Ionic Surfactant Enhancement of Clay Properties for Heavy Metals Adsorption: Kinetics and Isotherms

Adekeye Damilola Kayode[1*], Asaolu Samuel Sunday[1], Adefemi Samuel Oluyemi[1], Ibigbami Olayinka Abidemi[1], Akinsola Abiodun Folasade[2], Awoniyi Marcus Gbolahan[3], and Popoola Olugbenga Kayode[1]

[1]*Department of Chemistry, Ekiti State University, Ado-Ekiti, Nigeria*

[2]*Department of Industrial Chemistry, Ekiti State University, Ado-Ekiti, Nigeria*

[3]*Department of Biosciences, University of Nottingham, Nottingham, United Kingdom*

** **Corresponding author:***

email: damilola293@gmail.com

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Abstract: *The global health problems arising from ingesting toxic metals necessitate the quest for developing efficient materials for their remediation. Surface properties of raw kaolinite clay collected from Ire-Ekiti, South-western Nigeria, were improved by modification using sodium dodecyl sulphate (SDS) for the adsorptive removal of Pb, Cr, Ni and Cu from their respective aqueous solution. The raw and modified clays were characterized by X-ray fluorescence, Fourier transformed infrared spectrometry, Scanning electron microscope coupled with EDX and Particle induced x-ray emission technique. A batch adsorption study was used to examine the performance efficiency of the modified clay. Optimization of adsorption conditions like temperature, particle size, concentration, agitation time and pH was performed. The clay after modification showed improved surface properties such as increased pore diameter and number. Freundlich, Langmuir and Temkin isotherm models were applied to explicate the adsorption processes, while Pseudo-First order, Pseudo-Second order and the Elovich kinetic models were used to predict possible mechanisms driving the adsorption processes. The adsorption processes driven by chemical mechanisms involved series of complex mechanisms that include ion exchange, direct bonding and surface complexation other than precipitation. The percentage removal of the metals by the modified clay soil reached the values of 98.53, 94.50, 73.82, and 80.40 for Pb, Cu, Ni and Cr.*

Keywords: *kaolinite clay; heavy metals; clay modification; adsorption kinetics; adsorption isotherms*

INTRODUCTION

Environmental pollutants and their toxicity cause a major problem in the world. Water pollution is one of the biggest environmental issues causing serious problems to aquatic organisms and humans. Water bodies are majorly polluted by different industrial activities, including agrochemical production, dyeing, battery production, printing, mining, metallurgical engineering, electroplating, paint and pigment production, nuclear power operations, and electric appliances manufacturing, semiconductor production, cosmetics etc. [1-2]. The industries carrying out these operations generate various types of heavy metal pollutants in wastewater effluent. Heavy metals like chromium, nickel, cobalt, lead, arsenate and cadmium etc., in the aquatic environment, have been known to cause various health problems like chronic bronchitis, kidney problems, high blood pressure, reduced lung function, cancer of the lungs, intestinal cancer and fetal mortality [3-5].

To regulate the uncontrollable discharge of these heavy metals in wastewater, novel and recent water treatment technologies are being proposed globally. Several techniques like chemical precipitation, biological method, electrodialysis, ion exchange, electrochemical treatment and membrane filtration technologies, etc., have been used to remove hazardous pollutants [6-11]. The adsorption process is another suitable technique for heavy metal remediation in wastewater because of its significant advantages like low-cost, availability, profitability, ease of operation, high efficiency, and effectiveness over the other techniques [11-12].

Clays proposed as adsorption materials fulfill all requirements for low-cost chemical precursors for industrial applications [13-16]. Clays contain exchangeable cations and anions held to the surface [17-18]. The uptake of heavy metals by clay minerals involves a series of complex adsorption mechanisms such as direct bonding between metal cations with the surface of clay minerals, surface complexation, and ion exchange etc. [19]. In many studies, surface modification is required to enhance the adsorption capacity of clays in order to increase metal uptake [20]. Surface modification enhances the surface area, pore diameter, and the number of present active sites on the surface [21]. Several researches have shown that modified clay is a promising low-cost technology for efficient and effective removal of metals like Pb, Ni, Cr and Cu contaminated water [21-24].

Researches have also shown that both raw and modified clays from Nigeria could find application for the de-metallization of wastewater containing heavy metals [21,25]. A previous study by Adekeye et al. [26] showed low removal efficiency by the clay for metals like chromium and nickel. The authors recommended the improvement of the surface properties of the clay for enhanced performance efficiency. The low removal efficiency of the clay for metals like chromium and nickel immensely necessitates and motivates the quest for modification. The present study is tailored towards the surface modification of the Ire-Ekiti clay for improved heavy metals adsorption properties. It is also aimed at elucidating the kinetics to show the kind of reaction between the adsorbates and adsorbent and the isotherm to explicate the processes to which the adsorbates were adsorbed. This would be the study that showed the kinetics and isotherm of the modified form of Ire-Ekiti clay for heavy metals adsorption.

■ EXPERIMENTAL SECTION

Materials

Chemical and reagents used include copper(II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), nickel(II) sulphate heptahydrate ($NiSO_4.7H_2O$), potassium chromate K_2CrO_4, lead nitrate $Pb(NO_3)_2$, sodium dodecyl sulphate ($CH_3(CH_2)_{11}SO_4Na$), sodium hydroxide solution (NaOH), Hydrochloric acid solution (HCl). All reagents used were of analytical grade; hence, no further purification was carried out before use.

Instrumentation

Instrumentations applied in adsorption experiment and for the characterization of clay samples include Scanning Electron Microscope coupled with Energy Dispersive X-ray Spectrophotometer (JEOL JSM-7600F), pH meter (Jenway pH meter 3520), rotary orbital shaker with incubator (Biosan environmental shaker-incubator ES-20/60), laboratory oven, Flame Atomic Absorption Spectrophotometer (Agilent AAS 55AA), X-ray fluorescence (XRF), Fourier Transformed Infrared spectrophotometer (SHIMADZU FTIR-8400S) and Particle Induced X-ray Emission (PIXE) technique.

Study Area

The study area and trial (sample collection) site 'Ire-Ekiti' is a town in Oye local government area of Ekiti State, Southwestern Nigeria, located between latitude 7°47'N to 7°53'N and longitude 5°18'E to 5°24'E. The geological map is shown in Fig. 1. The town is known to have been the home of Ogun Onire, whom the Yoruba ethnic group of Nigeria recognizes as the "god of iron". Ire-Ekiti has naturally abundant clay deposits located within different settings of the town, which are mined both locally and industrially for different applications. The geological settings of Ekiti State are between latitude 7°20'N to 8°00'N and longitude 4°50'E to 5°50'E. The trial site showing the effects of mining activities (a depression filled with water) is shown in Fig. 2. The town possesses the most abundant clay deposits in Ekiti state, and the quality of the clay for making various industrial products

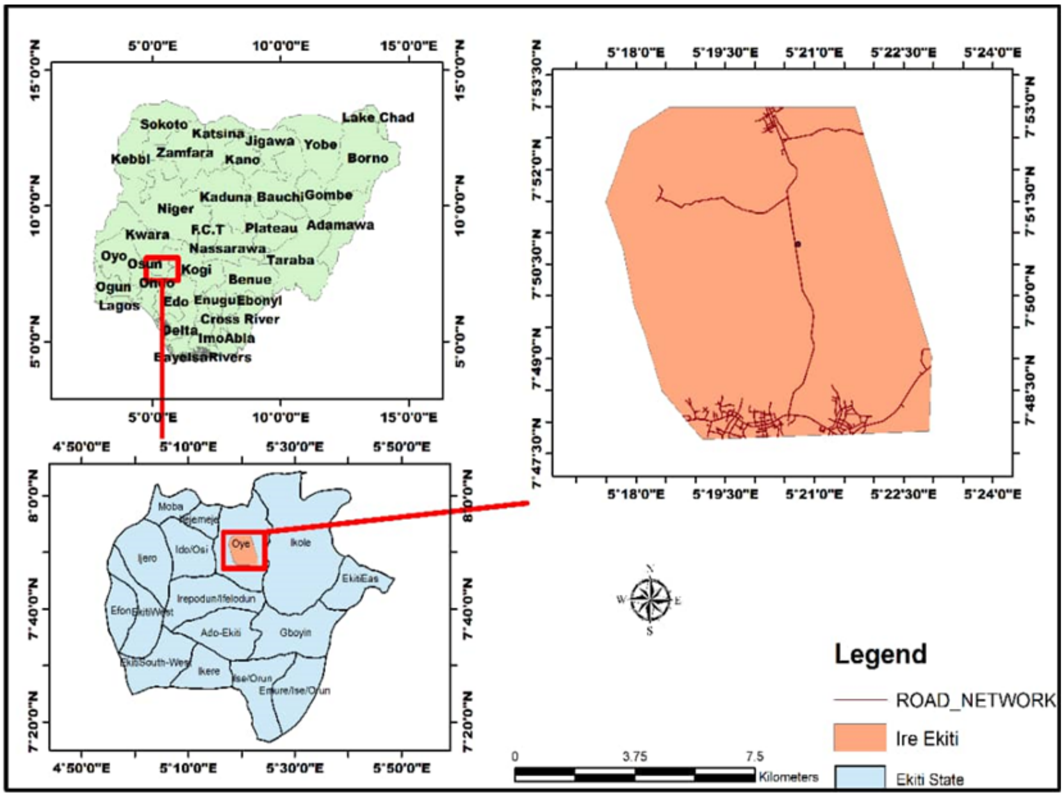


Fig 1. Geological map of Nigeria, Ekiti State, Oye local government area and Ire-Ekiti

Fig 2. Figure of the trial site showing effects of mining activities

such as bricks, tiles and ceramics have drawn the attention of different miners and establishment of a clay processing industry in the town.

Procedure

Collection and preparation of raw clay soil

The clay soil was collected from Ire-Ekiti, Southwestern Nigeria. An adequate amount for use was crushed and dispersed in deionized water; then, floating debris from plants was removed by handpicking and also by decantation. The suspension was thoroughly stirred in order to allow none clay materials to be separated from the clay; the clay soil was recovered from the water by centrifuging the suspension at 3000 rpm. The recovered clay soil was dried at 110 °C for about 12 h and cooled in a desiccator. After cooling, the dried clay soil was pulverized and sieved using sieves of different mesh sizes based on the experimental requirement. The sieved clay soils were stored in a black polyethylene bag prior to modification.

Modification of clay soil sample

An adequate amount of the raw clay sample to be used was modified with 100 mL of 0.01 M SDS in 100 mL 0.01 M NaCl solution at pH 5 by shaking for 90 min at 200 rpm on a rotary orbital shaker. The pH of the solution was adjusted using HCl and NaOH. After shaking, the mixture was centrifuged in order to collect the residue. The residue was collected and washed until the pH of leachate reached pH of 6.0, then dried in an oven at 105 °C for 12 h. The sample was crushed and sieved into the required particle sizes. The modified sample is called the surfactant (SDS) modified clay.

Preparation of metal solution

The stock solutions (1000 mg L^{-1}) of the adsorbates (Ni, Pb, Cu, and Cr) were prepared by dissolving known quantities of their metal salts (potassium chromate, lead nitrate, copper nitrate, and hydrated nickel sulfate) in deionized water and serially diluted to required concentration upon experimental requirement. The reagents used to prepare metal solutions were all extra pure analytical grades. The initial and equilibrium concentrations of metals were determined by Flame Atomic Absorption Spectrophotometer (Agilent AAS 55AA).

Characterization

Different characterizations were carried out for both the raw and modified clay to ascertain surface modification and enhanced adsorption properties of the clay material. The chemical compositions of the clay samples were determined by X-ray Fluorescence (XRF). Fourier Transformed Infrared spectrometry (FTIR) was used for functional group elucidation and to confirm the surface modification. Scanning Electron Microscopy (SEM) was used to show the surface morphology of both the natural and modified clay soil samples. The elemental make-up of the clay samples was determined by Particle Induced X-ray Emission (PIXE), while the relative abundance (%w) of some important ionic compositions as well as the carbon content of the raw and modified clay materials, were determined by Energy Dispersive X-ray Emission (EDX) technique.

Batch adsorption experiments

An adsorption experiment for the modified clay was carried out in batch by adding 50 mL of adsorbate solution 10 mg L^{-1} into conical flasks containing 0.50 g of the adsorbent [26]. Each adsorbent and adsorbate mixture was equilibrated at pH 5.0 by shaking at 200 rpm at a temperature of 298 K, using a rotary orbital shaker until equilibrium. The pH of each solution was adjusted using drops of HCl and NaOH when necessary. After equilibration, the mixtures were centrifuged for 15 min at 3000 rpm. Thereafter, the supernatants were collected and analyzed for equilibrium concentrations of the Cu, Ni, Pb, and Cr by an Atomic Absorption Spectrophotometer. The effect of pH on adsorption processes was studied at pH 3, 4, 5, 7, and 8 with an equilibration time of 90 min. The effect of agitation time on the adsorption process was investigated at the time varied between 10 and 80 min at a pH value of 5. Also, the adsorption of Cu, Ni, Pb, and Cr on the modified clay material was optimized at different concentrations (20, 40, 60, 80, and 100 ppm) with an equilibration time of 90 min at pH 5.

Data treatment

The percentage metal removal was calculated according to Eq. (1)

$$\%\ \text{Metal removal} = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (1)$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium adsorbate concentration, respectively.

■ RESULTS AND DISCUSSION

Surface Morphology

A scanning electron microscope image showing the morphology of the raw Ire-Ekiti clay soil is presented in Fig. 3(a). The image of the natural clay presents a very rough surface arising from a dense stacking and piling of particles upon one another and resulting in small-size inter-aggregate pores (10 µm). In this structure, the piling of the particles is in a consistent order, forming a tangled network with a highly dense arrangement of the

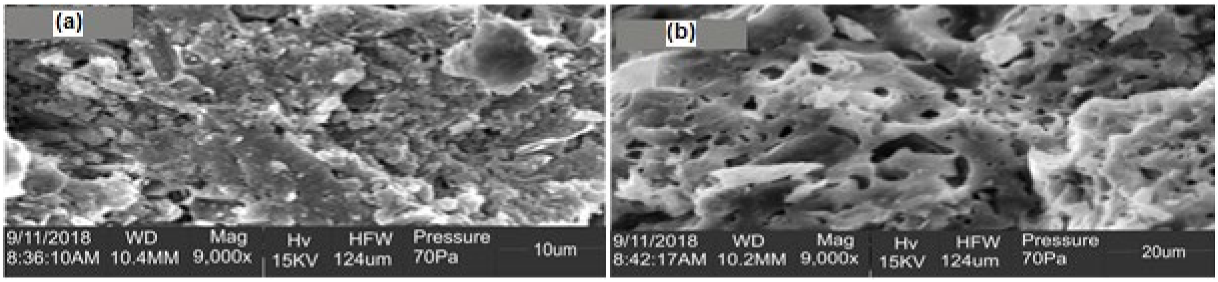


Fig 3. (a) Scanning electron microscope image of the raw clay; (b) Scanning electron microscope image of the modified clay

particles resulting in a reduced number of pores. The small pore size may hinder the permeability of adsorbates and result in low diffusion and reduced adsorption [26]. The SEM image of the modified clay is shown in Fig. 3(b). Modification of the raw clay changed its structure and surface morphology. The modified clay showed a honeycomb-like structure and surface morphology with improved surface adsorptive properties like increased pore number and size. The most notable improved properties are the pore diameter (20 µm) and number. The pore diameter increased from10 to 20 µm. Also, the pores are more numerous compared to those of the raw clay, as shown in Fig. 3(a) and 3(b). These properties make the modified clay more porous. The numerous pores and improved pore diameter have the potency to enhance permeation of the adsorbates during adsorption experiments. The highly porous structure of the SDS modified clay could improve intraparticle diffusion and permeation, resulting in higher adsorption of the adsorbate by enhancing the inner-sphere complexation reaction between the adsorbates and adsorbent.

FTIR Adsorption Spectroscopy Bands

The results of the FTIR analysis of the modified and raw clay are shown in Fig. 4(a) and 4(b), respectively.

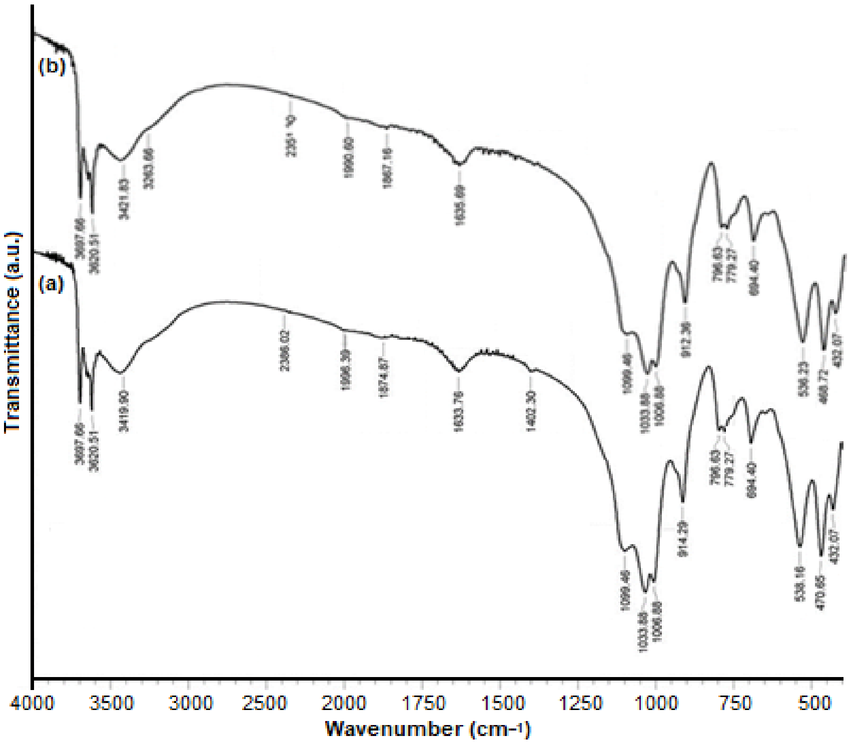


Fig 4. Fourier transform infrared spectra of (a) the SDS modified clay soil, and (b) the raw clay soil

The FTIR results showed absorption bands at 3620, 3421, 3263, 3697, 3620, and 3419 cm^{-1}, which are due to the hydroxyl group of the inner surface of the clays. The bands at 1099 and 1006 cm^{-1} correspond to the Si–O–Si group present in the clays; the band at 694 cm^{-1} is due to the bending mode of the same group. The absorption bands at 1633 and 1402 cm^{-1} are due to the presence of C=O and C=C of the organic components of the clay soils. The bands at 536 and 538 cm^{-1} showed the presence of the Si-O-Al group in the raw and modified clay. The presence of metallic oxide in the clay soil is indicated by the intensity bands at 468 and 432 cm^{-1} [27-28]. The appearance of a new intensity band at 1402 cm^{-1} assigned to the C=C in the modified clay soil, which is not present in the raw clay soil, is due to surface modification of the soil. The presence of the band 3263 cm^{-1} in the raw clay and its disappearance in the modified clay soil is a result of surface modification of the soil. Shifts in the adsorption bands from 2351, 1990, 1867, 912, and 468 cm^{-1} of the raw clay to higher intensity bands of 2386, 1996 1874, 914, and 470 cm^{-1} in the modified clay also confirm the surface modification. The changes in the FTIR results of the raw clay upon modification showed that modification with SDS might have possibly improved the negative charges of the clay surfaces and created more active sites for metal binding. The Si–O–Al and Si–O–Si structures of the soil were not affected by the modification.

Chemical Composition

The chemical composition presented in Table 1 showed that silica and alumina are the major constituents of the raw and modified clay with a percentage composition of 55.80 and 24.28; 56.31 and 27.07, respectively. The XRF results also showed that the metals are present in their oxide form rather than hydroxide. Silica (SiO_2) and alumina (Al_2O_3), being the major constituents of the clay soil, suggest that the clay soil is an alumino-silicate (kaolinite). The percentage of metal oxide compositions of the raw clay increased upon modification except for MnO. This showed that modification could also affect the chemical composition of clay soil. The results of this study are consistent and agreed with the result obtained from a study reported by Akinola et al. [29] and Awokunmi and Asaolu [30] on the modification of clay soil from Ekiti State for fluoride adsorption in an aqueous medium.

Table 1. Chemical composition of SDS modified Ire-Ekiti clay soil

Oxide	Chemical composition of the raw clay (%)	Chemical composition of the modified clay (%)
SiO_2	55.80	56.31
Al_2O_3	24.28	27.07
Fe_2O_3	4.16	4.89
Na_2O	2.91	2.92
K_2O	0.32	0.32
MgO	1.54	1.70
CaO	0.27	0.50
TiO_2	0.2	0.26
ZrO_2	0.06	0.07
MnO	0.03	0.03
LOI	10.30	5.65
Total	99.87	99.65

Elemental Composition

The result from the Proton Induced X-ray Emission technique (Table 2) showed that silicon (Si, 558138 ppm) and Aluminum (Al, 242444 ppm) are the major elemental composition with the highest concentration in the raw clay soil matrix. Al (271498 ppm) and Si (564580 ppm) are also the major elemental composition with the highest concentration in the modified clay soil matrix. These results corroborate the results of the XRF, which showed that silica and alumina are the major chemical composition of both the raw and SDS modified clay soils. The elemental composition of the raw and modified clays also showed that the clay soil samples contained a high concentration of some important exchangeable cations. The exchangeable cations for the modified clay include Na^+ (29473 ppm), Mg^{2+} (17018 ppm), Ca^{2+} (5056 ppm) and Fe^{2+} (49888 ppm). The presence of these exchangeable cations in the soil could bring about a cation exchange mechanism for removing the adsorbates from their respective solution. The concentration of each exchangeable cation of the modified clay is higher than those of the raw clay (Na^+ (28810 ppm), Mg^{2+} (15311 ppm), Ca^{2+} (2723 ppm), and Fe^{2+} (41320 ppm).

Table 2. Elemental composition and concentration of SDS modified Ire-Ekiti clay soil

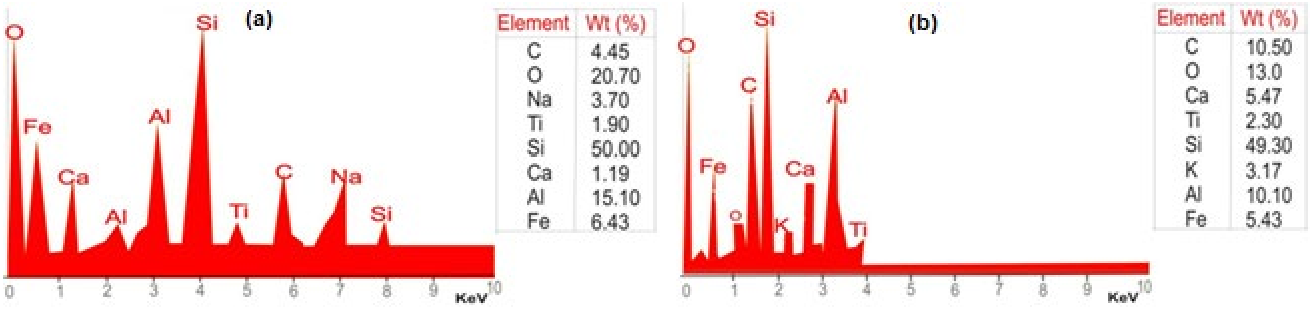
Z	Symbol	Elemental concentration of the raw clay (ppm)	Elemental concentration of the modified clay (ppm)
11	Na	28810	29473
12	Mg	15311	17018
13	Al	242444	271498
14	Si	558138	564580
15	P	329	400
17	Cl	281	386
19	Kf	3101	3154
20	Ca	2723	5056
22	Ti	2097	2687
24	Cr	261	309
25	Mn	312	318
26	Fe	41320	49888
29	Cu	381	452
30	Zn	138	180
38	Sr	35.8	187
40	Zr	562	690
46	Pd	20.5	35.7
47	Ag	217	273
48	Cd	91.6	107
50	Sn	218	283
82	Pb	13.8	13.2
83	Bi	-	45.9

Where Z is the atomic number

The metals were assumed to have undergone chemical multiplication or amplification reactions during the modification process, which resulted in their respective concentration increase. This improvement in the exchangeable cation concentrations could consequently increase the cation exchange capacity of the soil and enhance the adsorption of the adsorbates through an improved cation exchange mechanism. Bismuth (Bi) was present in the raw clay soil but absent in the modified clay soil. The absence of bismuth in the modified clay is probably due to the effect of modification of the raw clay soil.

Carbon and Ionic Composition of the Raw and Modified Soil Sample

Results of the EDX analysis of both the raw and modified clay soil samples (Fig. 5(a) and 5(b)) showed that aluminum, silicon, and oxygen are the most abundant ionic compositions of the soil matrixes and possessing the highest percentage by weight (%w). The value of Al, Si and O of the raw clay soil are 10.10, 49.30, and 13.0 %w, while that of the modified clay soil are 13.00, 50.00, and 20.70 %w, respectively. The absence of hydrogen and the presence of oxygen is an indication that the elements could be present in the form of oxides rather than hydroxide. This supports the results of the FTIR, PIXE, and XRF analysis obtained for the samples. In agreement with other techniques that have been applied for probing the properties and compositional characteristics of both the raw and modified clay samples in the present study, the EDX results of the raw clay sample also showed the presence of some important exchangeable cations such as K (3.17 %w), Ca (5.47 %w)



Element	Wt (%)
C	4.45
O	20.70
Na	3.70
Ti	1.90
Si	50.00
Ca	1.19
Al	15.10
Fe	6.43

Element	Wt (%)
C	10.50
O	13.0
Ca	5.47
Ti	2.30
Si	49.30
K	3.17
Al	10.10
Fe	5.43

Fig 5. EDX analytical results of (a) the raw clay soil, (b) the modified clay soil

and Fe (5.43 %w) while the modified clay showed the presence of Na (3.70 %w), Ca (1.19 %w) and Fe (6.43 %w). It was observed that modification has a significant influence on the ionic composition of the clay soil. For instance, K was present in the raw clay and absent in the modified clay. The absence of K in the modified clay may be due to the leaching of K from the clay during the modification process. The percentage composition of the elemental composition of the raw clay is different from that of the modified clay, as shown in Fig. 5(a) and 5(b). The carbon content of the raw and modified has the value of 10.50% and 4.45%, respectively. The relative abundance (percentage by weight) of Si and Al compared to other elements showed that the clay soil is typically kaolin confirming the results of the PIXE and XRF analysis.

Effect of pH

The pH of a solution determines the degree of ionization and speciation of metal ions and also affects the surface charge of an adsorbent in the process of metal uptake [31]. From the results in Fig. 6, it is shown that the optimum adsorption of Ni, Pb, and Cu was obtained at pH 4.0, while that of Cr was obtained at pH 5.0. This showed that optimum adsorption could be achieved at an acidic medium (usually, at pH greater than 2.0) without chemical precipitation of the hydroxide form of the metal adsorbates. This is in agreement with previously reported works by Erdemoglu et al. [32] and Chaari et al. [33]. The results obtained for the adsorption trend with increased pH showed that the adsorption process involved series of complex mechanisms, which include ion exchange, direct bonding, and surface complexation other than precipitation.

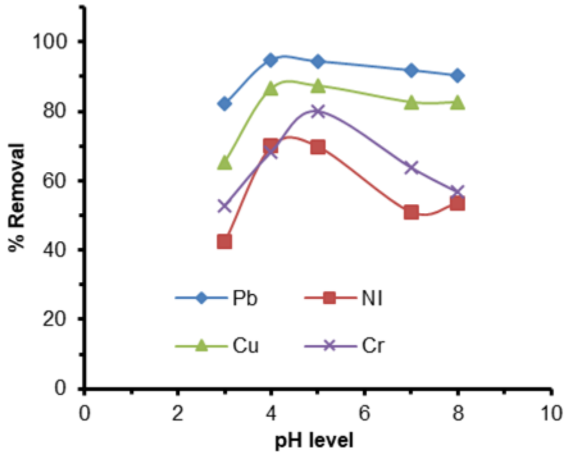


Fig 6. Adsorption trend with increase pH of the metals' solution

Effect of Agitation Time

The effect of agitation time on the adsorption potential of the modified clay material was investigated to show the suitability of the clay material for industrial applications. A good adsorbent suitable for industrial applications usually possesses a high adsorption capacity as well as a fast rate of removal. Equilibration time for adsorption of Cu and Pb was fast and achieved within 30 and 40 min respectively; then tended to be constant for 80 min. The fast adsorption rate of the adsorption process is probably due to the increased concentration gradient between the adsorbate in the solution and adsorbate in the adsorbent. This difference in concentration determined the number of vacant and available sites for metal binding and enhanced the increased uptake of the metals at the initial stages of the adsorption processes. This also implies that the nature of an adsorbent and its active sites determine the rate at which equilibrium is attained, as suggested by Dal Bosco et al. [34]. Similar results were observed in a study conducted by Jaiswal et al. [35]. Equilibration of Ni (50 min) and Cr (60 min) was achieved at a slower rate, as shown in Fig. 7. The slower rate of adsorption of Ni and Cr implies that the nature of adsorbates also plays a significant role in the rate at which equilibrium is attained or the rate of uptake. The progressive increase in adsorption and, consequently, the attainment of equilibrium adsorption may be due to limited mass transfer of the adsorbate particles from the adsorbate solution to the external surface of the clay material, initially and subsequently by slower internal mass transfer within the clay particles [36].

Effect of Adsorbate Concentration

The equilibrium adsorption trend for Ni, Pb, Cr and Cu by the modified clay material is shown in Fig. 8. Adsorptions of Ni, Pb, and Cu tend to increase as the concentration of the metals in the solution increased. It was observed that increasing the concentration of the metals in the solution resulted in higher uptake of the metal until equilibrium was achieved. This trend was attributed to the fact that when the transport of metals between the adsorbent's internal pores and external surface films tends to be equal, the transboundary movement of metals will not be significantly permissible; however, increasing concentration will re-initiate the movement, and for this reason, the adsorption process will be dependent [37]. Similar findings have been reported in the literature for similar and other pollutants' adsorption [38-39]. The effect of initial concentration on Cr adsorption by the modified clay showed that the percentage of Cr adsorbed decreased with increasing concentration. This decrease was a result of saturation of the active sites of the adsorbents at higher metal concentrations leading to less removal of chromium ions from the solution. This implies that at low concentrations, more chromium ions would be removed by the abundant active sites on the adsorbents. This result is in accordance with the findings by Akpomie et al. [21] in their study of the enhanced sorption of trivalent chromium unto novel cassava peel modified kaolinite clay.

Effect of Temperature

Temperature is one of the most important parameters of adsorption, and its effect on the metals uptake was investigated. The result of the study is shown in Fig. 9. The result showed that the adsorption process for all the metals increases with the increased temperature of the solution and suggesting endothermicity of the adsorption process. The adsorption trend is due to the ability of the metals in solution (lead, copper, chromium, and nickel) to overcome resistance to mass transfer with an increase in kinetic energy as they undergo interactions with active sites of the clay material. Increased temperature has been reported to favour the uptake of

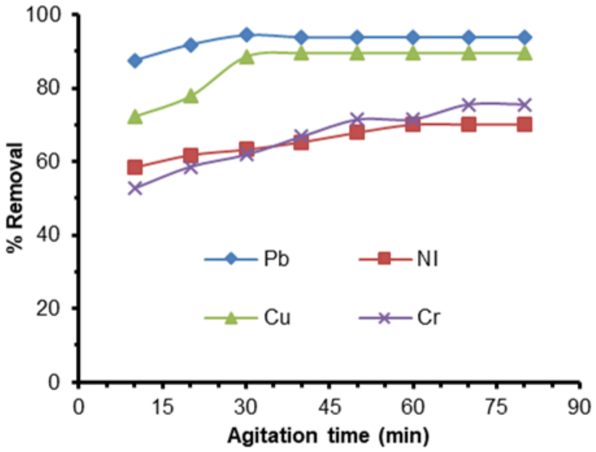


Fig 7. Adsorption trend with increase contact time for the metals

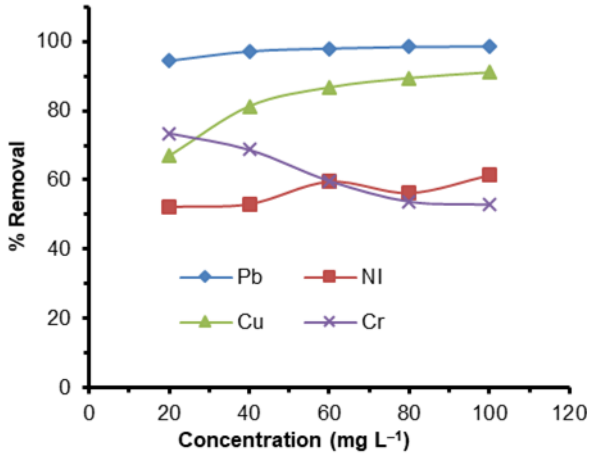


Fig 8. Adsorption trend with increase concentration for the metals

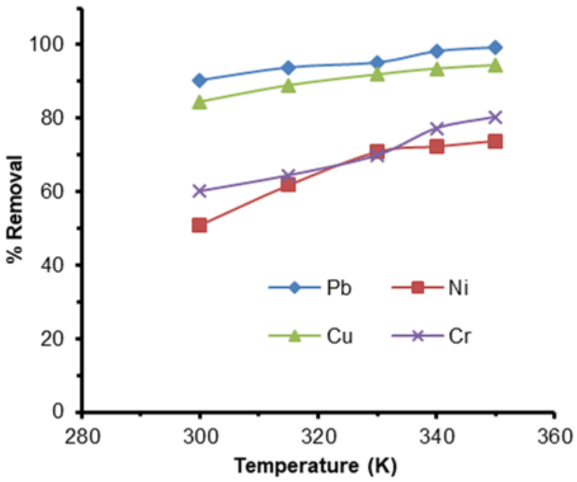


Fig 9. Adsorption trend with increase temperature for the metals

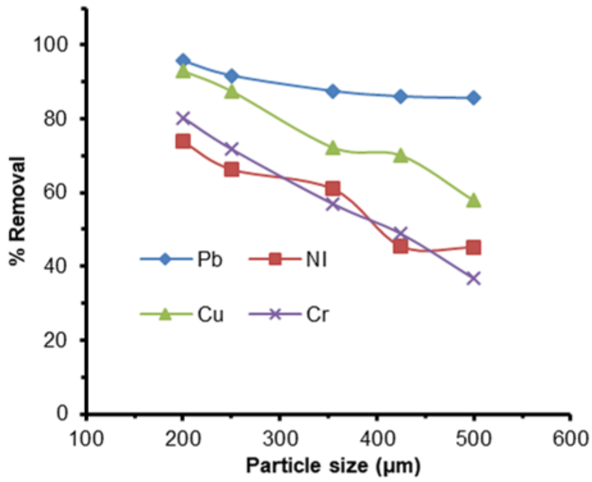


Fig 10. Adsorption trend with increase particle size for the metals

dyes and pigments Rattanaphani et al. [40] while the adsorption of metals was equally favored by increased temperature, as reported by Zouraibi et al. [41].

Effect of Adsorbate Particle Size

Adsorption processes have been known to be particle dependent. Results from this study showed that adsorption of Ni, Pb, Cu, and Cr by the modified clay material increased with decreased particle size (Fig. 10). This is due to the fact that a decrease in particle size of an adsorbent would yield larger surface areas and make available more active sites for metal binding [42].

Langmuir Adsorption Isotherm

The linearized Langmuir equation Kinniburgh [43] was used to show the surface binding properties of the metals on the modified clay soils.

$$\frac{1}{q}=\frac{1}{Q_o}+\frac{1}{Q_o K_L C_e} \tag{2}$$

where q_e (mg g^{-1}) represents the amount of ion adsorbed, C_e (mg L^{-1}) is the equilibrium concentration, Q_o (q_{max}) maximum is monolayer coverage capacity (mg g^{-1}), and K_L (L mg^{-1}) represents the Langmuir adsorption equilibrium constant. The values of K_L and q_{max} were determined from the slope and intercept of the Langmuir plot of $^1/q_e$ against $^1/C_e$. An essential feature of the Langmuir isotherm was also expressed in terms of equilibrium parameter R_L, known as the separation factor, which is a dimensionless constant and represented by Eq. (3).

$$R_L=\frac{1}{1+\left(1+K_L C_o\right)} \tag{3}$$

where C_0 represents the initial concentration and K_L is a constant related to the energy of adsorption. If the value of K_L is less than (<) 0, it implies that the adsorption process does not correlate to Langmuir isotherm. The adsorption nature is unfavorable if R_L is greater than 1, it is linear if $R_L = 1$, irreversible if $R_L = 0$, and favorable if $0 < R_L < 1$. A negative R_L value indicates that the adsorption process does not fit the Langmuir isotherm, and hence, it cannot be explained by the Langmuir isotherm.

The data presented in Table 3 shows that the K_L and R_L values for adsorption of Pb, Ni, and Cu on the modified clay are < 0. This showed that the adsorption processes do not fit the Langmuir isotherm. On the other hand, the K_L value for Cr on the modified clays is 26.88 L mg^{-1}. Also, an R_L value in the range of 3.7×10^{-5}–1.9×10^{-4} was also obtained for Cr adsorption on the modified clay material. The R_L value for chromium adsorption on and modified clay is greater than 0 but less than 1, which implies a favored Langmuir isotherm; the positive K_L values indicate that the adsorption processes correlate to the Langmuir isotherm. The R^2 values for the Cr, Pb, Cu, and Ni adsorption onto the modified clay are 0.9538, 0.5119, 0.9215, and 0.9864, respectively. The positive K_L values of Cr and other data obtained from all isotherms showed that chromium adsorption on the modified clay is in best compliance and correlates to the Langmuir

Table 3. Langmuir isotherm parameters for the modified clay material

Parameters	Ni	Pb	Cu	Cr
R^2	0.9864	0.5119	0.9215	0.9538
q_{max}	0.097	0.715	0.058	0.3378
K_L	-87.34	-1.517	-9.007	26.882
R_L	$-(1.15 \times 10^{-6}$-$3 \times 10^{-4})$	$-(6.64 \times 10^{-5}$-$3.41 \times 10^{-4})$	$-(5.6 \times 10^{-3}$- $1 \times 10^{-3})$	$(3.7 \times 10^{-5}$-$1.9 \times 10^{-4})$

isotherm as the negative K_L values (Table 3) of other metals showed their unfitness to the isotherm. These results imply monolayer adsorption of Cr on the clays' flat surfaces. The correlation was not only determined by the (coefficient of determination) linear regression coefficient parameter but also the K_L value as the R^2 value is not enough to describe the fitness and correlation of an adsorption process to Langmuir isotherm.

Freundlich Isotherm

Freundlich isotherm was used to predict a possible multi-layer adsorption of the metals on the clays' rough surfaces. The Freundlich isotherm was elucidated using Eq. (4) and (5) [44].

$$q_e = K_F C_e^{1/n} \tag{4}$$

where n is adsorption intensity, K_F is Freundlich isotherm constant (mg g^{-1}), and C_e represents the equilibrium concentration of adsorbate (mg L^{-1}). Hence,

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

where K_F and $^1/n$ are empirical constants, indicating the adsorption capacity and the strength of adsorption in an adsorption process, respectively. Parameters for the constants were obtained by plotting log q_e versus log C_e [45]. If the obtained value for $^1/n$ is below 1, it indicates normal adsorption. On the other hand, if the value of $^1/n$ is above 1, it implies cooperative adsorption [46].

Linear regression parameter is used to determine the fitness of kinetics and isotherm models [47]. From the data presented in Table 4, the values of $^1/n$ are greater than 1 for Cr, Pb and Cu adsorption by the modified clay material. This indicates that the adsorption processes are cooperative while the adsorption of Ni is more favored. The R^2 values of 0.9895 and 0.9806 were obtained for the Cu and Ni, respectively, from the Freundlich adsorption isotherm plot. The adsorption processes of the Cu and Ni on the modified clay fits best to the Freundlich isotherm than other tested adsorption isotherms. This implies that the adsorption process describes a heterogeneous system characterized by multi-layer adsorption on the rough surfaces of the clay material.

The Temkin Isotherm

The Temkin isotherm, which contains factors (Table 5) that explicitly takes into account 'adsorbent–adsorbate interactions', was used to show that heat of adsorption of Pb molecules in layers would decrease linearly rather than logarithmic with coverage by ignoring the extremely low and large value of the concentrations. The isotherm was computed using Eq. (6) and (7) [48].

$$q_e = \frac{RT}{b}\ln\left(A_T C_e\right)$$

$$q_e = \frac{RT}{b}\ln A_T + \left(\frac{RT}{b}\right)\ln C_e \tag{6}$$

$$B = \frac{RT}{b_T}$$

$$q_e = B \ln A_T + B \ln C_e \tag{7}$$

Table 4. Freundlich isotherm parameters for the modified clay material

Parameters	Cu	Ni	Cr	Pb
R^2	0.9895	0.9806	0.0452	0.8956
K_f	4.19×10^{-6}	9.56	1.778	7.863
n	0.149	1.25	0.131	0.097
$^1/n$	6.729	0.799	7.663	10.29

where A_T is Temkin isotherm equilibrium binding constant (L g^{-1}), b_T is Temkin isotherm constant, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is Temperature at 298 K, and B is Constant related to the heat of adsorption (J/mol). A_T and B were determined by plotting the quantity adsorbed q_e against ln C_e and the constants were determined from the slope and intercept [48].

The following values shown in Table 5 were estimated for the adsorption of Pb on the modified clay: A_T = 0.943 L g^{-1}, b_T = 47.87 and B = 52.11 J mol^{-1}. The parameters obtained from all the tested isotherms showed that the Temkin plot is the best fitting isotherm for the adsorption of Pb onto the modified clay with an R^2 value of 0.9655. This implies monolayer adsorption of the Pb particles in layers on the modified clay, whereas the heat of adsorption decreased linearly rather than logarithmic with coverage.

Pseudo-First-Order Kinetics

The adsorption data were modeled using the Lagergren pseudo-first-order kinetics given by:

$$\log(q_e - q_t) = \frac{K_1}{2.303}t + \log q_e \qquad (8)$$

The model was used to show that the physical adsorption mechanism was responsible for the metals' adsorption on the modified clay material. Where q_e represents the amount of metal adsorbed at equilibrium, q_t (mg g^{-1} min) represents the amount of metal adsorbed on the surface of the adsorbent at any time t (min), and K_1 min^{-1} represents the equilibrium rate constant of pseudo-first-order adsorption kinetics as given by Lagergren [49]. The rate constant K_1 was determined from the slope of log (q_e–q_t) versus time t for plots in which straight lines were obtained. An obtained straight-line graph of the plot of log (q_e–q_t) versus time t obtained, as well as closeness in values of q_{eCal} to q_{eExp}, suggests the applicability of the model.

The results of this study showed that straight line graphs were obtained for metals' adsorption on the modified clay material as shown in Fig. 11, but the values of q_{eCal} were not close to those of q_{eExp} as shown in Table 6. This suggests that the adsorption processes cannot be explained by the pseudo-first-order kinetic model.

Table 5. Temkin isotherm parameters for the modified clay soils

Parameters	Pb	Ni	Cu	Cr
R^2	0.9655	0.8927	0.9695	0.8648
B	52.11	3.53	26.90	1.546
b_T	47.87	7.44×10^2	92.72	1.6×10^3
A_T	0.943	1.231	0.1551	0.591

Table 6. Pseudo-first-order Kinetics parameters for the modified clay

Parameters	Pb	Ni	Cu	Cr
R^2	0.9033	0.5736	0.933	0.9078
K_1	0.1566	0.0836	0.0083	0.0299
q_{eExp}	0.4193	1.3424	0.2125	0.3334
q_{eCal}	0.988	0.680	0.790	0.699

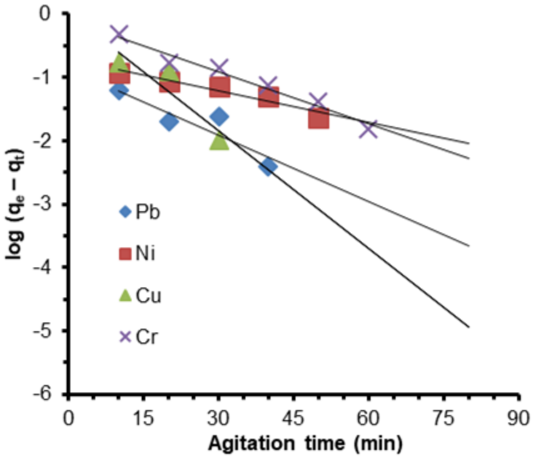


Fig 11. Plot of log (q_e–q_t) vs. agitation time (min) for modified clay

Pseudo-Second-Order Kinetics

The linearized form of the Pseudo-second-order kinetics was applied to explain the adsorption processes of the metals on the modified clay material. It is given by:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (9)$$

where h = kq_e^2 (mg/(g min)) [46].

Thus, the pseudo-second-order equation can be written as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

where k (g/(mg min)) represents the pseudo-second-order rate constant, q_t (mg g^{-1} min) represents the amount of metal adsorbed on the surface of the adsorbent at any time t, while q_e (mg g^{-1}) represents the amount of metal adsorbed at equilibrium [46].

The values of q_e, k, and h were determined experimentally by plotting $^t/q_t$ against t. The Pseudo-second-order kinetic plot of the modified clay is shown in Fig. 12. The values of q_{eCal} for the adsorption process of all the metals onto the modified clay correlate to those of q_{eExp}, as shown in Table 7. This implies that the adsorption process can be explained and represented by pseudo-second-order kinetics. The linear regression R^2 values of the pseudo-second-order kinetics for all the metals' adsorption processes are closer to unity than those of the pseudo-first-order plot. This showed that the adsorption processes best fit the pseudo-second-order kinetics. This fitting implies that there is a possible chemical interaction between the adsorbates and adsorbents during the adsorption processes. Hence, the adsorption process is driven by a chemical mechanism.

Elovich Kinetics

The Elovich equation was applied to test the suitability of the model. Elovich kinetic model shows the extent surface coverage and activation energy of chemisorptions of adsorbates on heterogeneous adsorbing surfaces. The Elovich kinetics was modeled using the linear form of the equation as represented in Eq. (11) [50].

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (11)$$

where α represents the initial adsorption rate (mg g^{-1} min), and β is related to the extent of surface coverage and the activation energy for chemisorption (g mg^{-1}). The constants α and β were obtained from the slope $(\frac{1}{\beta})$ and an intercept $[\frac{1}{\beta}\ln(\alpha\beta)]$ of the linear plot of q_t versus ln T. Elovich kinetic plots are represented by Fig. 13.

Generally, the R^2 value is used to show the suitability and applicability of the model. The results from Table 8 showed that the R^2 values obtained for adsorption processes are less close to unity than the pseudo-first-order and pseudo-second-order kinetics. This implies that the adsorption processes cannot be explained by the Elovich kinetic model.

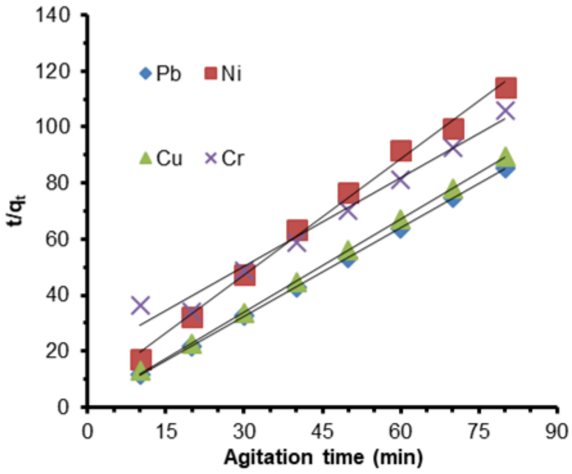


Fig 12. Plot of $^t/q_t$ vs. agitation time (min) for the modified clay material

Table 7. Pseudo-second-order kinetics parameters for the raw and modified clay soils

Parameters	Pb	Ni	Cu	Cr
R^2	0.9999	0.9952	0.9997	0.9786
K	1.4286	0.3615	1.2253	0.0950
q_{eExp}	0.948	0.7235	0.9089	0.9067
q_{eCal}	0.938	0.702	0.895	0.755

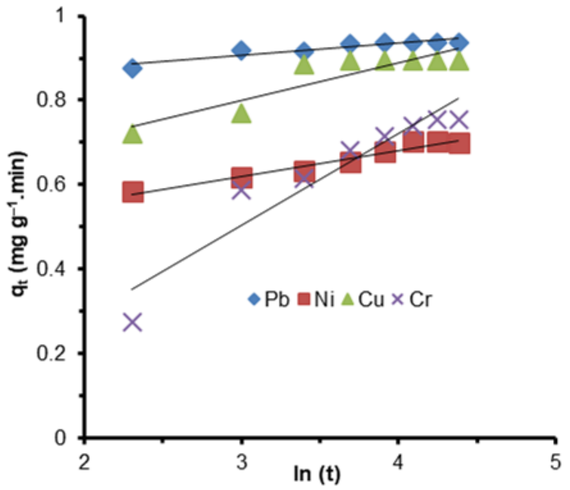


Fig 13. Plot of q_t (mg g^{-1} min) vs. ln (t) for the modified clay

Table 8. Elovich isotherm parameters for the modified clay material

Parameter	Pb	Ni	Cu	Cr
R^2	0.8697	0.9684	0.8249	0.9048

■ CONCLUSION

This study has investigated the enhancement of the adsorptive properties of Nigerian clay (Ire-Ekiti clay) for its potential application for the remediation of lead, chromium, nickel, and copper in their respective contaminated aqueous solution. Findings from this study showed that modification of the clay by anionic surfactant sodium dodecyl sulfate improved its heavy metals adsorption properties. The improved properties include pore diameter, pore numbers, exchangeable cations, surface morphology, and available active sites for metal binding. The instrumentations employed for the materials' characterization were able to give sufficient information on the subject matter. The results from the adsorption study showed a fast rate of the metals' removal by the modified clay material, and a very good percentage of the metals were adsorbed. Adsorption efficiency of the modified clay measured in the form of a percentage of metal removed reached the values of 98.5%, 94.5%, 80.3%, and 73.8% for the Pb, Cu, Cr, and Ni, respectively. The outcome of this research and information contained in this study showed that SDS modified clay is a promising material for remediation of heavy metal contaminated water and laden solution beyond an acceptable level. We recommend that other modification techniques be employed for surface modification of the clay for improved adsorptive properties and efficiency.

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