



FTIR Studies For The Removal Of Lead Ions From Aqueous Solution By Adsorption On Kankara Kaolinite Clay

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ABSTRACT

The aim of this research is to determine the effect of heat treatments on the structure and adsorption properties of kaolinite as a suitable adsorbent for removal of lead metal under some adsorption conditions. Heavy metals are toxic to health and environment, extensive endeavors are mandatory to economically remove them from contaminated water. Among viable options, clays of different characteristics are considered for the removal of heavy metals from polluted effluents. In this research, raw and thermally treated Kankara kaolin are investigated for the removal of lead from aqueous solution. The characterization of the clays was performed using Fourier-transform infrared spectroscopy (FTIR). The thermal activation period of 20 minutes and 300 minutes and the activation temperature of 100°C and 800°C were used. The FTIR spectra showed a strong family resemblance particularly over the 1110-1000 cm^{-1} and 3700-3600 cm^{-1} ranges, with variations in absorption pattern in the 1150-1100 cm^{-1} range arising from effects of particle size and shape. Results from adsorption studies showed that all the highest maximum adsorption capacity was achieved at the highest adsorption time of 180 mins, while low adsorption time (10 mins) leads to low adsorption capacity.

Keywords: FTIR, Lead, Adsorption, Kankara, Kaolinite clay

INTRODUCTION

Kaolinite is also known as China clay and has a structure that is dioctahedral 1:1 layer clay with alternating tetrahedral silica and octahedral alumina sheets, respectively. The chemical formula of Kaolin is $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ (Bawa, 2012). The charge within the structural unit is balanced. Kaolin is also referred to nonexpanding phyllosilicate as there is no expansion between the layers. There are small amounts of anatase, rutile, feldspar, iron oxide, mica, montmorillonite and quartz in almost all kaolinite clays (Vimonses *et al.*, 2009). Unuabonah, *et al.*, 2008, evaluated the adsorption of aniline blue on kaolinite and sodium tetraborate (NTB) modified kaolinite. The surface area of NTB-kaolinite was 15.84 compared to 10.56 m^2g^{-1} of raw kaolinite. The results indicate that on modification, the adsorption capacity of kaolinite increases which was explained by an increase in surface area after modification.

Kaolinite clay is widely used in the paper industry for its high whiteness and low abrasion and it is also used in the other industry branches like construction, ceramics, rubber, paint and porcelain manufacturing (Arias, *et al.*, 2002). The theoretical chemical compositions in kaolinite are SiO_2 , 46.50 %; Al_2O_3 , 39.50 %; and H_2O , 14.00 % as reported by Bhattacharyya and Gupta, (2008). Jorge, *et al.*, 2003, concluded that most of the negative surface charge on kaolinite is pH independent and is likely to be due to isomorphous substitution. Arias, *et al.*, (2002), concluded that the surface negative charge of kaolinite is derived mainly from broken bonds around the edges and from exposed basal hydroxyls. Unlike broken bonds, the hydrogen of exposed hydroxyls is an integral part of the structure and may be replaced by an exchangeable cation (Sajidu *et al.*, 2006). However, Wang and Wang, (2008), also

suspected that such hydrogens would probably be relatively held tightly compared with those associated with broken bonds and hence, in the main, not be replaceable. They narrated that the exchange capacity from exposed hydroxyls would be important for kaolinite because of the presence of sheet of hydroxyls on one side of the basal crystal or cleavage surface. In a number of isotopically labeled ion-exchange experiments, it was found that cation uptake by kaolinite depends upon the cation chosen, the solution concentration, the time of contact and the modification technique (Spark, *et al.*, 1995). The aim of this research is to determine the effect of heat treatments on the structure and adsorption properties of kaolinite as a suitable adsorbent for removal of lead metal under some adsorption conditions.

Kankara Kaolin and Location of Some Kaolin Deposits in Nigeria

Kankara is located in Katsina state of Nigeria precisely around longitudes 7°26E and 7°28E and latitude 11°53N. It is the local government headquarters of Kankara Local Government Area, Katsina State. The clay is a weathering product of a unit of the basement rocks in this area, most likely feldspar. The clay sequence overlies mica schist and underlain by marble (Lori, *et al.*, 2007). This deposit has a grit context averaging 32-50%. The plasticity index approximates 13%. The linear and volume drying shrinkage ranges from 9% to 12% and 18% to 30% respectively (Bawa, 2012). The color is off-white with pink or brown patches.

Lead

Lead is rarely found as the free metal in nature, but it is present in several minerals, principally galena (PbS), the main source for lead production. It is also found as anglesite (Pb(SO₄)₂) and cerussite (Pb(SO₃)₂). Lead is one of the most commonly used non-ferrous metals that has many applications; its largest use is in making storage batteries, most of which are recycled. As a result of its resistance to corrosion and its malleability, it finds use in building constructions, storage tank lining and corrosive liquid containers. Other uses of lead are for radiation shielding, ammunition, solder, cable sheathing and pipework. Lead compounds are used as pigments in paints and ceramics, catalysers, antibacterial substances and wood preservatives (Jorge, *et al.*, 2003). A major use is in the production of anti-knock compounds for addition to petrol, particularly tetraethyl lead, Pb(C₂H₅)₄.

The exhausts from vehicles are a major source of the environmental contamination by lead. Lead is present in exhaust gases mainly as lead halides and oxides, but incomplete combustion results in about 10% of alkyl lead compounds also being present (Ademorati, 1996). Other sources of lead emissions are copper and nickel smelters, iron and steel production etc. Lead exist in the oxidation states Pb²⁺ and Pb⁴⁺, with the divalent form being the more stable in most aquatic environments. The speciation of lead compounds in water is complicated and depends upon a number of factors, principally pH, dissolved oxygen and the concentration of other organic and inorganic compounds. In surface waters, lead is present as hydrated Pb²⁺, or [PbCO_{3(aq)}] in the pH range 7-9. At pH 6, Pb²⁺ and Pb(OH)₂ are in equal concentration, whereas at higher pH values there is an increase in Pb in form of PbCO₃, Pb(OH)₂ and concentration of lead in waters is usually limited by the solubility of PbCO₃, and by its adsorption onto particulate matter (Waid and Hossam, 2007).

As reported by Khan, *et al.*, (1995), the extent of adsorption depends upon the following factors:

1. Nature of adsorbate and adsorbent
2. The surface area of adsorbent
3. Activation of adsorbent
4. Experimental conditions, such as temperature, pressure, concentration, contact time, adsorbent dosage, etc.

Characterization of Kaolinite Clay

Mark and Onyemaobi (2009), conducted a study on the mineralogical and chemical analyses of four clay deposits in Abia State, Nigeria namely Ibere, Oboro, Ohiya and Uzuakoli clays, with a view to assessing their potentials for numerous industrial applications. The analyses were performed using X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM), X-ray Fluorescence (XRF), and Atomic Absorption Spectrophotometer (AAS). It was observed that the Clays are predominantly

kaolinite. The chemical analysis showed that the silica (SiO₂) and alumina (Al₂O₃) contents of the Clays meet the requirements specified for fireclay refractory applications. The Clays were also found to have high adsorption capacity for metals removal. They concluded that the Clays have economic potentials as adsorbents and as industrial raw materials for ceramic, paper, paint, fertilizer, and pharmaceutical applications.

FTIR Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. An FTIR spectrometer simultaneously collects high resolution spectral data over a wide spectral range. The infrared (IR) spectrometer measures the absorption of IR radiation by materials as the atoms vibrate about their bonds. It is primarily used to identify bond types, structures and functional groups in organic and inorganic compounds (Serkan, 2007). IR sensitive vibrations are associated with changes in dipole moments. IR spectroscopy measures vibrational energy levels in molecules. It can be used for both qualitative and quantitative analysis, to identify molecules and compounds, and to determine the presence or absence of certain types of bonds and functional groups (Ozcan, *et al.*, 2007). For example, double and single bonds associated with carbon-hydrogen and carbon-oxygen bonding (=C-H, -C-H, C-O and C=O) can be distinguished by IR absorption. When functional groups can be bonded at different locations on molecules, IR spectroscopy can frequently identify the positions at which the functional groups are attached (Sajidu *et al.*, 2006), the reason is that vibrational frequencies differ when functional groups are attached at different sides in molecules. When illuminated by IR radiation of the appropriate frequencies, atoms, ions, and functional groups in molecules will vibrate about their bonds and energy will be absorbed (Dinger, 2005).

METHODOLOGY

FTIR Spectroscopic Technique

FTIR characterization of raw (unmodified), modified and spent clays were performed with Nicolet Magna 550 FTIR Spectrometer instrument with a frequency range of 4000-400 cm⁻¹. The samples were prepared in the forms of potassium bromide (KBr) disk. Approximately 40-60 mg of each powdered sample and 120 mg of KBr were mixed and crushed together in an agate mortar and pestle for 10 min. Approximately 40 mg of the mixture were compacted using an IR hydraulic press at a pressure of 8 tons for 60s. The disk was conditioned in a desiccators placed in an oven at 80°C for 16 hours before analysis. The spectra of raw, modified and spent kaolinite clay samples (in the forms of KBr disk) were obtained with a frequency range of 4000-400 cm⁻¹.

Experimental Procedure for Atomic Absorption Spectrometry (AAS)

The detailed experimental procedures followed in the course of this work were similar to those described by Kamel *et al.* (2004), Sajidu *et al.* (2006) and Serkan (2007). At each experimental trial, 5.00g of the appropriate adsorbent (modified kaolinite clay sample) was treated with 50cm³ of the adsorbate solution (Pb (II)) of appropriate concentration (1000ppm or 10,000ppm). The mixture was then stirred at 100 rpm at a room temperature and for a given time as reflected in the design table of experiment (Table 1). The mixture was then filtered and the filtrate made to 100 cm³ in a volumetric flask. Concentration of the analyte left in the filtrate was determined by AAS and the amount adsorbed was determined by difference.

Analysis of Aqueous Solutions using Atomic Absorption Spectrometry

Lead (II) ions were measured by using Flame AAS (Atomic Absorption Spectrometer), Model Analyst, Sens AA, using air/acetylene (10:2.51 min⁻¹) flame under optimized conditions. Element content of aqueous solutions was determined with hollow cathode lamps.

The amount of metal adsorbed onto the kaolinite clay (q_e , = μgmg⁻¹) was calculated from the equation below.

$$q_e = \frac{(C_o - C_e)}{m} V$$

Where C_e (μgml^{-1}) is the equilibrium concentration of metal in solution, C_o (μgml^{-1}) is the initial metal concentration, m (mg) is the amount of adsorbent and V is the solution volume (ml). All analytical experiments were conducted in triplicate and the mean values were reported.

RESULT AND DISCUSSION

Infrared (IR) Spectroscopy of Kankara Kaolinite Clay

As obtained from the FTIR analysis, the IR Spectrum for unmodified Kaolinite has major bands observed at 3622cm^{-1} and 3694cm^{-1} for OH groups and 1030cm^{-1} and 1108cm^{-1} for Si-O groups. However, Al-Si-O bond showed characteristic absorption at 540 per cm in the unmodified clay sample as evident in Figure 1.1 below. Similarly, the IR spectra of thermal modified kaolinite were obtained in the range from $4000\text{-}400\text{ cm}^{-1}$ to investigate the effect of thermal treatment on the raw kaolinite as shown below (figure 1.2 to 1.5).

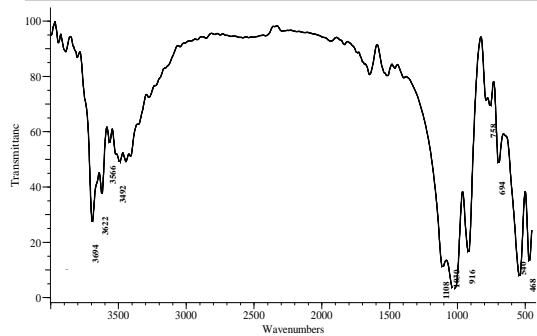


Figure 1.1: Infrared Spectrum for Unmodified (Raw) Kankara Kaolinite

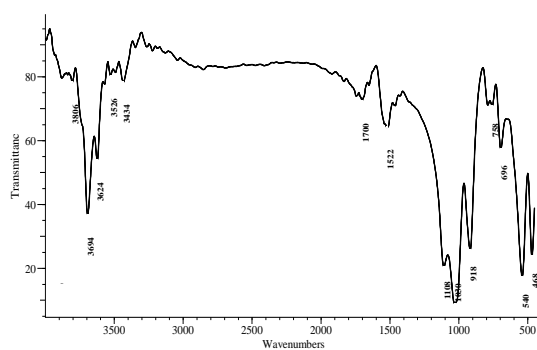


Figure 1.2: IR Spectrum for Modified kaolinite at 100°C for 20 mins

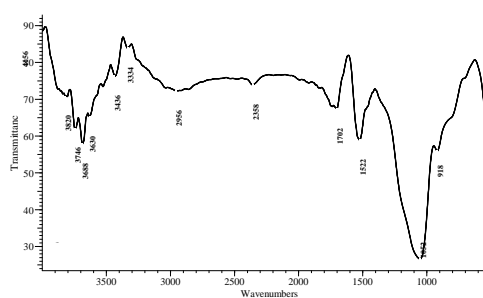
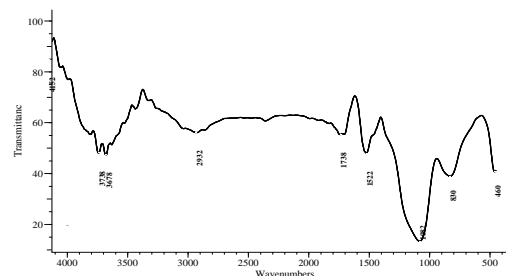
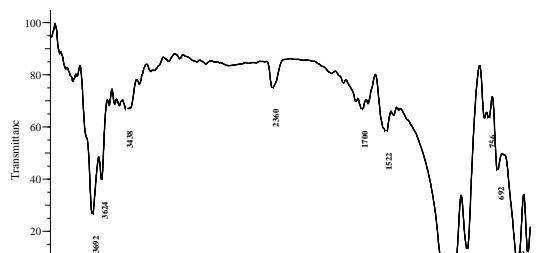


Figure 1.4: IR Spectrum for Modified Kaolinite at 800°C for 20 mins



The Infrared spectra of unmodified and modified Kaolinite clay samples exposed to different thermal treatment regimes were obtained; the result shows that the minerals of kaolinite group are frequently encountered in the studied clay samples. Kaolinite of variable order and crystallinity are obtained. Spectra of all members shows a strong family resemblance particularly over the 1110-1000 cm^{-1} and 3700-3600 cm^{-1} ranges, with variations in absorption pattern in the 1150-1100 cm^{-1} range arising from effects of particle size and shape which is similar to the result of Lori, *et al.*, 2007. The four samples of modified kaolinite clays can be readily distinguished by differences in position and relative intensity of their OH-stretching bands (Figure 1.2, 1.3, 1.4 and 1.5). As reported by Manjot (2010), it is generally

accepted that the band near 3620 cm^{-1} arises from internal OH groups, and that near 3700 cm^{-1} arises from internal surface OH groups. Disorder in kaolinite was detected mainly in the OH-stretching region as in figure 1.3, although some general broadening of all bands in the spectrum has also occurred.

Kaolinite modified at 100°C for 20mins shows significant broadening of bands throughout its spectrum (Figure 1.2), particularly for the 3694 and 3624 cm^{-1} for OH-stretching bands because of structural distortion caused by variable hydration. The Si-O group was observed at 1108 and 1030 bands. The Si-O group and OH^- for other kaolinite samples modified at 100°C for 300mins (Figure 1.3) shows almost similar absorbance compared to 100°C for 20mins modified kaolinite (Figure 1.2). The OH deformation bands of kaolinite at $3688, 3630\text{ cm}^{-1}$ and $3738, 3678\text{ cm}^{-1}$ (Figure 1.4 and 1.5) are also typical for the kaolin group, and arise from vibrations of the inner and inner surface OH groups, respectively.

In the modified kaolinite at 100°C for 20 mins (Figure 1.2), Al-Si-O bond maintained the characteristic absorption at 540 per cm which exhibit a slight change in the modified kaolinite at 100°C for 300 mins (Figure 1.3) with absorption band of 542 cm^{-1} . The band has been shifted to 538 cm^{-1} as a result of the increase in the activation temperature of 800°C for 20 mins (Figure 1.4). As the activation time increases to 300 mins at the same 800°C temperature, the Al-Si-O bond was found to disappear as evident in Figure 1.5. The IR Spectra for modified Kaolinite samples after adsorption were also obtained as shown below:

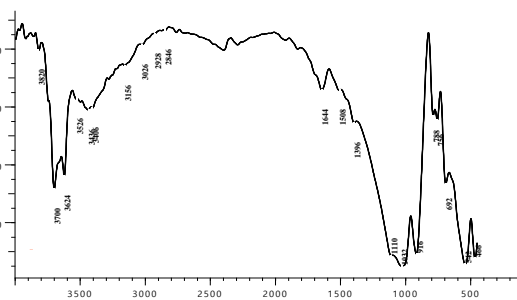


Figure 2.1: IR Spectrum for Modified Kaolinite at 100°C for 20mins after Adsorption

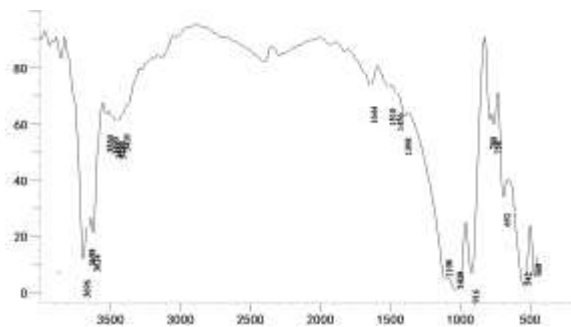


Figure 2.3: IR Spectrum for Modified Kaolinite at 800°C for 20 mins after Adsorption

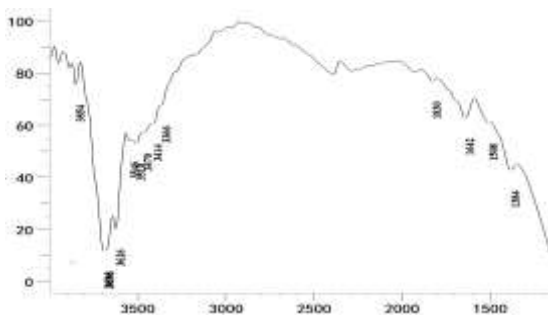


Figure 2.2: IR Spectrum for Modified Kaolinite at 100°C for 300 mins after Adsorption

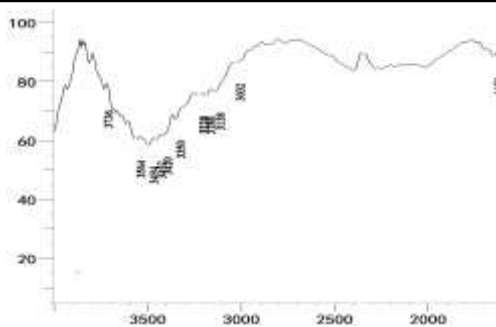


Figure 2.4: IR Spectrum for Modified Kaolinite at 800°C for 300 mins after Adsorption

After adsorption, the modified kaolinite at 100°C for 20 mins (Figure 2.1) shows a slight shift in the absorption band from 540 cm^{-1} to 542 cm^{-1} for Al-Si-O bond, while modified kaolinite at 100°C for 300 mins after adsorption (Figure 2.2), maintained the same characteristic absorption band of 542 per cm. The modified clay at 800°C for 20 mins which has a band at 538 cm^{-1} before adsorption (Figure 1.4), has been shifted to 542 cm^{-1} after adsorption (Figure 2.3) for the same bond type. The Al-Si-O bond was not found in the modified clay at 800°C for 300 mins after adsorption (Figure 2.4) which was also similar to the spectrum obtained before adsorption at the same temperature and time as evident in figure 1.5.

Statistical Design of Experiment

For studying the Lead (II) adsorption on modified kaolinite, the amount of adsorbed metallic ion (q) could depend on the mass of adsorbent, the time of contact between the adsorbate and adsorbent, the initial metal concentration (Pb^{2+}), activation temperature, activation time, etc as reported by Sajidu *et al.*, (2006). A full 2^4 factorial design was given in table 1 for treatment of datum in which the Minitab statistical software 15.1.1.0 was employed throughout in order to obtain the factor effects, effect of coefficients, standard deviation of coefficients and other statistical parameters of the fitted models.

In this work, the factors screened were, activation temperature, activation time, time of contact between the kaolinite and Pb (II) ions, and initial metal ion concentration for best metallic ion uptake using a batch adsorption system.

The experiments on table 1 were carried out to obtain the highest metallic ion uptake (q) in microgram of Lead (II) per milligram of kaolinite due to factor effect.

Table 1: Screening Experiment of Factor Effect on Lead (II) Adsorption on Kaolinite clay

S/N	StdOrder	RunOrder	CenterPt	Blocks	TempC	TimeC	TimeS	ConcS	Qe_Pb
1.	13	1	1	1	100	20	180	10000	82.95
2.	28	2	1	1	800	300	180	1000	9.9
3.	26	3	1	1	800	20	180	10000	85.798
4.	9	4	1	1	100	20	180	1000	10
5.	18	5	1	1	800	20	10	1000	10
6.	10	6	1	1	800	20	180	10000	87.374
7.	22	7	1	1	800	20	10	10000	85.368
8.	16	8	1	1	800	300	180	10000	88.402
9.	12	9	1	1	800	300	180	1000	10
10.	30	10	1	1	800	20	180	1000	10
11.	31	11	1	1	100	300	180	1000	9.728
12.	24	12	1	1	800	300	10	1000	9.492
13.	32	13	1	1	800	300	180	10000	87.898
14.	29	14	1	1	100	20	180	10000	85.824
15.	5	15	1	1	100	20	10	1000	9.736
16.	6	16	1	1	800	20	10	10000	85.976
17.	25	17	1	1	100	20	180	1000	9.342
18.	1	18	1	1	100	20	10	10000	87.81
19.	17	19	1	1	100	20	10	10000	85.924
20.	14	20	1	1	800	20	180	1000	9.694
21.	27	21	1	1	100	300	180	10000	86.05
22.	15	22	1	1	100	300	180	1000	9.65
23.	4	23	1	1	800	300	10	10000	86.234
24.	2	24	1	1	800	20	10	1000	9.728
25.	3	25	1	1	100	300	10	1000	10
26.	23	26	1	1	100	300	10	10000	86.686
27.	21	27	1	1	100	20	10	1000	9.754
28.	11	28	1	1	100	300	180	10000	88.16
29.	20	29	1	1	800	300	10	10000	87.046
30.	7	30	1	1	100	300	10	10000	87.674
31.	8	31	1	1	800	300	10	1000	9.216
32.	19	32	1	1	100	300	10	1000	10

It can be observed from Table 1 that the maximum adsorption capacity of the modified kaolinite, Q_e (μgmg^{-1}) at equilibrium in sorption of the Pb (II) ions was found to reach highest maximum adsorption capacity of $10 \mu\text{gmg}^{-1}$ which occur in both the four modified kaolinite samples. This indicates a complete removal of the metal from aqueous solution by the clay. This can also be seen from Table 1 in each run with the initial Pb (II) concentration of 1000 ppm. Similarly, lowest adsorption capacity in sorption of Pb (II) ions with initial metal concentration of 1000 ppm was $9.216 \mu\text{gmg}^{-1}$ which occur in kaolinite modified at 800°C for 300 mins. However, for the run order with initial Pb (II) concentration of 10,000 ppm, the highest maximum adsorption was $88.4 \mu\text{gmg}^{-1}$ which occur in modified kaolinite activated at 800°C for 300 mins, while the lowest adsorption capacity was $82.95 \mu\text{gmg}^{-1}$ that occur in the modified kaolinite sample activated at 100°C for 20 mins.

The results of this analysis agreed with the results of Sajidu, *et al.*, (2006), in that the mixed clay from Tundulu demonstrated strong affinity for the complete adsorption of Pb (II) and Cr (III) from aqueous solutions. The findings of this work are also in agreement to that of Chaari *et al.* (2008), who studied the adsorption of lead on thermal activated clays, the results revealed that adsorption of lead on the smectite clay increased with the increase in activation temperature due to the removal of physisorbed water and then decreased with further increase in temperature because of decrease in surface area. It was also observed from the screening of factors effect experiment in Table 1 that all the highest maximum adsorption capacity were achieved at the highest adsorption time of 180 mins, while low adsorption time (10 mins) leads to low adsorption capacity, except for the first run order that has a low adsorption capacity of 82.95 μmg^{-1} with initial Pb (II) concentration of 10,000 ppm.

CONCLUSION

Raw Kankara kaolin obtained from Kankara kaolinite quarries manifested acceptable adsorption performance regarding the removal of heavy metal ions particularly lead (II) ions. Heat modification of kaolin at different temperatures and time, as conducted in this research had detrimental effect on adsorption performance of Kankara kaolin as compared to its raw form. However, the activated kaolinite clay sample used in the present study was found to be an effective cheap source of scavenging material for heavy metal removal.

REFERENCES

- Ademorati, CMA. (1996). Environmental Chemistry and Toxicology. Pollution by heavy metals. Foludex press, Ibadan. pp. 171-172.
- Arias, M., Barral, M.T. and Mejuto, J. C. (2002), Enhancement of Copper and Cadmium Adsorption on Kaolin by the Presence of Humic Acids. *Chemosphere* 48, 1081–1088.
- Bawa, G.S. (2012). Development of gamma alumina from Kankara kaolin for potential application as catalysts support. An MSc. Thesis submitted to the Department of Chemical Engineering, School of Postgraduate Studies, Ahmadu Bello University, Zaria.
- Bhattacharyya, K. and Gupta, S. (2008). Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Advances in Colloid and Interface Science*, 140, 114-131.
- Chaari, I., Fakhfakh, E., Chakroun, S., Bouzid, J., Boujelben, N., Feki, M., Rocha, F. and Jamoussi, F. (2008). Lead removal from aqueous solution by Tunisian smectite clay. *Journal of Hazardous Materials*, 156, 545-551.
- Dinger, D.R., (2005). *Characterization Techniques for Ceramics*. Morris Publishing, U.S.A, pp. 3-224.
- Jorge, C., Miranda, T. and Cynthia, A.C. (2003). Kaolinite properties, structure and influence of metal retention on pH. *Applied Clay Science*. 23, 133– 139.
- Kamel, M.M., Ibrahim, M.A., Ismael, A.M. and El-Motaleeb, M.A. (2004). Adsorption of some heavy metal ions from aqueous solutions by using kaolinite clay. Assiut University, *Bulletin of Environmental Resource*. 7, 1, 101-110.
- Khan, S.A., Rehman, R. and Khan, M.A. (1995). “Adsorption of Cr(III), Cr(VI) and Ag(I) on bentonite”, *Waste Management*. 15, 271–282.
- Lori, J.A., Lawal, A.O. and Ekanem, E.J. (2007), Characterisation and optimisation of deferration of Kankara clay. *Journal of Engineering and Applied Sciences*. 2, 5, 1-7.
- Manjot, K. (2010), Enhancing adsorption capacity of bentonite for dye removal: Physiochemical modification and characterization. Thesis submitted for the degree of Masters in Engineering Science, School of Chemical Engineering, University of Adelaide. pp 10-105.
- Mark, U. and Onyemaobi, O.O. (2009). Assessment of the industrial potentials of some Nigerian kaolinitic clay deposits. *International Research Journal of Engineering Science and Technology (IREJEST)*. 6, 1, 244-257.
- Ozcan, A., Ömeroğlu, C., Erdoğan, Y., Özcan, A.S. (2007). Modification of bentonite with a cationic surfactant: An adsorption study of textile dye reactive blue 19. *Journal of Hazardous Materials*. 140, 173-179.

- Sajidu, S., Persson, I., Masamba, W., Henry, E. and Kayambazinthu, D. (2006). Removal of Cd^{2+} , Cr^{3+} , Cu^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+} cations and AsO_4^{3-} anions from aqueous solutions by mixed clay from Tundulu in Malawi and characterisation of the clay. *Water Society of America*. 32, 4, 519-526.
- Serkan, K. (2007). Comparative adsorption studies of heavy metal ions on chitin and chitosan biopolymers. MSc Thesis Submitted to the Post Graduate School of Engineering and Science of Izmir Institute of Technology, pp 11-36.
- Spark, K.M., Wells, J.D. and Johnson, B.B. (1995). Characterizing trace metal adsorption on kaolinite. *European Journal of Soil Science*. 46, 633– 640.
- Unuabonah, E. I., Adebowale, K. O., Dawodu, F. A. (2008). Equilibrium, kinetic and sorber design studies on the adsorption of aniline blue dye by sodium tetraborate modified kaolinite clay adsorbent. *Journal of Hazardous Materials*. 157, 397-409.
- Vimonses, V., Lei, S., Jin, B. Chow, C.W. and Saint, C. (2009). Kinetic study and equilibrium isotherm analysis of congo red adsorption by clay materials. *Chemical Engineering Journal*, 148, 354-364.
- Waid, O. and Hossam, A. (2007). Removal of Pb^{2+} ions from aqueous solutions by adsorption on kaolinite clay. *American Journal of Applied Sciences*. 4, 7, 502-507.
- Wang, L. and Wang, A. (2008). Adsorption properties of Congo red from aqueous solution onto surfactant-modified montmorillonite. *Journal of Hazardous Materials*. 160, 173-180.