolinite clay as reported by Adebowale et al. [2] and Unuabonah et al. [10]. The observed decrease of pH of the unmodified feldspar clay was in the range of 1-1.5 units as the concentration of adsorbed metal ions increased from 100-600 mg/L. This was found to support findings by Unuabonah et al. [10]. No plausible reason can be given yet for the increase in pH of equilibrium metal ion solution for CPS-modified sample, although it is believed that CPS-modified feldspar clay sample shows some anionic characters which may definitely have strong affinity for a soft base like Cu (II) as against a hard base like Pb (II) [25,26].

Thus, it is also possible to suggest that the lone pairs of electrons introduced on the adsorbent's surface by papaya seed chemical constituents could possibly be involved in coordinate covalent reactions with the metal ions in the form of Pb (II) and Cu (II) [27]. This simply implies that there would be no release of H^+ in the process and no monovalent specie of both metal ions will be adsorbed. This may have led to an observed increase in the pH of the adsorbate solution.

The decrease in pH for the unmodified feldspar clay adsorbent became fairly constant with increase in metal ion concentrations. This inference is supported by the adsorption studies carried out on removal of Pb (II) and Cd (II) using CPS-modified and unmodified kaolinite clay [2,28].

Effect of time on metal adsorption

From Figure 6, it was observed that modification of feldspar clay enhanced adsorption of the metal ions as well as altered the rate of adsorption of these metal ions by the adsorbent. Unlike the unmodified

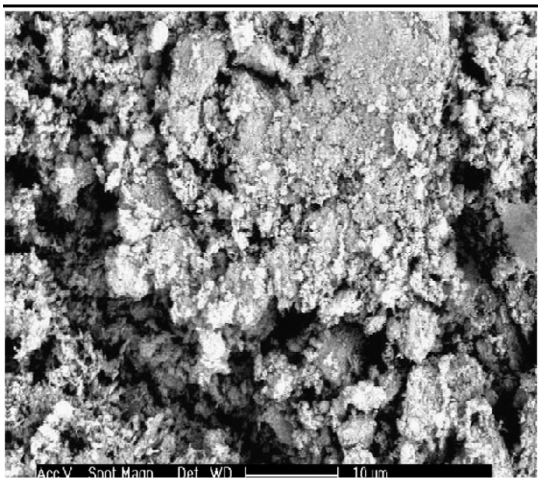

Figure 4: Scanning Electron Microscope scan for CPS-modified felspar clay.

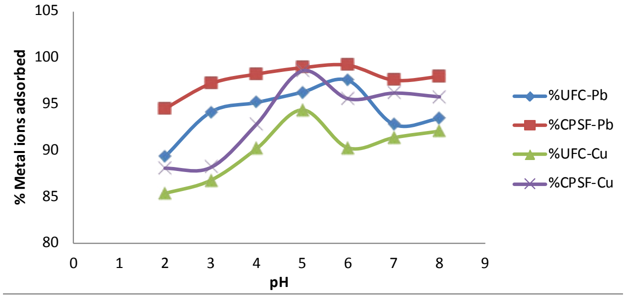

Figure 5: The effect of pH on the adsorption of Pb^{+2} and Cu^{2+} onto CPS-modified and unmodified feldspar clay sample.

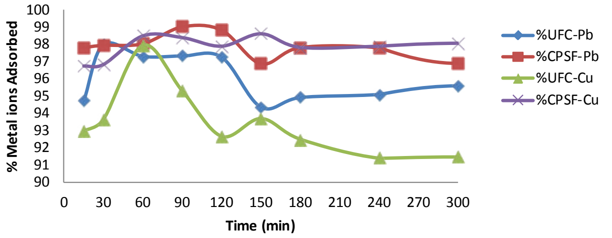

Figure 6: The effect of Time on the Adsorption of Pb^{+2} and Cu^{2+} onto CPS-modified and unmodified feldspar clay sample.

adsorbents, there was a sharp increase in the adsorption of both metal ions on the CPS-modified adsorbents within the first 15 min of the reaction [29]. For adsorption of lead on CPS-modified adsorbent, equilibrium was reached after 15 min with 94.8% adsorption while for the unmodified adsorbent, equilibrium was attained after 30 min with 78.7% adsorption. However, for copper adsorption, equilibrium condition was attained after 30 min for the CPS-modified adsorbent and 60 min for the unmodified adsorbent with 92.5 and 78.6% adsorption, respectively.

This accelerated adsorption of these metal ions onto CPS-modified clay may be as a result of the blocking of some pores on the surface of the feldspar clay mineral by anionic constituent of the papaya seed. This is because the size of pores at the surface of the grinded papaya seed (0.25 nm in radius) is larger than the sizes of Pb^{2+} (0.133 nm) and Cu^{2+} ions (0.078 nm). It is therefore possible for negative ions at the surface of the modified adsorbent to diffuse into and block the pores after modification. As a result, Pb and Cu ions may not be able to diffuse further into the pores and this will increase the overall rate of adsorption [30,31]. A similar observation was reported by Adebowale et al. [2].

Effect of adsorbent dose on metal adsorption

Figure 7 shows the effect of adsorbent dose on the adsorption capacity of the CPS-modified feldspar clay. Increase in the dosage of both adsorbents from a range of 0.5-3.0 g resulted in a decrease in equilibrium adsorption capacity, q_e, of the adsorbents (Figure 7). However it was observed that the percentage of adsorbate adsorbed increased with increase in adsorbent dose. This observation has similar trend to those reported in study of the unmodified kaolinite sample [10] as well as by Ofomaja and Ho in the adsorption of Pb (II) by palm kernel fiber and Gupta and Bhattacharyya in the adsorption of Ni (II) on kaolinite clay as cited by Unuabonah et al. [10]. The increased percentage adsorption of these metal ions with increasing adsorbent dose is possibly due to increased surface negative charge and decrease in the electrostatic potential near the solid surface that favors sorbent–solute interaction [32-35].

However, the decreased equilibrium adsorption capacity q_e of the modified clay sample for the metal ions, as its dosages were increased, could be attributed to two reasons. There is decreasing total surface area of the adsorbent and an increase in diffusion path length, which is the result of aggregation of adsorbent particles [2]. This aggregation becomes increasingly significant as the weight of the adsorbent is increased [10].

The relationship between the adsorbent dose and equilibrium adsorption capacity, q_e, was found by linear regulation and obtained by coefficient of determination (r^2). It can be expressed as:

$$Q_e = Sm_s + Y \tag{5}$$

Where the constant, Y, is the maximum adsorption capacity of the adsorbents, and m_s is the adsorbent dose and S is related to the adsorption potential of the adsorbents. The negative values of S show that with the increase in adsorbent dose, the equilibrium adsorption capacity q_e was decreased. Eq. (5) can be used to predict the amount of metal ion that will be adsorbed by a particular weight of both adsorbents used in this study [2,36].

The values of Y and S for the adsorption of Pb (II) onto the modified feldspar clay sample were calculated from plots using Eq. (5), to be, 65.69 mg/g and-36.47 for CPS-modified clay and 9.84 and -6.72 for the unmodified feldspar clay sample. For the adsorption of Cu (II), Y and S gave values of 55.70 mg/g and -43.60 for CPS-modified sample and 8.75 and -4.72 for the unmodified sample. This suggests the CPS-modified feldspar clay has a better potential for the adsorption of both metals from aqueous solutions than the unmodified kaolinite clay. This innovative explanation was adopted from Unuabonah et al. [10].

Effect of initial metal ion concentration on metal adsorption

It was observed from Figure 8 that increasing initial metal ion concentration from 100 to 600 mg/L resulted in an increase in the metal ions adsorbed for both CPS-modified and unmodified feldspar adsorbent. At very low initial concentrations 94.7% of Pb ions were adsorbed on CPS-modified feldspar clay compared with 85.5% of Pb ions on the unmodified sorbent. However, 89.6% Cu ions were adsorbed on CPS-modified feldspar clay whereas 68.1% of Cu ions were adsorbed on unmodified feldspar clay samples.

Although not shown, the fraction of metal ions adsorbed decreased with increasing metal ion concentration. This indicates a decrease in the active sites on the sorbents as more metal ions are adsorbed. With increasing metal ion concentration, there is increase in the amount of metal ion adsorbed due to increasing driving force of the metal ions towards the active sites on both the modified and unmodified adsorbents.

Plots of the K_R (separation factor) values for the metal ions as given in Figure 9 indicated that sorption is more favorable for higher initial metal ion concentrations with respect to lower ones. The sorption of both metals is more favorable on the CPS-modified sorbent than on the unmodified adsorbent. The results are comparable to those obtained by Ofomaja et al. [6], Jimoh et al. [13] and Adebowale et al. [2].

Effect of binary solutions on metal adsorption

The effect of the presence of one heavy metal ion in solution of another (binary solution of metal ions) on the adsorption of heavy metal ions unto both modified and unmodified adsorbents is shown in Figure 10. It may be represented by the ratio of the sorption capacity for one metal ion in the presence of the other metal ion, Q_{mix} to the sorption capacity for the same metal when it is present alone in the solution, Q_o, so that for:

$Q_{mix}/Q_0>1$ 6

the sorption is promoted by the presence of other metal ions:

$Q_{mix}/Q_0=1$ 7

there is no observable net interaction:

$Q_{mix}/Q_0<1$ 8

sorption is suppressed by the presence of other metal ions.

The values of Q_{mix}/Q_0 are found to be less than one as shown in Table 1 which suggest that sorption of either metal ion is suppressed by the presence of the other metal ion. However, the % drop in adsorption capacities of both CPS-modified and unmodified adsorbents for the binary metal ion solutions are less than those obtained during adsorption of metal ions in the presence of electrolytes. This may therefore suggest that the negative effect of an electrolyte on the adsorption capacities of both CPS-modified and unmodified feldspar clay for Pb and Cu ions is more pronounced than the negative effect produced by binary solution of both metal ions during their adsorption onto the adsorbents [37].

Effect of ionic strength of electrolyte

The effect of electrolyte on the adsorption of Pb (II) and Cu (II) onto CPS-modified and unmodified feldspar clay adsorbents is shown in Table 2. It is observed that the simultaneous presence of electrolytes with both Pb (II) and Cu (II) in aqueous solutions reduced the equilibrium adsorption capacity of both adsorbents for either metal ion. For the adsorption of Pb (II) and Cu (II) onto unmodified adsorbent, there was a decrease of 0.19-18.38% and 33.7-52.76% respectively for Na electrolyte.

In the presence of Ca-electrolyte the adsorption of Pb (II) gave a decrease of adsorption capacity in the range of 5.05-36.51% while Cu (II) adsorption gave a decrease of 10.51-35.53%. Ca-electrolyte has a more negative impact on the adsorption capacity of unmodified feldspar clay adsorbent. This is due to the divalent nature of cation in the Ca-electrolyte which is preferred to the monovalent cation of the Na-electrolyte [2].

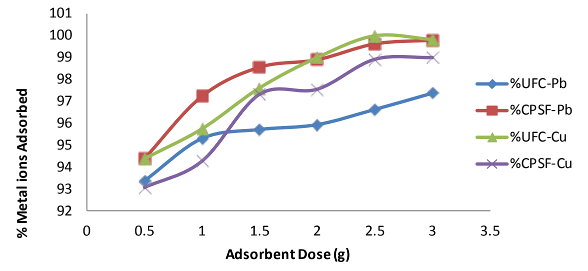

Figure 7: The effect of adsorbent dose on the adsorption of Pb^{+2} and Cu^{2+} onto CPS-modified and unmodified feldspar clay sample.

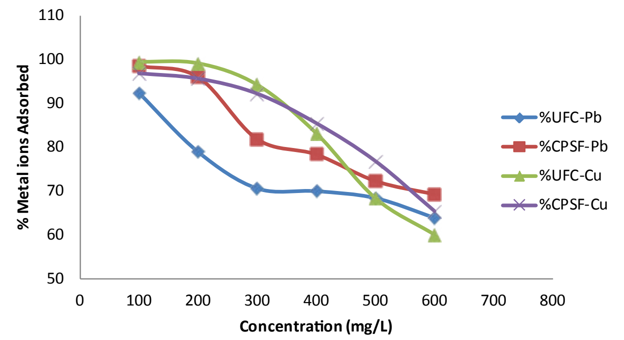

Figure 8: The effect of initial metal ions concentration on the % adsorption of Pb^{+2} and Cu^{2+} onto CPS-modified and unmodified feldspar clay sample.

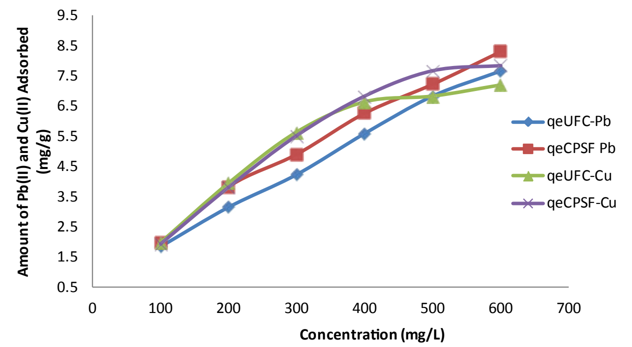

Figure 9: The effect of sorbate concentration on the adsorption of Pb^{+2} and Cu^{2+} onto CPS-modified and unmodified feldspar clay sample.

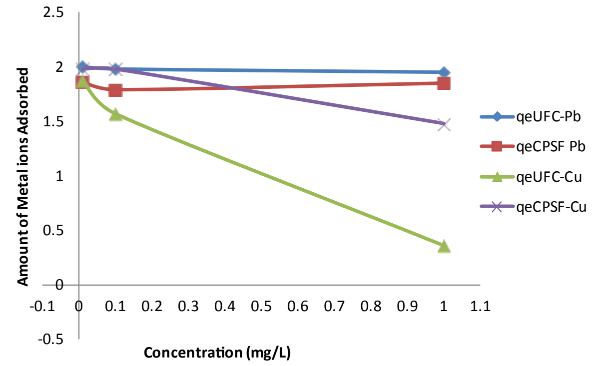

Figure 10: The effect of ionic strength on the adsorption of Pb^{+2} and Cu^{2+} onto CPS-modified and unmodified feldspar clay sample.

CPS-modified feldspar clay sample gave a decrease in the range of 4.31-25.88% for the adsorption of Pb (II) and 5.66-23.60% for the adsorption of Cu (II) when Na-electrolyte was used (Table 3).

With Ca-electrolyte, the decrease was in the range of 9.92-45.04% for Pb (II) and 31.27-58.08% for Cu (II). Similar trends mentioned above have been observed by Naidu et al. [14] for adsorption of Cu (II) on soils, Adebowale et al. [2] for adsorption of Pb (II) and Cd (II) on orthophosphate-modified and unmodified kaolinite, and Spark et al. [15] for the adsorption Cu^{2+}, Zn^{2+}, Co^{2+} and Cd^{2+} on kaolinite.

Thermodynamics of adsorption

Thermodynamic parameters for the adsorption of Pb (II) and Cu (II) are shown in Tables 4 and 5. The plots used to obtain data for the various thermodynamic parameters are shown in Figure 11. The enthalpy of the adsorption ΔH_{mean} is a measure of the energy barrier that must be overcome by reacting molecules. The values for ΔH_{mean} were found to be in the range of 4.35-10.84 J K^{-1} mol^{-1} and were all positive. This suggests that the adsorption reactions of Pb (II) and Cu (II) onto Unmodified and CPS-modified adsorbents are endothermic in nature meaning that increasing temperature will favor the adsorption both metals onto both adsorbents [38].

The value of ΔS mean is an indication of whether or not the adsorption reaction is by associative or dissociative mechanism. The entropy measures the width of the saddle point of the potential energy surface over which reactant molecule must pass as activated complexes. Entropy change N-10 J $K^{-1}mol^{-1}$ generally implies dissociative mechanism. Entropy values obtained in this study (Table 5) are below this value except that for the adsorption of Cu (II) onto unmodified clay sample. This could suggest associative mechanism of adsorption of both metal ions onto the adsorbents except for the adsorption of Cu (II) onto unmodified clay sample.

This abnormality may not necessarily mean that the adsorption of Cu (II) onto unmodified feldspar clay adsorbent is dissociative in nature but that there could be some structural changes in the adsorbate and adsorbent during the adsorption reaction. ΔG_{mean} values obtained were all small and positive which suggests that the adsorption of Pb (II) and Cd (II) onto unmodified and CPS-modified feldspar clay samples require some small amount of energy to convert reactants into products.

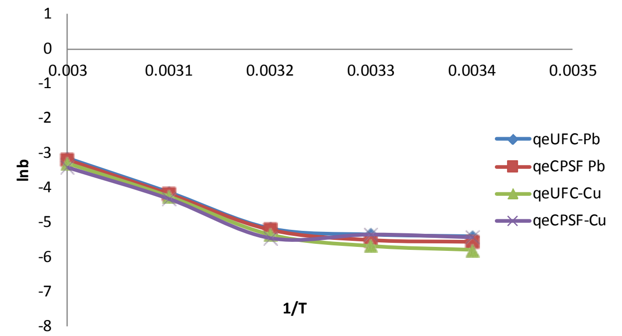

Figure 11: Thermodynamics plot of lnb against 1/T for the adsorption of Pb(II) and Cu(II) onto unmodified and CPS-modified feldspar clay samples.

Adsorbents	Q_o (mg/g)			b (L/g)		
Lead ions	308°K	318°K	328°K	308°K	318°K	328°K
Unmodified	18.26	20.9	22.86	9.08×10^{-3}	8.89×10^{-3}	8.54×10^{-3}
CPS-Modified	45.81	48.56	53.60	1.38×10^{-3}	1.42×10^{-3}	1.45×10^{-3}
Copper ions						
Unmodified	12.57	14.38	16.06	3.20×10^{-3}	3.58×10^{-3}	4.84×10^{-3}
CPS-Modified	46.18	50.66	55.78	2.51×10^{-3}	2.64×10^{-3}	2.95×10^{-3}

Unmodified feldspar clay sample CPS-Mod: *Carica papaya* seed modified feldspar clay sample.

Table 1: Data for adsorption (q_o) of Pb (II) and Cu (II) ion for the unmodified and CPS-modified feldspar clay samples and their corresponding Langmuir constants b.

Parameters	Nacl			CaCl			*
Lead ions	0.1M	0.01M	0.001M	0.1M	0.01M	0.001M	-
Q_o (mg/g)	33.78	37.06	42.86	24.21	27.76	37.75	42.91
b(L/g)	0.0089	0.0083	0.0068	0.010	0.0099	0.0056	0.0250
R2	0.9986	0.9745	0.9433	0.9115	0.9328	0.9389	0.9686
Copper ions							
Q_o (mg/g)	34.05	36.09	48.05	18.00	23.55	26.46	44.05
b(L/g)	0.0096	0.0095	0.0095	0.022	0.016	0.012	0.0126
R^2	0.9604	0.9813	0.9828	0.9588	0.9673	0.9708	0.9686

Q_o: Maximum Adsorption Capacity; b: Binding energy constant; R: Correlation Coefficient; *Without electrolyte

Table 2: Effect of indifferent electrolyte on metal ions adsorption onto CPS-modified feldspar clay sample.

Metal ions	Adsorbents type	Qmx (mg/g)	Qmx/Qo	b/L(g)	R^2
Lead ions	Unmodified	18.38	0.96	0.005	0.8747
	CPS-Modified	15.14	0.95	0.002	0.9495
Copper ions	Unmodified	14.23	0.91	0.006	0.8836
	CPS-Modified	9.35	0.88	0.003	0.8356

Unmodified feldspar clay sample CPS-Mod: *Carica papaya* seed modified feldspar clay sample

Table 3: Effect of binary solution on adsorption of Pb (II) and Cu (II) ions onto the Unmodified and CPS- modified feldspar clay.

Adsorbents	Lead ions			Copper ions		
	308°K	318°K	328°K	308°K	318°K	328°K
Unmodified	+11.65	+11.96	+12.32	+14.53	+14.68	+14.51
CPS-Modified	+10.86	+11.18	+11.41	+9.43	+9.51	+9.73

Unmodified feldspar clay sample CPS-Mod: *Carica papaya* seed modified feldspar clay sample

Table 4: ΔG ($kJmol^{-1}K^{-1}$) obtained from ΔG=-RTlnb for the two adsorbents.

This is further supported by the positive ΔH_{mean} values obtained for the adsorption of Pb (II) and Cu (II) onto both adsorbents (Table 5). This may not suggest that the adsorption of Pb (II) and Cu (II) onto both adsorbents is non-spontaneous, rather it could indicate that both adsorbents may show better performance in the adsorption of Pb (II) and Cu (II) from aqueous solutions when such solutions have temperature up to 323°K. This indicates the presence of an energy barrier in the adsorption process. Ozcan and Ozcan [16] have suggested that positive values for ΔG are quite common with ion-exchange mechanism of adsorption of metal ions because of the activated complex of the metal ion formed with the adsorbent in the excited state [37-39].

Besides, estimation of thermodynamic parameters using linear plots of thermodynamic models could introduce some errors that could shift values from the border of one extreme to another. When this occurs, adsorption reactions that have small but negative ΔG could shift to small but positive ΔG. This is case with the unmodified clay sample which indicates a small negative ΔG when the rate constants of the adsorption of Pb (II) and Cu (II) onto the adsorbent were used in the estimation of ΔG [9].

Adsorbents	**Lead ions**			**Copper ions**		
	ΔH_{mean} (kJmol^{-1})	ΔS_{mean} (Jmol^{-1}K^{-1})	r^2	ΔH_{mean} (kJmol^{-1})	ΔS_{mean} (Jmol^{-1}K^{-1})	r^2
Unmodified	+5.42	-22.13	0.9908	+15.08	-1.23	0.9426
CPS-Modified	+4.38	-21.75	0.9845	+3.81	-18.32	0.9992

Unmodified feldspar clay sample CPS-Mod: *Carica papaya* seed modified feldspar clay sample

Table 5: Thermodynamic parameters obtained from plots of lnb vs. 1/T for the various adsorbents.

Conclusion

The modification of kaolinite clay mineral was found to be on both silanol (Si-O) and aluminol (Al-OH) sites of the clay mineral and not on the edge -hydroxyl groups on the surface of the sorbent. Modification of feldspar clay with *Carica papaya* seed biomass decreased its PZC from 4.43 to 3.50. The feldspar clay sample was observed to be an organo-clay surface modified as there was no any crystallographic change in the crystal lattice of the feldspar clay adsorbent.

Modification of kaolinite clay with papaya seed biomass increased the Specific Surface Area (SSA) of feldspar clay from 12.58 $m^2 g^{-1}$ to 18.64 $m^2 g^{-1}$. The presence of Na-and Ca-electrolytes reduced the adsorption of the metal ions on both CPS-modified and unmodified adsorbents. Adsorption reaction carried out on binary solutions of both metal ions reveals that adsorption of both metal ions is suppressed by the presence of either metal ion.

There was an observed increase in the adsorption capacity of the feldspar clay after modification with papaya seed which corresponds to its increase in cation exchange capacity. Adsorption of Pb (II) and Cu (II) on modified and unmodified clay was endothermic and accompanied by a decrease in entropy. Furthermore, a synergy was observed when both clay and *Carica papaya* seed were made into a composite: increased cation exchange capacity and no "bleeding" of the column when the modified clay- composite adsorbent was left in aqueous solution for over 10 days as compared with *Carica papaya* seeds.

Modeling data obtained with Langmuir and Freundlich isotherms indicated that very good fits were produced with the Freundlich model at high metal ion concentration. Poor fit was however obtained with Langmuir models. This implies that the sites on both modified and unmodified feldspar clay adsorbents available for the adsorption of high concentrations of Pb^{2+} and Cu^{2+} may be heterogeneous in nature.

In view of the above, the CPS-modified feldspar adsorbent has the potential of holding heavy metal ions from industrial waste waters even in the presence of low concentrations of electrolytes. It also offers an application in the in situ treatment of heavy metal contaminated soils and replacing commercial activated carbon in treatment of wastewater in the developing world.

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