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Sawdust-kaolinite composite as efficient sorbent for heavy metal ions

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Abstract

The improvement of the adsorption capacity of clay minerals using chemicals though effective is expensive, results in secondary contamination and noxious to the environment. This study was therefore aimed at the development of a new sawdust clay modified adsorbent (SDKC) as an alternative means of improving the adsorption capacity of kaolinite. The adsorbents were characterized by the Fourier transform infrared spectroscopy and X-ray diffraction analysis. Batch sorption was employed to determine the effect of pH, metal concentration, sorbent dose, time and temperature on the removal of Pb (II) and Cd (II) ions from solution by the adsorbents. Optimum operating conditions of pH 6.0, metal concentration 200mg/L, sorbent dose 0.1g was obtained. Equilibrium isotherm analysis indicated the Langmuir, Temkin and Flory-Huggins models to be more suitable than the Freundlich, Dubinin–Radushkevich (D-R). The kinetic data were analyzed using the pseudo-first order, pseudo-second order, the Elovich and intraparticle diffusion models. The analysis revealed that the adsorption process followed pseudo second order model. The calculated thermodynamic parameters showed an endothermic, spontaneous and a physisorption process between both metal ions and the adsorbents. The obtained result of the experiment indicated a significant improvement in the uptake of Pb (II) and Cd (II) ions on the sawdust modified kaolinite adsorbent than the untreated kaolinite clay. This could be utilized as an alternative to chemical treatment methods

Keywords: Heavy metals; Sawdust-kaolinite composite; New adsorbents; Characterization

Introduction

Environmental degradation as a result of pollution with toxic substances has been on the increase in recent years due to rapid growth of industries. This rapid growth of industries has resulted to an increase in discharge of wastewaters containing heavy metals, which is a serious environmental problem. These heavy metals are usually toxic at certain concentrations to living organisms, persistent in nature, non-biodegradable and tend to accumulate in the food chain (Ahluwalia and Goyal, 2007). It is therefore necessary to remove these metals from industrial effluents before their discharge into receiving water bodies. The heavy metals present in solutions commonly include Pb, Cd, Zn, Cu, Ni, Cr, Mn, Fe, Hg and As (El-Eswed *et al.*, 2012). Cadmium is

a potent enzyme inhibitor and causes kidney and liver damages in animals and humans (Politi and Sidiras, 2012). Cadmium is responsible for kidney tubular impairment, affects ion regulation, calcium metabolism and skeletal calcification. Cadmium poisoning also causes severe abdominal pain, vomiting, diarrhea and a choking sensation. Lead is a general metabolic poison, enzyme inhibitor and affects the functioning of the blood, liver, kidney and brains of humans; it can also cause behavioral problems, learning disabilities, seizures and death (Guerra *et al.*, 2013; Farghali *et al.*, 2013). The permissible level for lead in drinking water is 0.05 mg/L.

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The permissible level for lead in drinking water is 0.05 mg/L. The permissible limit (mg/L) for Pb(II) in wastewater according to Bureau of Indian Standards (BIS) is 0.1 mg/L. (BIS, 1981).The recommended limits for Pb (II) and Cd (II) in drinking water as per World Health Organization (WHO) are 0.010 mg/L (Lalhruaitluanga *et al.,* 2010) and 0.005 mg/L (Solisio *et al.,* 2008) respectively. Therefore, it is of great relevance to remove lead and cadmium from aquatic environment using biosorbents. Therefore, the concentrations of these metals must be reduced to levels that satisfy environmental regulations for various bodies of water.

The conventional methods for removing lead and cadmium from wastewater include membrane filtration, chemical precipitation, ion-exchange, chelation, reverse-osmosis, solvent extraction, evaporation , electroplating and adsorption (Sari and Tuzen, 2009). Among these, adsorption is effective and economical (Ahmad *et al*., 2009). Many heavy metal adsorption studies have focused on the application of activated carbons (Kikuchi *et al*., 2006; Malik *et al*., 2002). However, it is quite expensive with relatively high operating costs. Hence there is a growing demand to find low cost and efficient adsorbents to remove heavy metals from aqueous solution. Recently, many industrial, agricultural and forestry sources are used as biosorbents such as, sawdust (Shukla and Roshan, 2005), clay (Akpomie *et al.,* 2012), zeolite (Biserka and Boris, 2004), kaolinite (Chantawong *et al.,* 2001), illite (Echeverria *et al.,* 2005), sepiolite (Brigatti *et al.,* 2000), biomass materials (Kiran *et al.,* 2005; Ucun *et al.,* 2003; Jionlong *et al.,C* 2001; Marshal and Champagne, 1995), soil (Das and Mondal, 2011), montmorillonite (Barbier *et al.,* 2000) and bentonite (Naseem and Tahir, 2001). Nigeria is abundantly rich in clay minerals which can be used as cheap alternative adsorbent for the removal of heavy metals from solution. However, clay minerals usually have low adsorption capacity, but its modification with acids or alkaline have greatly improved the adsorption capacity due to the removal of impurities and increasing in surface area of clays (Akpomie and Dawodu, 2014). Unfortunately, the use of these chemicals for modification is expensive and leads to secondary contamination. Therefore, it is necessary to look for other low cost alternative means of clay modification for improving the adsorption capacity for heavy metals. In this study, the use of sawdust to modify kaolinite (sawdust-kaolinite composite), being a novel adsorbent for the removal of Pb (II) and Cd (II) ions from contaminated solution was investigated. The sawdust is also very cheap as clay and is present in large quantity in Emene, Enugu east local government area, Enugu State, Nigeria. Batch adsorption technique was applied and the effect of solution pH, initial metal ion concentration, adsorbent dose, agitating time and temperature were investigated. Equilibrium, kinetic and thermo-dynamic parameters were also determined to help provide a better understanding of the sorption process.

Materials and methods

Preparation of adsorbents

The Kaolinite clay was purchased from Aloji in Kogi state of Nigeria. It was dissolved in excess de-ionized water in a pretreated plastic container with proper stirring to ensure proper dissolution and after which it was filtered through a 300μm sieve and the filtrate allowed to settle for 24hrs.The excess water was decanted and the clay residue sundried for several days, and then dried in an oven at 105°C for 4hrs. The dried clay was pulverized and passed through 100μm mesh sieve to obtain the Kaolinite Clay (KC). The saw dust was obtained from a saw mill in Enugu state of Nigeria. It was then washed with de-ionized water to remove unwanted materials more especially heavy metals attached to the surface. The saw dust was sundried for several days, after which it was ground or pulverized to powdery form. The sample was then passed through 100μm mesh sieve to obtain the saw dust (SD). To prepare the composite adsorbent, the kaolinite was modified with saw dust using the method described by Akpomie and Dawodu (2014b). The raw saw dust was added to the raw clay at a ratio of 10:90, 20:80, 30:70, 40:60 and 50:50 by weight. Distilled water was added to form a solid paste of the mixture, which was compounded using a pestle and a mortar to aid the coming together of the particles and to ensure proper blending. After a while, it was sundried, pulverized and heated in a muffle furnace at 300⁰C and passed through 100μm mesh sieve to obtain the saw dust-kaolinite clay (SDKC) composite adsorbent.

Preparation of adsorbates

A laboratory solution of lead (II) and Cadmium (II) ions were prepared by dissolving appropriate amounts of $Pb(NO_3)_2$ and $Cd(NO_3)_2$, respectively in a beaker. Thereafter, the solution was placed in 1 liter volumetric flask and made up to the meniscus mark with de-ionized water to obtain a stock solution of concentration 1000mg/L of the metal ions. Several lower concentrations of the metal ions which include 200, 400, 600, and 800mg/L were then prepared from the stock solution by serial dilution.

Physicochemical characterization

The physicochemical analysis of the solution was determined using standard methods (AOAC, 2005) by the use of analytical grade chemicals obtained from Sigma Aldrich. The heavy metal concentration of the solution was determined by

the use of the Atomic Absorption Spectrophotometer (AAS) (Buck scientific model 210VGP).X-ray diffraction (XRD) analysis was determined using a model MD 10 Randicon diffractometer operating at 25 kV and 20 mA. The scanning regions of the diffraction were 16–72 °C on the 2angle. The Fouriertransforminfrared spectrophotometer (FTIR; Shimadzu 8400s) was used to investigate the surface functional groups on the adsorbents, while scanning electron microscope (SEM; HitachS4800) was utilized to access the morphology.

Batch adsorption studies

Batch adsorption experiment was performed to determine the effect of pH, initial metal ion concentration, adsorbent dose, temperature and agitation time. The experiment was performed by adding 0.1 g of the adsorbent to 20 ml of a given solution in a pretreated glass bottle at room temperature of 300 K. The influence of pH (2.0–8.0) studied by varying the pH of the solution by the drop wise addition of 0.1 M HCl or 0.1 M NaOH, initial metal concentration (200, 400, 600, 800 and 1000 mg/L), adsorbent dose (0.1, 0.2, 0.3,0.4 and 0.5 g), agitation time (10, 20, 30, 40, 50, 60, 90 and 120 min) and temperature (300, 313, 323 K) were evaluated. The bottles were placed in a thermo-stated water bath for temperature regulation when the effect of temperature was studied. In order to evaluate the effect of a particular parameter, that parameter was varied while others were kept constant at the optimum conditions. At the end of the given agitation time for a particular sorption, the mixed solution was filtered and the residual metal ion concentration in the filtrate was determined by the AAS. The following equations were utilized in the calculation of percentage removal of metal ions and the adsorption capacity of the adsorbent for metal ions respectively:

$$Removal\ (\%) = \frac{100(C_o-C_e)}{C_o} \tag{1}$$

$$q_e\ (mg/g) = v\frac{(C_o-C_e)}{m} \tag{2}$$

where *qe* (mg/g) is the adsorption capacity, *Co* (mg/L) is the initial metal ion concentration in solution, *Ce* (mg/L) is the metal ion concentration remaining in solution at equilibrium, *v* (litres) represents the volume of solution used for the adsorption and *m* (g) is the mass of the adsorbent used.

Isotherm modeling

The equilibrium isotherm modeling was carried out by the application of the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R), Scatchard and Flory-Huggins

isotherm model presented in the equations respectively (Langmuir, 1918).

$$\frac{C_e}{q_e} = 1/q_L K_L + C_e/q_L \tag{3}$$

$$logq_e=logK_F+[1/n]logC_e \tag{4}$$

$$q_e=BlnA+BlnC_e \tag{5}$$

$$lnq_e=lnq_m-\beta\varepsilon^2 \tag{6}$$

$$q_e/C_s=q_sb-q_eb \tag{7}$$

$$log(\theta/C_i)=logK_{FH}+nFHlog(1-\theta) \tag{8}$$

Where qe (mg/g) and K_L (L/mg) are related to the adsorption capacity and energy of adsorption respectively. K_F (L/g) and *n* are Freundlich adsorption constants representing the adsorption capacity and intensity of the adsorbent respectively. $B = RT/b_T$, *T* is the temperature (K), *R* is the ideal gas constant (8.314 J/mol K) and *A* and b_T are Tempkins constants. q_m(mg/g) is the theoretical saturation capacity, β (mol²/J²) is a constant related to the mean free energy of adsorption per mole of the adsorbate and ε is the Polanyi potential (). q_S (mg/g) and b (L/mg) represent the Scatchard isotherm sorption parameters. $\theta = (1 – Ce/C_i)$ is the degree of surface coverage, K_{FH} (L/g) and n_{FH} represent the Flory-Huggins equilibrium isotherm constant and model exponent, respectively

Kinetic modeling

The kinetic modeling was carried out by the application of the pseudo-first order, pseudo-second order, Elovich equation and intraparticle diffusion models represented in the given equations respectively (Low, 1960; Taffarel and Rubio, 2009):

$$log(q_e-q_t)=logq_e-(K_1t/2.303) \tag{9}$$

$$t/q_t = 1/K_2q_e^2 + t/q_e \tag{10}$$

$$q_t=[1/\beta]ln(\alpha\beta)+[1/\beta]lnt \tag{11}$$

$$q_t=K_dt^{1/2}+C \tag{12}$$

Where qt (mg/g) and qe (mg/g) are the amounts of metal ions adsorbed at time t and equilibrium, respectively. K_l is the pseudo-first order adsorption rate constant (min^{-1}). h = K_2qe^2 is the initial sorption rate (mg/g min), K_2 (g/ mg min) is the rate constant of pseudo second order reaction. α is the initial sorption rate constant (mg/g min) and the parameter $β$ is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg). K_d(mg/gmin$^{1/2}$) is the intraparticle diffusion rate constant and C represents the intercept. If the plot of q_t versust$^{1/2}$ is linear then the intraparticle diffusion is involved in the mechanism (Guler and Sarioglu, 2013).

Adsorption thermodynamics

The thermodynamic parameters such as the standard free energy($ΔG^o$),enthalpy change ($ΔH^o$) and entropy change($ΔS^o$)were determined to evaluate the feasibility of adsorption by the application of the following equations (Dawodu and Akpomie, 2014)

$$\Delta G^o = -RTlnK_c \tag{13}$$

$$lnK_c = -(\Delta H^o/RT) + (\Delta S^o/R) \tag{14}$$

where Kc = Ca/Ce is the distribution coefficient, Ca (mg/L) and Ce (mg/L) represent the concentration of heavy metals adsorbed and that remaining in solution at equilibrium, respectively. T (K) is the absolute temperature and R is the gas constant. ($ΔH^o$) and ($ΔS^o$) were evaluated from the slope and intercept of the linear plot of lnKc versus 1/T.

Results and discussion

Selection of optimum sawdust-kaolinite clay adsorbent

In order to select the appropriate mixing ratio for kaolinite and sawdust, five composites were prepared which comprises of 10% sawdust and 90% kaolinite clay (10SD-90KC), 20% sawdust and 80% kaolinite clay (20SD-80KC), 30% sawdust and 70% kaolinite clay (30SD-70KC), 40% sawdust and 60% kaolinite clay (40SD-60KC) and 50% each of sawdust and kaolinite clay(50SD-50KC). The adsorbents were utilized for the adsorption of the metal ions from the binary solution at a metal concentration of 200 mg/L as shown in Fig. 1. From the graph it was observed that the addition of sawdust increased the adsorption potential of the kaolinite compared to when the kaolinite was used alone (100KC). An increase in percentage removal of both metal ions with increase in the amount of sawdust in the composite was noticed. Optimum adsorption

of Pb (94.95% and 37.98 mg/g) and Cd (90.9% and 36.36 mg/g) was obtained using the 50SD-50KC adsorbent. The increase in metal adsorption with SD concentration is simply due to increase in the number of active binding (Akpomie and Dawodu, 2014b). The 50SD-50KC adsorbent was then chosen and utilized in this study for adsorption due to its higher percentage removal recorded than the other composites.
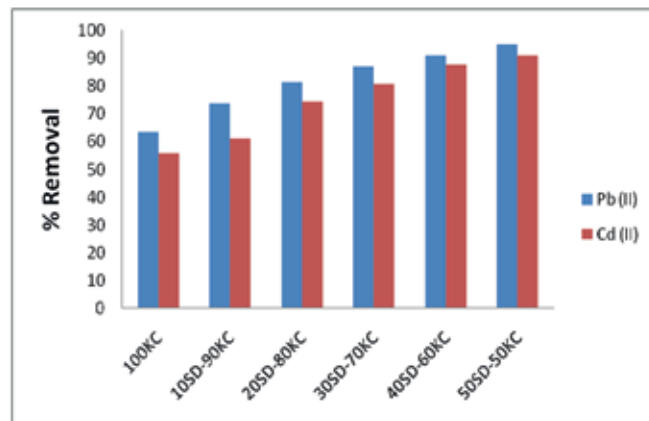
Fig. 1. Effect of sawdust addition to kaolinite and calcination on the percentage adsorption of heavy metals (pH 6.0, dosage 0.1g, temperature 300K, metal concentration 200mg/L, contact time 120min)
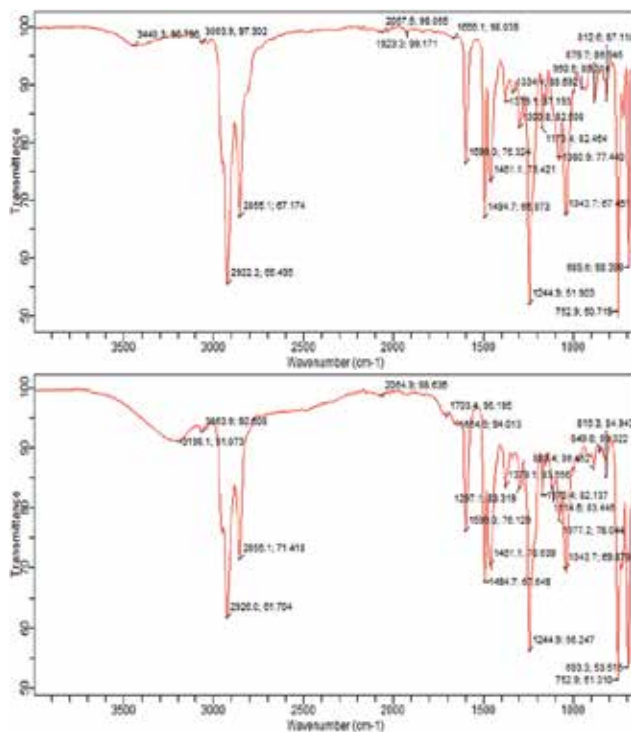
Fig. 2. Fourier transform infrared spectra of (a) kaolinite clay (b) calcined sawdust-kaolinite composite

FTIR and SEM analysis

The adsorbents were characterized to evaluate the surface nature and functional groups, the mineral identification and the morphology of the adsorbents using the Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron microscopy (SEM) respectively. The spectra illustrating the characterization of the adsorbents are shown in Fig. 2 and 3. The FT-IR analysis is useful in the spectrophotometric observation of adsorbent surface within the range of $400 - 4000$ cm^{-1} and therefore assist in the identification of the functional groups on the surface. A close examination of the adsorbent surface before and after modification provides information regarding the surface groups involved in the modification and confirms the modification of the adsorbent. The FT-IR spectrum of KC is shown in Fig 2a; several bands were observed which suggest that the kaolinite is composed of various functional groups responsible for binding of metal ions. Absorption bands at 3440.3 cm^{-1}corresponds to the outer surface OH stretching vibration of kaolinite (Dawodu and Akpomie, 2014). The band at 2057.5 - 2922.2 cm^{-1} represents the P-OH stretching vibration, while bands at $1334.0 - 1666.1$ cm^{-1} are due to the OH bending vibration of water and can also be attributed to the symmetric COO stretching vibration (Li *et al*, 2013). The Si-O bending vibration was observed at $1043.7 - 1170.4$ cm^{-1} while the stretching vibration was observed at 752.9 cm^{-1} - 689.6 cm^{-1} (Dawodu and Akpomie, 2014). The FTIR spectrum of SDKC is shown in Fig 2b, changes in the absorption bands of the kaolinite after sawdust modification were observed in the spectrum which is an indication of the successful modification of the adsorbent. The P-OH stretching bands were also observed at $2064.9 - 2064.9$ cm^{-1}, while the OH bending vibration of water or the symmetric COO stretching was observed at $1297.1 - 1654.9$ cm^{-1}. The Si-O bending vibration was observed at 1043.7-1170 cm^{-1}. The Si-O stretching vibration of the sawdust-kaolinite was also observed by bands at $693.3 - 752.9$ cm^{-1}(Dawodu and Akpomie, 2014).

Scanning electron microscopy (SEM) of the adsorbents are shown in Fig 3. The SEM is used to examine the surface morphology and the porous nature of the material responsible for adsorption of metal ions. From the SEM images, it is observed that the adsorbents revealed a porous nature, considerable number of heterogeneous pores, an irregular surface and particle aggregation of various shapes and sizes (Meitei and Prasad, 2013). The presence of pores helps in the diffusion of metal ions into the adsorbents during the sorption of metal ions from solution (Dawodu and Akpomie, 2014. However, an increase in porosity of SDKC was observed in the SEM images when compared to KC and may suggest

higher removal of metal ions by SDKC than KC. Also, the SEM image of KC showed some white clumps or particles on the surface, these were probably due to the presence of non-clay minerals like potassium, iron, magnesium, sodium, calcium and manganese (Unuabonah, 2007). In general, the porous nature of the adsorbents more especially the composite (SDKC) revealed their suitability for adsorption of Pb (II) and Cd (II) from aqueous solution.
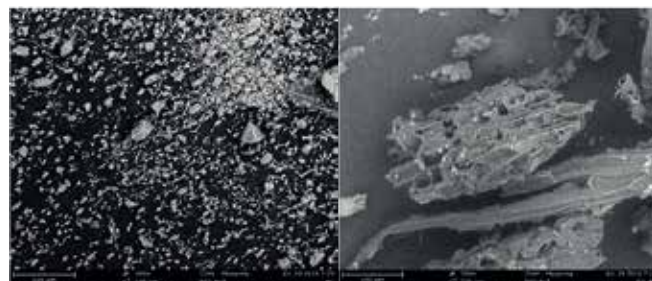
Fig. 3. Scanning electron microscopy of (a) kaolinite clay (b) calcined sawdust-kaolinite composite

Effect of solution pH

The pH of the solution has an important effect on heavy metals sorption since the pH of the solution controls the magnitude of electrostatic charges and the degree of ionization of the adsorbate (Abdelwahab and Amin, 2013). Therefore, the amount of metal adsorbed will vary with the pH of an aqueous medium. The effect of pH on the simultaneous adsorption of Pb (II) and Cd (II) ions unto the adsorbent is shown in Fig.4. It was observed that the percentage removal of both metal ions on all the adsorbents showed an increase with increase in initial pH of solution. With an increase in initial pH of solution from 2.0 to 8.0, the
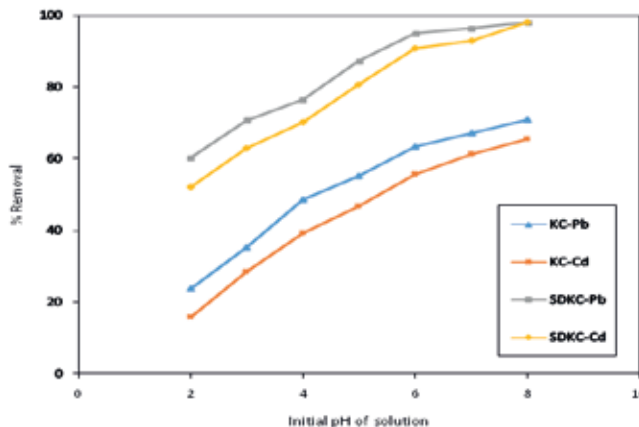
Fig. 4. Effect of initial pH of solution on the percentage removal of heavy metals (Dosage 0.1g, temperature 300K, metal concentration 200mg/L, contact time 120min)

percentage removal of Pb (II) increased from 23.7 to 67.1% and 60.3 to 97.95%, for KC and SDKC, respectively. Similarly, with an increase in the initial pH of solution from 2.0 to 8.0, the adsorption of Cd (II) showed a percentage increase from 15.8 to 65.45% and 52.1 to 97.95%. The low adsorption recorded at lower pH values is simply due to excess H^+ ions in solution which competes with the metal ions for the active sites of the adsorbent, resulting in a low removal. As pH of the solution increases, the concentration of H^+ ions in solution decreases, this reduces the competition between the metal ions and H^+ ions for the active sites of the adsorbents leading to an increase in percentage removal of metal ions. Notably, at pH > 6.0, metal ions may precipitate from solution in the form of hydroxides (Taffarel and Rubio, 2009) . Therefore, precipitation may have accounted for some of the metal ions adsorbed, especially at higher pH 7.0 and 8.0.The pH value of 6.0 was chosen in this study for all subsequent experiments and not 8.0, despite the highest removal obtained at 8.0. This was done in order to avoid metal precipitation associated with higher pH values (7.0-8.0) and ensure that adsorption phenomena accounted for the optimum adsorption recorded at 6.0. Furthermore, comparing the adsorption potential of the two adsorbents for metal ions, it was found that at all pH values for both Pb (II) and Cd (II) ions, the adsorption followed the order SDKC>KC. This result obviously showed that the addition of SD to KC and calcinations would improve the adsorption of the clay which is desired in this research. This is expected since biomass materials usually have higher adsorption potentials than clay minerals. Similar result on improving the adsorption capacity of clay using rice husk and has been reported (Akpomie and Dawodu, 2014). The increase in adsorption potential of SDKC when compared to KC is simply as a result of increase in the effective active sites and increase in the heterogeneous nature of the composite.

Also, comparing the adsorption of the two metal ions at all pH values on the two adsorbents, the following trend was observed Pb (II)> Cd (II). The difference in this adsorption trend of Pb (II) and Cd (II) may be attributed to differences in behavior of these metals or their ions in solution (Barka et al, 2013).The difference in the adsorption trend of Pb (II) and Cd (II) may be as a result of differences in behavior of these metals or their ions in solution. These include the smaller hydrated radius of Pb (II) (0.401 nm) compared to Cd (II) (0.426 nm), the higher electronegativity of Pb (II) (2.10) than Cd (II) (1.69), whereas Pb (II) is adsorbed as hydrolysed species Cd (II) is not. These factors accounts for the higher adsorption of lead than cadmium on adsorbents (Barka et al, 2013). Similar result has been reported (Nessim et al, 2014).

Effect of initial metal ion concentration

The investigation of initial metal ion concentration is a very important in adsorption studies, as most contaminated wastewaters usually have different concentration of metal ions, and therefore, the determination of its effect is necessary for an elaborate adsorption study. The effect of initial metal ion concentration on the percentage removal and adsorption capacity of Pb (II) and Cd (II) ions on KC and SDKC are shown in Fig. 5. A decrease in percentage removal of both metal ions on the adsorbents with increase in initial metal ion concentration was observed. This decrease in percentage removal is due to the fact that at lower concentrations, more of the metal ions would be removed by the abundant active sites on the adsorbent. At higher concentrations, more metal ions would be left un-adsorbed due to saturation of the active sites of the adsorbents. Unlike the decrease observed in percentage removal, an increase in adsorption capacity for both metal ions on all the adsorbents with increase in initial metal ion concentration was recorded. The increase in adsorption capacity of Pb (II) from 25.32 to 80.34 mg/g and 37.98 to 121.52 mg/g for KC and SDKC respectively and also increase in adsorption capacity of Cd (II) from 22.26 to 75.72 mg/g and 36.36 to 112.04 mg/g for KC and SDKC respectively with increase in metal ion concentration from 200 to 1000 mg/L was observed. This was attributed to the increasing concentration gradient which acts as a driving force to overcome the resistances to mass transfer of metal ions between the aqueous and solid phase (Kumar *and* Tamilarasan 2013). In fact, higher concentration in solution implies higher metal ions fixed at the surface of the adsorbent and maximum utilization of the active sites (Barka *et al*., 2013). The adsorption of metal ions on the adsorbents at all concentrations also followed the order SDKC>KC, while the metal ions adsorption on by the adsorbents followed the trend Pb>Cd. The metal concentration of 200 mg/L was utilized in this study due to the high percentage removal recorded.
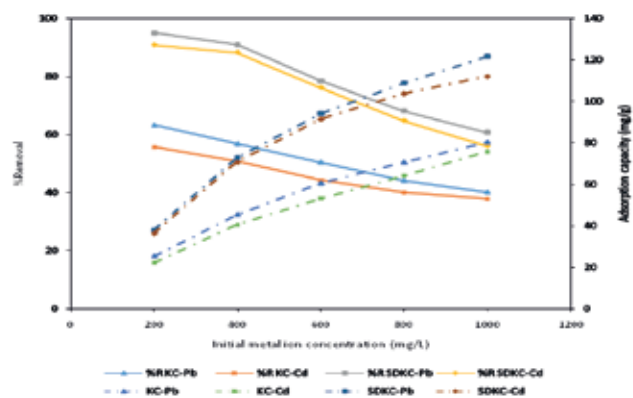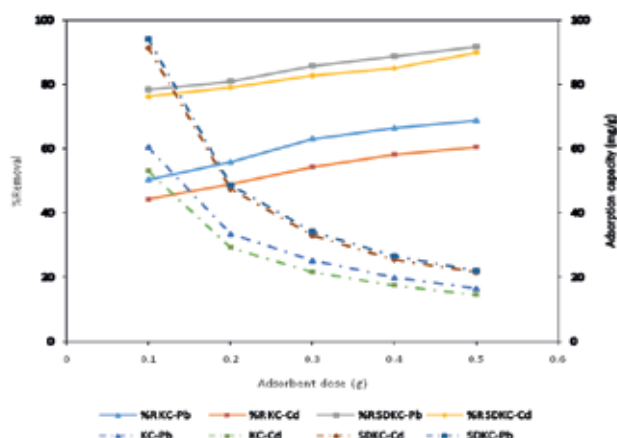

Fig. 5. Effect of initial metal ion concentration on the adsorption of heavy metals (pH 6.0, Dosage 0.1g, temperature 300K, contact time 120min)

Effect of adsorbent dose

The adsorbent dose affects the number of sites available for binding metals in a solution. In this study, five different adsorbent dosages were selected ranging from 0.1 to 0.5 g while the lead and cadmium concentrations were fixed at 200 mg/L. The effect of adsorbent dosage on the percentage removal and adsorption capacity of Pb (II) and Cd (II) ions are shown in Fig. 6. It was observed that percentage removal of Pb (II) increased from 50.45 to 68.76% and 78.43 to 91.78% for KC and SDKC respectively and also removal of Cd (II) increased from 44.30 to 60.55% and 76.20 to 89.93% for KC and SDKC respectively with increase in adsorbent


Fig. 6. Effect of adsorbent dose on the adsorption of heavy metals (pH 6.0, metal concentration 200mg/L, temperature 300K, contact time 120min)

dose. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent (Nasuha , 2010). However, the equilibrium adsorption capacity showed an opposite trend. As the adsorbent dosage was increased from 0.1 to 0.5 g, there was a decrease in adsorption capacity of Pb (II) from 60.54 to 16.50 mg/g and 94.12 to 22.03 mg/g for KC and SDKC respectively and also decrease in adsorption capacity of Cd (II) from 53.16 to 14.53 mg/g and 91.44 to 21.58 mg/g for KC and SDKC respectively. This may be due to the decrease in total adsorption surface area available to lead and cadmium ions resulting from overlapping or aggregation of adsorption sites (Crini, 2007; Akar, 2009). This decrease in equilibrium adsorption capacity per unit mass of adsorbent may also be due to the higher adsorbent dose providing more active adsorption sites, which results in the adsorption sites remaining unsaturated during the adsorption reaction (Li, 2011). The adsorption trend of metal ions on the adsorbents was also in the order SDKC>KC, while that for metal ions was Pb>Cd. The adsorbent dose of 0.1 g was chosen in this study due to its high adsorption capacity for metal ions recorded.

Effect of Agitation time

The time it takes metal ions and adsorbent to reach equilibrium is of considerable importance in adsorption experiment because it depends on the nature of the system used and can provide information on the process mechanism. The effect of agitation time on the percentage removal of the heavy metals from the solution was studied as shown in Fig. 7. An increase in percentage removal of the metal ions with increase in contact time was recorded. The fast adsorption at the initial stages is attributed to an increased availability in the number of available active sites on the adsorbents. The sorption rapidly occurs and is controlled by the diffusion process from the bulk to the surface of the adsorbent. In the later stages the adsorption diminished and attained equilibrium due to the utilization and subsequent saturation of the active sites, the sorption in this stage is likely an attachment controlled process due to less available adsorption sites (Das and Mondal, 2011). Similar findings for lead (II) adsorption onto other adsorbents have been reported by other investigators (Badmus *et al.,* 2007). It was also observed that different equilibrium times were attained for the two metal ions on all the adsorbents. Equilibrium sorption time of 50 and 40 min were obtained for Pb (II) and Cd (II) ions on the adsorbents respectively. A contact time of 120 min was utilized in this study to ensure equilibrium sorption of both metal ions on all the adsorbents was attained. The faster rate of adsorption of Cd (II) when compared to Pb (II) is due to the smaller ionic radii of Cd (II) (0.097 nm) than Pb (II) (0.12 nm) which makes it to diffuse faster to the surface of adsorbents due to its smaller size than the bulkier Pb (II) ion (Akpomie and Dawodu, 2014).
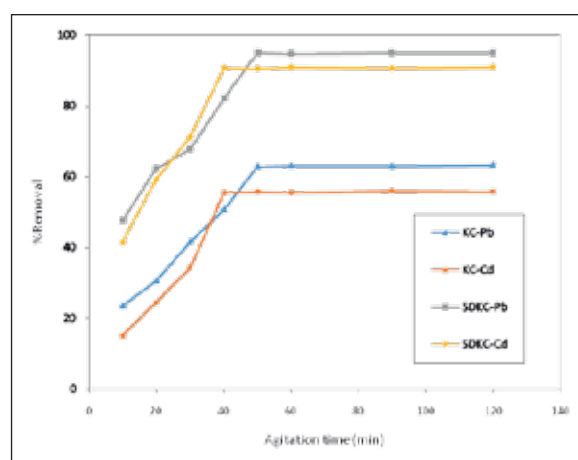
Fig. 7. Effect of agitation time on the percentage removal of heavy metals (pH 6.0, dosage 0.1g, metal concentration 200mg/L, temperature 300K,)

Table 1. A comparison of the Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich (D–R), Scatchard and Flory-Huggins isotherm constants for the adsorption of Pb(II) and Cd(II) ions unto KC and SDKC

Isotherm models	KC		SDKC	
	Pb(ll)	Cd(ll)	Pb(ll)	Cd(ll)
Langmuir				
q_L (mg/g)	125	125	142.86	125
K_L (L/mg)	3.5×10^{-3}	2.4×10^{-3}	2.7×10^{-2}	2.4×10^{-5}
R^2	0.998	0.987	0.994	0.998
Freundlich				
K_F	2.54	1.46	21.09	16.26
$1/n$	0.547	0.616	0.301	0.331
N	1.83	1.62	3.32	3.02
R^2	0.985	0.992	0.951	0.907
Tempkin				
A (L/g)	0.035	0.024	0.630	0.345
B (mg/g)	26.00	26.58	21.80	22.86
R^2	0.997	0.985	0.991	0.973
Dubinin-Radushkevich				
qm (mg/g)	68.306	62.802	100.283	98.003
β (mol^2/J^2)	—	0.001	2.0×10^{-5}	6.0×10^{-5}
R^2	0.895	0.885	0.879	0.935
Scatchard				
q_s (mg/g)	147.333	152.000	121.930	124.958
b (L/mg)	0.003	0.002	0.043	0.024
R^2	0.996	0.974	0.960	0.960
Flory-Huggins				
K_{FH}	4.80×10^{-5}	2.66×10^{-5}	2.80×10^{-4}	2.20×10^{-4}
n_{FH}	-4.123	-5.636	-0.927	-1.188
R^2	0.995	0.991	0.981	0.963

Equilibrium isotherm analysis

In order to effectively analyze and design an adsorption process it is important to understand the equilibrium isotherm application. Adsorption isotherms provide basic physicochemical data for evaluating the applicability of the adsorption process as a unit operation. In this study, Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (D-R), Scatchard and Flory-Huggins isotherms were applied to the experimental data. The regression coefficient (R^2) was utilized to determine the best fitted model and the closer the R^2 value to 1, the best the model fit. The equilibrium isotherm parameters calculated are presented in Table I. Higher R^2 values (> 0.962) were obtained in Langmuir as well as in Temkin and Flory-Huggins indicating that the models gave good fit to the adsorption data. Furthermore, higher R^2 value of Langmuir depicts that sorption process is attributed to a monolayer adsorption on a homogeneous surface. However, the Langmuir dimensionless separation factor (R_L) values obtained for the two metal ions with initial metal concentration from 200 to 1000 mg/L is in the range of 0.04 – 0.74 for Pb (II) and 0.03 – 0.99 for Cd (II) indicating that the adsorption of the Pb (II) and Cd (II) unto KC and SDKC are favorable processes. The Langmuir equilibrium constant (K_L)

of KC for Pb (II) and Cd (II) are 3.5×10^{-3} and 2.4×10^{-3} L/mg respectively, while that of SDKC for Pb (II) and Cd (II) are 2.7×10^{-2} and 2.4×10^{-5} L/mg respectively.

On the other hand, Freundlich, Dubinin–Radushkevich (D-R), and Scatchard generally gave low R^2 values indicating that the models did not fit in well to the adsorption data, except for the adsorption of Cd (II) unto KC in Freundlich and also Pb (II) unto KC in Scatchard which showed high values of R^2. While the fitness in Freundlich suggests heterogeneous multilayer adsorption of Cd (II) unto KC, the fitness in Scatchard as a result of high linearity obtained from the Scatchard plot of qe/Ce against qe suggests homogeneous monolayer adsorption of Pb (II) unto KC and as well confirms the good fit to the experimental data obtained by the Langmuir model.

Kinetic model analysis

Kinetic analysis helps in the prediction of the mechanism involved in sorption and identification of the rate limiting step of the process (Das and Mondal, 2011). The pseudo-first order, pseudo-second order, Elovich equation and intraparticle diffusion models were applied to evaluate kinetic

Table II. A comparison of the pseudo-first order, pseudo-second order, elovich equation and intraparticle diffusion constants for the adsorption of Pb(II) and Cd(II) ions unto KC and SDKC

| Kinetic models	KC		SDKC	
	Pb(ll)	Cd(ll)	Pb(ll)	Cd(ll)
qe_{exp} (mg/g)	25.32	22.38	37.98	36.36
Pseudo-first-order				
qe_{cal} (mg/g)	38.99	77.09	57.68	23.88
K_I (min^{-1})	0.074	0.113	0.094	0.083
R^2	0.761	0.825	0.708	0.628
Pseudo-second-order				
h (mg/g min)	1.39	1.00	3.48	3.80
K_2 (g/mg min)	1.33×10^{-3}	1.09×10^{-3}	1.84×10^{-3}	2.19×10^{-3}
qe_{cal} (mg/g)	32.26	30.30	43.48	41.67
R^2	0.970	0.916	0.990	0.988
Elovich equation				
α (mg/g min)	2.620	1.896	8.625	8.058
β (g/min)	0.1330	0.1322	0.1161	0.1166
R^2	0.884	0.819	0.886	0.828
Intraparticle diffusion				
K_d (mg/g min$^{1/2}$)	2.235	2.195	2.548	2.448
C	4.669	2.581	14.55	14.54
R^2	0.790	0.697	0.783	0.682

data. The calculated constants obtained from these models are given in Table II. It was observed from the linear regression coefficient (R^2) values that the adsorption process showed a greater conformity to the pseudo-second order model than the pseudo-first order modeling the adsorption of Pb (II) and Cd (II) ions on the adsorbents, as R^2 values were all greater than 0.9. Also the values of qe_{cal} were closer to the values of qe_{exp} than those presented by the pseudo-first order model. This good fit presented by the pseudo-second order model implies that chemisorptions mechanism is the rate controlling step for the sorption of these metal ions on the adsorbents (Barka et al, 2013). However, in this study, Elovich equation was found to present a poor fit to the sorption experiment as revealed by its highest R^2 value of 0.886, even though several researchers have found the Elovich model to be more suitable in the description of kinetic mechanism of sorption (Wu et al., 2009; Piccin et al., 2012).

The pseudo-first order, pseudo-second order and Elovich equation models could not identify the diffusion mechanism, therefore the kinetic result was further analyzed with the intraparticle diffusion model. The low R^2 values presented by the intraparticle diffusion model suggest that this mechanism did not play a major role in the overall sorption of the metal ions.

Thermodynamic analysis

The result on the effect of temperature on the simultaneous adsorption of Pb(II) and Cd(II) ions unto KC and SDKC is presented in Fig.8 A slight increase in the percentage removal and adsorption capacity of both metal ions with KC was observed while no significant increase was observed with SDKC, with increase in solution temperature from 300 to 323K. This indicates that a high temperature favors the adsorption of both metal ions unto KC. The improved adsorption capability with increasing temperature suggests that the adsorption is an endodermic one. This may due to the creation of more additional adsorption sites on the adsorbent surface with increase in temperature as a result of the
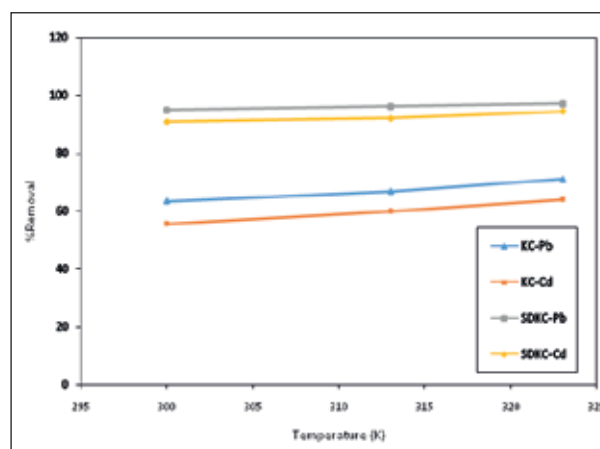
Fig. 8. Effect of solution temperature on the percentage removal of heavy metals (pH 6.0, dosage 0.1g, metal concentration 200mg/L, contact time 120min,)

Table III. Comparison of thermodynamic parameters for the adsorption of Pb(II) and Cd(II) ions from solution unto KC and SDKC

				KC			
Metal ion	T(K)	Kc	ΔG^o(KJ/mol)		ΔH^o(KJ/mol)	ΔS^o(KJ/mol)	R^2
Pb(II)	300	1.72	-1.36		12.09	0.04	0.970
	313	2.01	-1.81				
	323	2.49	-2.40				
Cd(II)	300	1.25	-0.57		12.12	0.04	0.993
	313	1.50	-1.06				
	313	1.78	-1.55				
				SDKC			
Metal ion	T(K)	Kc	ΔG^0(KJ/mol)		ΔH^0(KJ/mol)	ΔS^0(KJ/mol)	R^2
Pb(II)	300	18.80	-7.32		20.58	0.09	0.978
	313	24.64	-8.34				
	323	34.09	-9.48				
Cd(II)	300	9.99	-5.74		18.07	0.08	0.884
	313	11.58	-6.37				
	313	17.02	-7.61				

dissociation of some of the surface components on KC (Bhattacharyya and Gupta, 2006)

The designer of an adsorption system usually takes into account changes in the reaction based on thermodynamics. The parameters, enthalpy change (ΔH^o), entropy change (ΔS^o) and standard free energy (ΔG^o), denote the features of the final state of the system and their values are shown in Table III. The positive values of ΔH^o obtained for both metal ions with KC and SDKC indicate an endothermic adsorption process, which explains the fact that adsorption efficiency increased with increase in temperature. The magnitude of the enthalpy change (ΔH^o) provides information about the type of sorption. The heat evolved during physisorption generally lies in the range of 2.1–20.9 kJ/mol, while the heat of chemisorptions generally falls in the range of 80–200 kJ/mol (Liu and Liu, 2008). From table III, the values of ΔH^o for Pb(II) and Cd(II) ions with KC are 12.09 and 12.12 kJ/mol, while that of SDKC are 20.58 and 18.07kJ/mol, representing physisorption process. The positive values of ΔS^o for both metal ions indicate an increase in randomness at the solid/liquid interface during the sorption process (Guler and Sarioglu, 2013). The negative values of ΔG^o obtained for both metal ions at all temperatures indicate the spontaneous nature of the adsorption process (Meitei and Prasad, 2013). The magnitude of the free energy change ΔG^o can be used to classify adsorption as physical or chemical: the free energy change for physical adsorption is −20 and 0 kJ/mol, while that for chemical adsorption is −80 to −400 kJ/mol [40]. Therefore, ΔG^ovalues obtained indicate a physical adsorption

process with KC and SDKC for both metal ions. Physical adsorption is desirable because there is a lower energy barrier to be overcome by metal ions, which allows easy desorption from the surface of the adsorbent during recycling (Dawodu and Akpomie, 2014).

Conclusions

The removal of heavy metals from aqueous solution was carried out by batch adsorption technique using KC and SDKC, as a low-cost adsorbents. These adsorbents which are present in great amount in Eastern Nigeria can be utilized for treatment of solution containing high concentration of Pb(II) and Cd(II) ions, hence reducing the toxic effects they pose to the environment. Solution pH, initial metal concentration, agitation time, adsorbent dose, and temperature were the determining factors in adsorption. Optimum removal of both metal ions was obtained at a pH of 6.0, agitation time of 120 min and an adsorbent particle size of 100 μm. The Langmuir, Temkin and Flory-Huggins models showed a better fit with higher R^2 values than those of Freundlich, Dubinin–Radushkevich (D-R) and Scatchard models.The analysis showed that the adsorption process followed pseudo second order model. The calculated thermodynamic parameters showed an endothermic, spontaneous and a physisorption process between both metal ions and the adsorbents. The research generally revealed that the addition of sawdust to kaolinite clay enhanced its adsorption capacity for lead and cadmium ions and therefore could be efficiently utilized for the removal of the metal ions.

This provides a cheaper alternative means of clay modification rather than the excessively used chemical means which is expensive and noxious to the environment.

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