

Adsorptive Behaviour of a Nigerian Natural Clay for the Removal of Lead and Cadmium from Aqueous Solutions

Aminu Koko Rabi^{*}, Murtala Maidamma Ambursa, Yakubu Yahaya, Faruk Umar Maiahu, Farooq Abubakar Atiku

Department of Pure and Applied Chemistry, Kebbi State University of Science and Technology, Aliero, Nigeria

Email address:

arkoko2003@gmail.com (A. K. Rabi), murtalamaidamma@ymail.com (M. M. Ambursa), yalmo72@gmail.com (Y. Yahaya), maiahu208@gmail.com (F. U. Maiahu), atikufarooq@gmail.com (F. A. Atiku)

*Corresponding author

To cite this article:

Aminu Koko Rabi, Murtala Maidamma Ambursa, Yakubu Yahaya, Faruk Umar Maiahu, Farooq Abubakar Atiku. Adsorptive Behaviour of a Nigerian Natural Clay for the Removal of Lead and Cadmium from Aqueous Solutions. *Science Journal of Chemistry*.

Vol. 10, No. 4, 2022, pp. 93-102. doi: 10.11648/j.sjc.20221004.11

Received: June 13, 2022; **Accepted:** June 29, 2022; **Published:** July 12, 2022

Abstract: The occurrence of heavy metals in water constitute a major threat to both humans and aquatic animals. The current research work investigated the adsorptive behavior of a natural clay obtained from Goronyo Local Government, Sokoto state, Nigeria for Pb(II) and Cd(II) ions removal from aqueous solution. The clay sample was characterized using different techniques (X-ray fluorescence, X-ray diffraction, and Fourier transform infrared spectroscopy). Batch adsorption method was employed at room temperature to investigate the amount of metal ion adsorbed per gram of clay as a function of solution pH, contact time, adsorbent dosage and metal ion concentration. Optimum adsorption was attained at solution pH of 5.5 and 6 for Pb(II) and Cd(II) ions, respectively, contact time of 60 min, adsorbent dosage of 0.5 g/50 mL and metal ion concentration of 50 mg/L. Kinetic analysis revealed that the adsorption conform to pseudo-second order kinetic model. Among the different isotherms tested, the Freundlich and Langmuir isotherms gave the best fit, illustrating that the interaction was predominantly chemical in nature but the adsorption sites were heterogeneous. The maximum adsorption amount per gram of the clay adsorbent was found to be 49.72 and 31.63 mg/g for Pb(II) and Cd (II) ions, respectively. These results suggest that GN clay can be efficiently utilized as a low-cost adsorbent for metal ions removal from aqueous systems.

Keywords: Adsorption, Clay, Heavy Metals, Kinetics, Adsorption Isotherm

1. Introduction

The contamination of natural water resources by heavy metals has continued to attract global attention due to its widespread and potential health effects on living organisms [1–3]. Most environmental contamination by heavy metals is often associated with anthropogenic activities such as mining and agriculture, discharge of untreated wastewater from domestic and industrial processes, etc. [2, 4]. Unlike organic contaminants, heavy metals do not biodegrade and tend to accumulate in the environment and living organisms [5]. Lead (Pb) and cadmium (Cd) are among the most toxic metals and have received significant attention. Exposure to these metals even at trace levels can cause detrimental health disorders like neurological and gastrointestinal distress,

kidney and liver disease, lung cancer and several other health problems [6, 7]. Hence, the elimination of heavy metals from drinking water and from effluents discharged from various industries is extremely important in order to protect the health of the people and the environment. Among the numerous processes available for the removal of heavy metals from water, adsorption-based process has proven to be more versatile and widely used because it is economical, effective, as well as flexible in design and operation [8]. Various adsorbents, including activated carbon, carbon nanotubes and mesoporous organosilica have been employed for the adsorption of different types of pollutants (organic and inorganic) [9, 10]. Although activated carbon has been the most commonly used, but it is expensive and difficult to regenerate [11]. Thus, research efforts have been directed towards finding low-cost, effective and easily available

adsorbents for the removal of heavy metals from water and wastewater.

Clay, a fine-grained naturally occurring material, has received much attention recently as an adsorbent material for the removal of different kinds of contaminants from water/waste water due its abundance and low cost [12, 13]. The applicability of the clay material as adsorbent is associated with its high chemical and mechanical stability, high specific area, high porosity, high cation exchange capacity, layered structure and a variety of surface and structural properties [9].

Nigeria has large deposits of inexpensive natural clay, which are distributed across different regions of the country. However, there is a paucity of information related to utilization of the abundant Nigerian clays for applications in water and waste water treatment. Therefore, the present study was aimed at evaluating the potentials of a large clay deposit located in Goronyo area of Sokoto state, Nigeria for adsorptive removal of lead and cadmium metal ions from aqueous solution. To keep the process simple and inexpensive, the natural clay was used without much purification or modification. The efficiency of the natural clay for adsorptive removal of lead and cadmium was evaluated at different pH, adsorbent amount, and metal ion concentration. The adsorption data were analyzed using relevant linear isotherm and kinetic models.

2. Materials and Methods

2.1. Clay Sample

The natural clay sample used in this study was obtained from a clay deposit in Goronyo Local Government area of Sokoto State, Nigeria. The raw clay was pretreated to remove stones and debris then sun dried for 3 days. The clay sample was crushed into fine powder using ceramic mortar and pestle and passed through 76 μm mesh. Soluble impurities were removed by soaking 100 g of the clay sample in 1 dm^3 of distilled water for 48 h. The obtained slurry was centrifuged at 4000 rpm for 30 min. The recovered clay was oven dried, crushed and stored in plastic container.

2.2. Chemicals

All chemicals used in this study were of analytical reagent grade and were products of Sigma Aldrich. Stock solutions of Cd(II) (1000 mg/L) and Pb(II) (1000 mg/L) were prepared by dissolving appropriate amount of $\text{Cd}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ in double distilled water. Standard solutions of the metal ions were prepared by diluting the stock solutions. The pH of the test solutions was adjusted using 0.1 M HNO_3 and 0.1 M NaOH solutions.

2.3. Characterization of the Clay Sample

Powdered X-ray diffraction (XRD) analysis of the clay sample was performed using PANanalytical Empyrean XRD with monochromated $\text{CuK}\alpha$ radiation (40 kV and 40 mA) with reflections recorded for 2θ positions in the range 4° to 75°

with step size 0.026° . The chemical composition of the bulk clay sample was determined using X-ray fluorescence (XRF) spectrometer. Fourier transform infrared (FTIR) spectroscopic analysis was performed on a Shimadzu IRPrestige-21 using attenuated total reflection (ATR) method. The spectrum was recorded from $4000\text{--}650\text{ cm}^{-1}$ wavenumber range at a resolution of 2 cm^{-1} .

2.4. Batch Adsorption Experiments

The adsorption of Cd(II) and Pb(II) ions on the natural clay adsorbent was tested in a batch method by mixing appropriate amount of the clay sample with a metal ion solution in a 100 mL plastic bottle. The content was agitated on an orbital shaker at 150 rpm for a given time. The mixture was centrifuged at 3000 rpm for 30 min and the metal ion remaining unadsorbed was determined using atomic absorption spectroscopy (AAS). The effect of contact time (1–240 min), pH (2–6), initial metal ion concentration (50–300 mg/L), and clay amount (0.1–0.9 g) was investigated for the metal ions. All experiments were conducted at room temperature ($29 \pm 2^\circ\text{C}$). The amount (q) of metal ion adsorbed per unit mass of clay adsorbent (mg/g) was calculated using the expression:

$$q = (C_o - C_e)/m$$

Where, C_o (mg/L) and C_e (mg/L) are the initial and final metal ion concentration, respectively and m (g) is the mass of adsorbent.

3. Results and Discussion

3.1. Characterization of the Natural Clay

Table 1 shows the chemical composition of GN clay obtained from X-ray fluorescence analysis. The data in Table 1 indicated that the major oxides present in the clay sample are SiO_2 (61.77%), Al_2O_3 (20.36%), Fe_2O_3 (6.19%) and MgO (5.51%), while the remaining oxides are in trace amounts.

The mineralogical composition of the GN clay was determined by XRD and the obtained pattern is shown in Figure 1. The diffractogram showed the dominance of kaolinite and quartz minerals in the natural clay sample. Kaolinite was identified by its reflections at 7.18 \AA and 3.57 \AA , corresponding to Bragg's angle (2θ) of 12.32 and 24.91 respectively, while the reflections at 3.35 ($2\theta = 26.65$) is associated with quartz.

FTIR spectroscopy is commonly utilized for the identification of minerals present in raw clays. The major absorption bands identified in the GN clay sample were those typical of kaolin group (Figure 2, Table 2). The peaks recorded in the $3600\text{--}3700\text{ cm}^{-1}$ range are characteristic kaolinite peaks attributed to OH stretching vibrations while the two peaks in the $900\text{--}950\text{ cm}^{-1}$ range are attributed to OH bending vibrations [13–15]. The peaks at 3621 and 934 cm^{-1} are due to inner hydroxyl groups in the octahedral sheet while those at 3697 and 911 cm^{-1} are due to inner surface hydroxyl groups

that form the bonds between the sheets [15]. The peak at 1629 cm^{-1} is attributed to the bending of adsorbed water. The peaks observed in the 1200–600 cm^{-1} region are characteristic of silicate minerals and were assigned to various vibrational transitions (Table 2) [16].

3.2. Batch Adsorption

Batch adsorption were carried out to investigate the effect of operating conditions, adsorption isotherms and kinetics of Pb(II) and Cd(II) adsorption onto the GN clay.

3.2.1. Effect of Contact Time

The effect of contact time (1 – 240 min) on the sorption of Pb(II) and Cd(II) ions onto the GN clay is presented in Figure 3. The initial pH of the solution was adjusted to 4, while the clay amount was 0.5 g/50 mL and the initial metal ion concentration was 100 mg/L. The sorption amount of the clay for both metal ions increased rapidly with increasing contact time up to 30 min and then slowed down as the equilibrium was approached. Equilibrium was achieved within 60 min, which indicated that all the adsorption sites on the clay have been saturated by the metal ions. Similar trend was observed by [8, 17]. Thus, the contact time of 60 min was found to be appropriate for maximum adsorption of both Pb(II) and Cd(II) ions and was selected for the remaining experiments.

3.2.2. Effect of Solution pH

The aqueous solution pH is one of the most important factors influencing metal ions adsorption process because it controls the surface charge on the clay adsorbent and the chemistry of the adsorbate ions [8]. The effect of solution pH on the adsorption of Pb(II) and Cd(II) ions onto the natural clay is shown in Figure 4. As the pH of the aqueous solution was raised from 2 to 6, the uptake amount of the metal ions by the clay increased, with optimum adsorption occurring at $\text{pH} > 5$ for both metal ions. The improved sorption of the metal ions by the clay with increase in solution pH could be explained on the basis of competition for adsorption sites on the clay surface between the adsorbate metal ions and H_3O^+ ions. At low pH, the concentration of H_3O^+ ions present in

the solution outweighed that of the metal ions and the clay surface was more likely to be covered by the H_3O^+ ions, thus restricting the adsorption of Pb(II) and Cd(II) ions. When the solution pH was increased, the binding sites became more available for adsorption of the metal ions to occur. At solution pH greater than 5.5 and 6 for lead and cadmium ions, respectively, precipitation of the metal ions was observed. This is usually associated with the formation of $\text{Pb}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ [18]. As a result of this, an apparent increase in the amount of the metal ions adsorbed would be observed. In the present study, the experiments were not performed at pH greater than 5.5 and 6 for lead and cadmium ions, respectively to avoid any uncertainties arising from the precipitation of the metal ions.

3.2.3. Effect of Adsorbent Amount

The effect of different clay amounts (0.1–0.9 g/50 mL) on the sorption of Pb(II) and Cd(II) ions at fixed initial metal ion concentration (100 mg/L), contact time (60 min), temperature ($29 \pm 2^\circ\text{C}$) and pH (6 for Cd(II) and 5.5 for Pb(II)) is shown in Figure 5. It is evident that the amount of Pb(II) and Cd(II) adsorbed per unit mass decreased from 11.55 mg/g and 10.27 mg/g to 3.77 mg/g and 3.52 mg/g, respectively when the adsorbent amount was increased from 0.1–0.9 g/50 mL. Similar trend has been reported by [19]. The decrease in the adsorption amount with increase in adsorbent dosage may be associated to increased number of adsorption sites that remained unsaturated during the adsorption process [20]. It may also be due to aggregation of adsorbent particles leading to a decrease in the total surface area and an increase in diffusional path length [21]. However, the removal efficiency exhibit a reverse trend. For both metal ions, the efficiency increased from 23.11% and 20.55% at 0.1 g adsorbent mass to 96.27% and 82.56% at 0.5 g adsorbent mass for Pb(II) and Cd(II) ions respectively. This increase in efficiency is due to availability of more adsorption sites, which increased with increase in adsorbent dose. The observed trend is similar to that reported by other workers [11, 22]. In order to obtain maximum adsorption efficiency, an adsorbent dose of 0.5 g was employed at a fixed aqueous solution volume of 50 mL for all subsequent studies.

Table 1. Oxide chemical composition of the clay sample.

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	CaO	SO ₃	CuO	ZnO	TiO ₂	MnO	Na ₂ O	P ₂ O ₅	V ₂ O ₅	Cr ₂ O ₃
Weight%	61.77	20.36	6.19	5.51	1.77	1.45	0.34	<0.01	0.01	0.69	0.09	0.05	0.16	0.02	0.03

Table 2. Assignment of FTIR absorption peaks for GN clay.

Frequency (cm^{-1})	Assignment
688	Perpendicular Si-O vibration
778	Perpendicular Si-O vibration
911	Inner-surface –OH bending
934	Inner –OH bending
1005	Asymmetric in-plane Si-O-Si stretching
1030	Asymmetric in-plane Si-O-Si stretching
1116	Apical Si-O stretching
3621	Inner –OH stretching
3697	Inner-surface –OH in-plane stretching

3.2.4. Effect of Initial Metal Ion Concentration

The effect of initial metal ion concentration (50 – 300 mg/L) on the adsorption of Pb(II) and Cd(II) ions obtained at constant clay amount (0.5 g/50 mL), contact time (60 min), pH (6 for Cd(II) and 5.5 for Pb(II)) is shown in Figure 6. It can be observed that increasing the metal ion concentration resulted in a decrease in metal ion removal efficiency. When the metal ion concentration was increased from 50 mg/L to 300 mg/L, the removal efficiency decreased from 91.17% and 81.67% to 78.05% and 71.65% for Pb(II) and Cd(II) ions respectively. This decrease may be associated to the increase in the ratio of the number of metal ions in solution to the number of available adsorption sites which resulted in increased competition for the adsorption sites [23]. However, the increase in adsorption amount per unit mass (q_e) with an increase in metal ion concentration can be explained considering the fact that increased number of metal ions were supplied per unit mass of the clay.

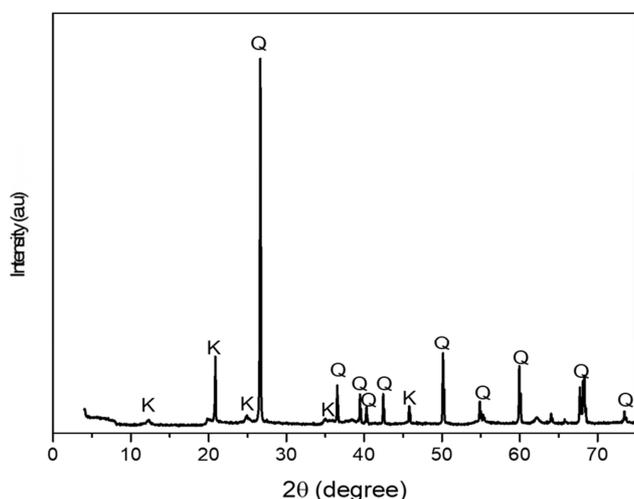


Figure 1. X-ray diffraction pattern of the clay sample.

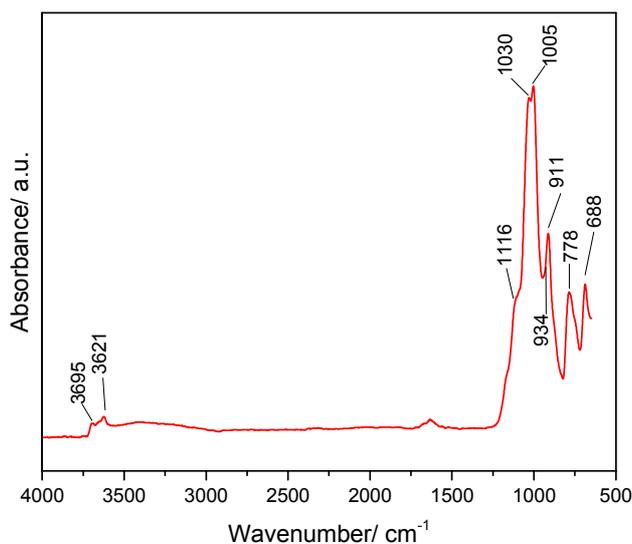


Figure 2. FTIR spectrum of natural clay sample.

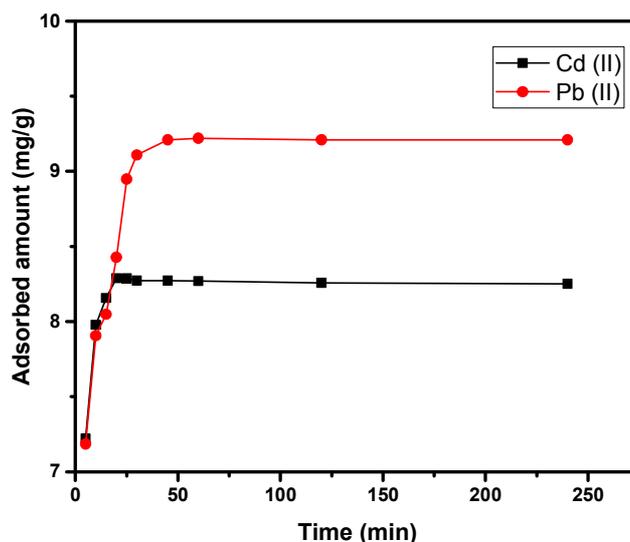


Figure 3. Effect of contact time on the amount of Pb(II) and Cd(II) ions adsorbed per unit mass of natural clay at room temperature ($29 \pm 2^\circ\text{C}$), pH of 4, metal ion concentration of 100 mg/L, and clay dosage of 0.5 g/50 mL.

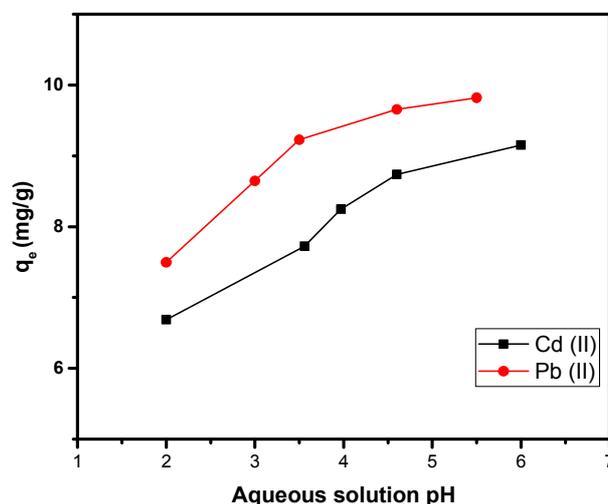


Figure 4. Effect of pH on the amount of Pb(II) and Cd(II) ions adsorbed per unit mass of natural clay at room temperature ($29 \pm 2^\circ\text{C}$), contact time of 60 min, metal ion concentration of 100 mg/L, and clay dosage of 0.5 g/50 mL.

3.3. Adsorption Isotherm

Adsorption isotherm expresses the relationship between the equilibrium concentration of the solute in solution and the equilibrium adsorption amount on the adsorbent at a particular temperature [24]. The adsorption isotherm variables give detail information on surface properties, adsorbent affinity and adsorption mechanism. Proper analysis and design of adsorption processes requires relevant adsorption equilibria as one of the important information. A number of adsorption isotherm models, originally employed for gas-phase adsorption, have been readily applied to equilibria of heavy metals in solution. Some of the commonly used models such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms have been evaluated in the present work.

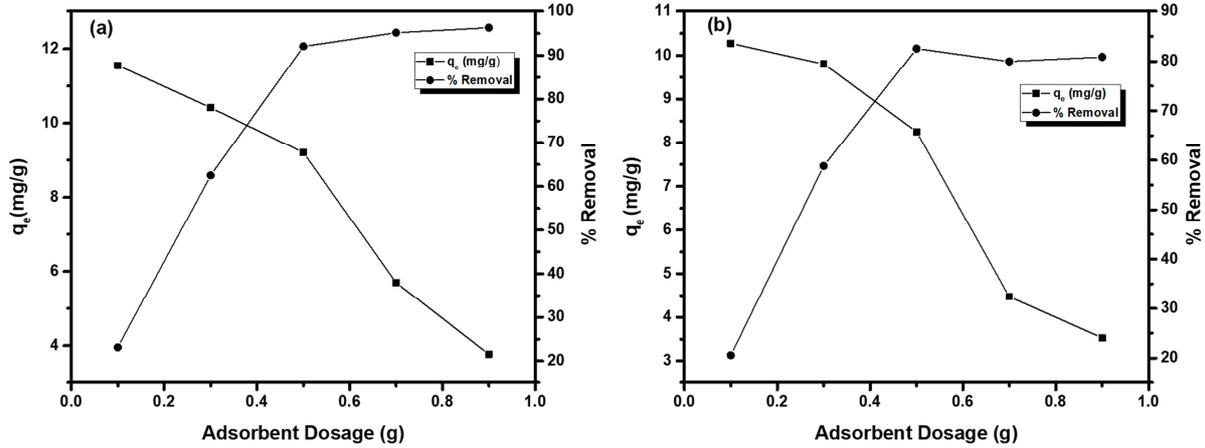


Figure 5. Effect of Adsorbent dosage on the amount of (a) Pb(II) and (b) Cd(II) ions adsorbed per unit mass of natural clay at room temperature (29±2°C), pH of 5.5 for lead and 6 for cadmium ions, metal ion concentration of 100 mg/L, and contact time of 60 min.

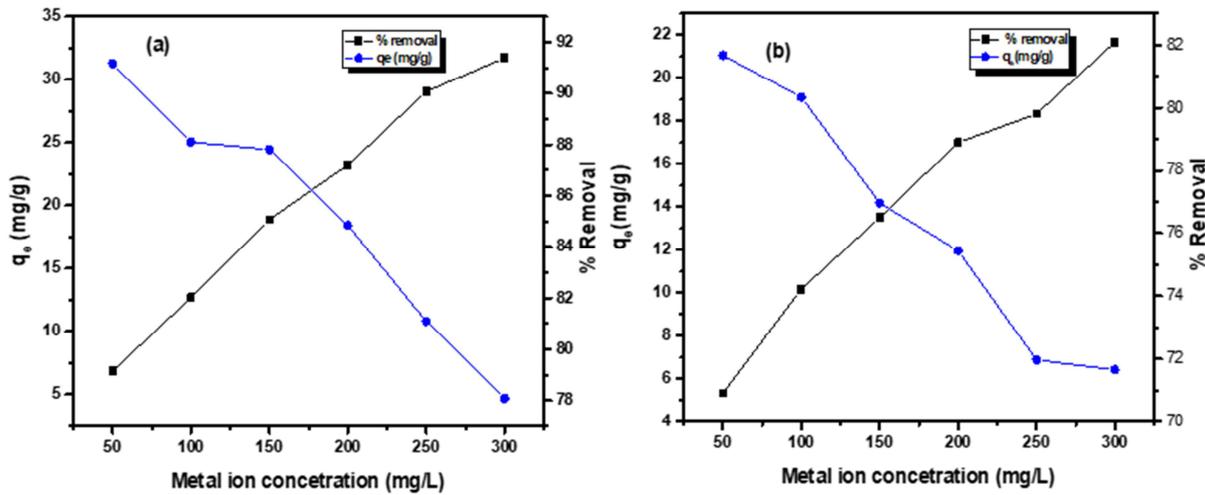


Figure 6. Effect of metal ion concentration on the amount of (a) Pb(II) and (b) Cd(II) ions adsorbed per unit mass of natural clay at room temperature (29±2°C), pH of 5.5 for lead and 6 for cadmium ions, adsorbent dosage of 0.5 mg/50mL, and contact time of 60 min.

3.3.1. Langmuir Isotherm Model

The Langmuir adsorption isotherm is based on the assumption that adsorption occurs at specific homogeneous sites within the adsorbent. The model has been successfully applied to many adsorption processes involving monolayer adsorption [5, 12]. The linearized form of Langmuir isotherm is expressed as [25]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e$$

where q_e is the amount of the metal ion adsorbed per gram of adsorbent (mg/g); C_e is the equilibrium concentration of the metal (mg/L); K_L is Langmuir constant (L/mg); and q_m is the maximum adsorption capacity (mg/g). The constants, K_L and q_m can be computed from the slope and intercept of plot of C_e/q_e vs. C_e, respectively.

The Langmuir isotherm equation is also used to determine the dimensionless equilibrium parameter commonly referred to as the separation factor, R_L, using the relation:

$$R_L = \frac{1}{1 + K_L C_0}$$

where C₀ is the adsorbate ion initial concentration. The value of R_L is indicative of whether the adsorption is favorable, linear, unfavorable or irreversible. The adsorption is favorable if 0 < R_L < 1, linear if R_L = 1, unfavorable if R_L > 1 and irreversible if R_L = 0 [21, 26].

From the data presented in Table 3 and Figure 7a, it can be observed that the Langmuir isotherm fairly fits the adsorption data well (R² > 0.96). The maximum monolayer adsorption capacity estimated at room temperature (29±2°C) for Pb(II) and Cd(II) ions were 49.72 and 31.63 mg/g respectively. The q_m values obtained for the Pb(II) and Cd(II) ions removal by the clay adsorbent were higher than the maximum adsorption capacities reported by Chaari et al. [23] for Tunisian smectite clay and Jiang [27] for natural kaolinite clay, but lower than those reported by [28]. The K_L values calculated were 0.99 and 0.87 for Pb(II) and Cd(II) ions, respectively. The larger value of K_L with respect to lead adsorption indicated that the interaction between Pb(II) ions and the GN clay were stronger

than that between Cd(II) ions and the clay adsorbent. The values of the dimensionless separation factor, R_L (0.0033 – 0.0046) calculated for both adsorbate ions were < 1 , suggesting that the metal ions adsorption onto the clay surface is favorable [29]. This further confirms the fitness of the data to Langmuir isotherm model.

3.3.2. Freundlich Isotherm Model

The Freundlich isotherm takes into account the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy of adsorption [30, 31]. The linear form of the Freundlich isotherm is described as [30]:

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

where K_F and n are Freundlich constants, which can be determined from the intercept and slope of the linear plot of $\log q_e$ vs. $\log C_e$. The Freundlich isotherm model provided the best fit to the equilibrium data for both metal ions ($R^2 > 0.98$), which is indicative of nonspecific or multilayer adsorption on a heterogeneous adsorbent surface [8, 21]. At room temperature ($29 \pm 2^\circ\text{C}$), the value of the Freundlich constant, K_f (Freundlich adsorption capacity), obtained from the linear fit (Figure 7b) for Pb(II) and Cd(II) ions were 1.78 mg/g and 1.03 mg/g, while the coefficient, n (adsorption intensity), had values of 1.59 and 1.66, respectively (Table 3). The obtained values of n , which are greater than 1 for both ions indicated that the adsorption was favorable [25]. Similar results have been reported for the adsorptive removal of Pb(II), Cr(IV) and Cd(II) ions from aqueous solutions by waste clay [8].

3.3.3. Temkin Isotherm Model

The Temkin isotherm model was put forward to take into account the effects of adsorbate-adsorbate interactions [32]. The model assumes that due the adsorbate-adsorbate interactions, the heat of adsorption of all adsorbate molecules or ions in the layer decreases linearly with surface coverage [32, 33]. The linearized Temkin isotherm model has the form [34]:

$$q_e = B \ln k_T + B \ln C_e$$

Where, $B = (RT/b)$ and denotes the Temkin constant which is related to the heat of adsorption (J/mol), T is the absolute temperature (K), R is the gas constant (J/mol K), b is another Temkin isotherm constant and k_T is the Tempkin isotherm equilibrium binding constant (L/mg) corresponding to the maximum binding energy [31, 35]. These constants can be estimated from the slope and intercept of the plot of q_e vs. $\ln C_e$, respectively.

Figure 7c shows the fittings of the lead and cadmium ions equilibrium adsorption data obtained at $29 \pm 2^\circ\text{C}$ to the Temkin isotherm model. The plots were also linear with good coefficient of determination ($R^2 > 0.97$). The higher value of the Temkin constant, B , (3.91 kJ/mol) for Pb(II) ions compared to 1.06 kJ/mol for Cd(II) ions (Table 3) suggests that the Pb(II) ions had higher heat of adsorption than the Cd(II) ions. The similar k_T values obtained for both ions might indicate that the strength of the interaction between the GN

clay and the ions of Pb(II) and Cd(II) is similar.

Table 3. Isotherm parameters for the sorption of Pb(II) and Cd(II) ion on natural clay.

Isotherm	Adsorbate ion	
	Pb(II)	Cd(II)
Langmuir Isotherm		
q_m (mg/g)	49.72	31.63
K_L (L/mg)	0.99	0.87
R_L (mg/g)	0.0033	0.0046
R^2	0.968	0.980
Freundlich		
K_f (mg/g)	1.78	1.03
n	1.59	1.66
R^2	0.987	0.985
Temkin Isotherm		
k_T (L/mg)	0.995	0.985
B (kJ/mol)	3.9509	1.0592
R^2	0.977	0.984
D-R Isotherm		
q_s (mg/g)	23.85	17.25
k_{ad} (mol ² /J ²)	1.80×10^{-5}	6.67×10^{-5}
E (kJ/mol)	0.167	0.087
R^2	0.789	0.876

3.3.4. Dubinin–Radushkevich (D–R) Isotherm Model

The D–R isotherm assumes that the adsorption of metal ions occurs in the pores of the adsorbent rather than on its surface and the distribution of the pores in the adsorbent follows the Gaussian energy distribution [24, 31]. The model is commonly applied to distinguish between chemical and physical metal ions adsorption process [31]. The linear model is represented as

$$q_e = q_s - k_{ad} \varepsilon^2$$

Where

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$

q_s (mg/g) is the theoretical saturation capacity; k_{ad} (mol²/J²) is Dubinin–Radushkevich isotherm constant. q_s and k_{ad} can be obtained from the intercept and slope of the plot of q_e vs ε^2 respectively. The mean free energy of adsorption, E (J/mol), is expressed as [24]:

$$E = \left(\frac{1}{\sqrt{2k_{ad}}} \right)$$

The value of E is used to predict the adsorption type. The adsorption process could be described as physical if the value of E is less than 8 kJ/mol and chemical if the value of E is 8 – 16 kJ/mol [36].

The D – R isotherm model was used to determine the kind of interaction that occurred between the clay adsorbent and the adsorbate metal ions at room temperature. The theoretical saturation capacities, q_s , (Table 1) for Pb(II) ions was higher (23.85 mg/g) than that of Cd(II) ions; this was similar to the trend observed for the case of Langmuir isotherm model. The mean adsorption energy, E , was found be 0.167 kJ/mol for Pb(II) ions and 0.087 kJ/mol for Cd(II) ions, suggesting physisorption as the most feasible path for

adsorption of both Pb(II) and Cd(II) ions on GN clay. However, as indicated by the coefficient of determination (Table 1) and the linear plots (Figure 7d), the fitting of the D–R isotherm to the Pb(II) and Cd(II) adsorption process was only fair as compared to all other isotherm models investigated in the present study.

3.4. Adsorption Kinetic Models

Kinetic models can provide valuable information on the mechanism and rate of the adsorption process, which in turn defines the efficiency of the adsorbent [37]. In this study, four kinetic models were evaluated: pseudo-first order, pseudo-second order, Elovich equation and intra-particle diffusion models.

Table 4. Kinetic model parameters for the sorption of Pb(II) and Cd(II) ions on natural clay.

Kinetic Model	Coefficients	Adsorbate ion	
		Pb(II)	Cd(II)
Pseudo-first order	k_1 (min ⁻¹)	0.12	0.15
	q_e (mg/g)	4.76	1.59
	R^2	0.9067	0.9401
Pseudo-second order	k_2 (g/mg min)	0.088	0.047
	q_e (mg/g)	9.28	8.28
	R^2	0.9999	0.9999

3.4.1. Pseudo-First Order Kinetics

The pseudo-first order rate is represented as [38]

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

Where, q_t (mg/g) is the amount of adsorbate adsorbed at time t (min) and q_e is the amount of adsorbate (mg/g) adsorbed at equilibrium; k_1 (min⁻¹) is the pseudo-first order rate constant.

The linearized form of the equation is given by [34]:

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303$$

The values of q_e and k_1 can be obtained from the slope and intercept of the plot of $\log(q_e - q_t)$ vs. t , respectively. Figure 8a shows the plot of the pseudo-first order model. The values of the constants and the coefficient of determination are presented in Table 4. The plots were linear with coefficient of determination (R^2) greater than 0.9. However, since the experimental adsorption capacity ($q_{e\text{ exp}}$) is very different from the calculated adsorption capacity ($q_{e\text{ cal}}$) with large deviations of 46% for Pb(II) ions and 66% for Cd(II) ions, the pseudo-first order mechanism becomes unsuitable [21].

3.4.2. Pseudo-Second Order

The linear form of the pseudo-second order rate is represented as [38, 39]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where q_e and q_t are the amount of adsorbate ion adsorbed (mg/g) at equilibrium and at any time t ; k_2 (g/mg min) is the pseudo-second order rate constant. The plot of t/q_t vs. t can be used to obtain the pseudo-second order rate constant.

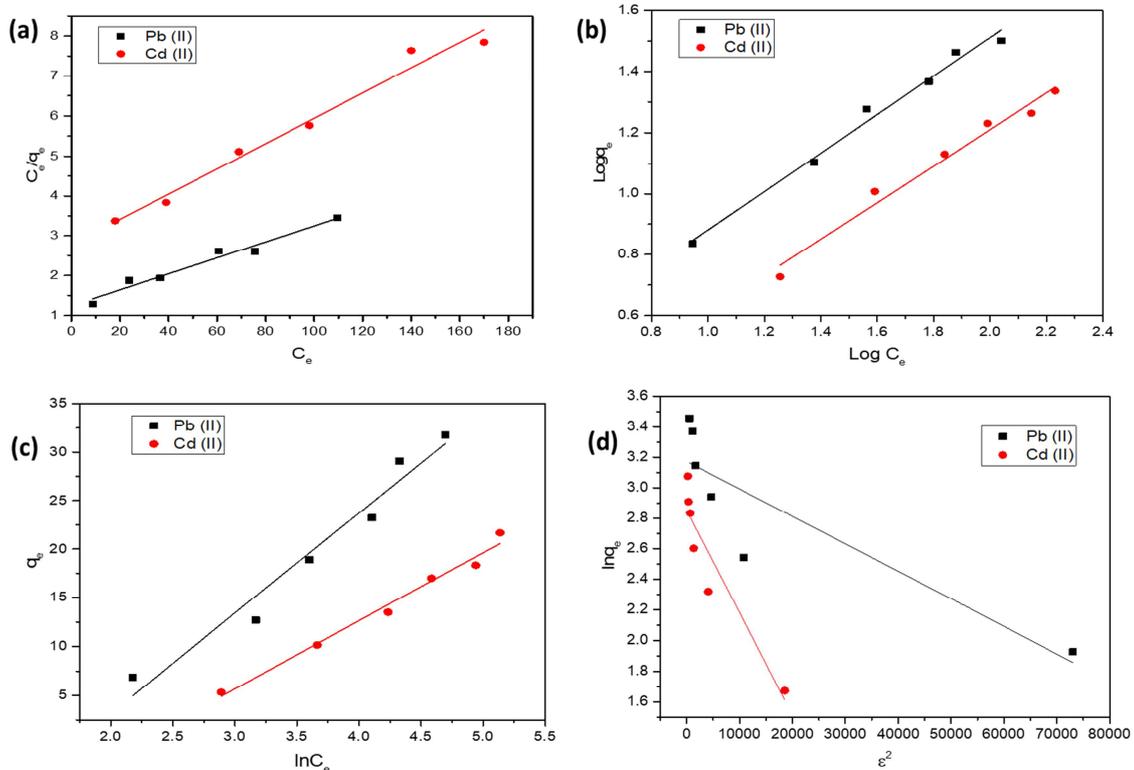


Figure 7. Plots of linearized Langmuir (a), Freundlich (b), Tamkin (c) and D-R (d) isotherms for the adsorption Pb(II) and Cd(II) ions on GN clay.

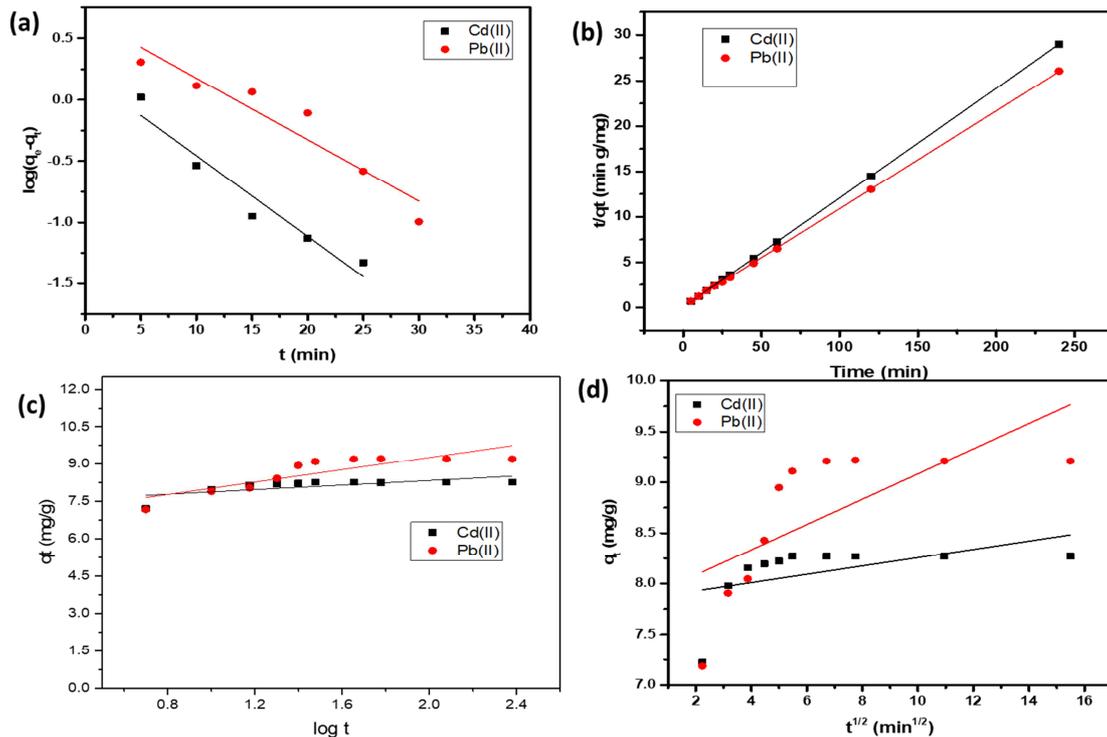


Figure 8. Pseudo first order (a) pseudo second order (b), Elovich (c) and intra-particle diffusion kinetic model plots for the adsorption of Pb(II) and Cd(II) ions on GN clay.

Figure 8b shows the plots of the pseudo-second order kinetics for the adsorption of Pb(II) and Cd(II) ions on natural clay. The corresponding kinetic parameters and coefficient of determination are presented in Table 4. Based on the coefficient of determination (R^2) values, the adsorption process is best described by the pseudo second-order equation when compared to pseudo-first order rate equation. Moreover, the values of $q_{e \text{ exp}}$ and $q_{e \text{ cal}}$ are similar; the maximum deviation between the two sets of values were 7% and 1.1% for Pb(II) and Cd(II) ions, respectively. The obtained result is in good agreement with the findings reported by [40] and [41] for the adsorption of Pb(II) and Cd(II) ions on montmorillonite clay and orange peels respectively, where the adsorption process was found to be best fitted by pseudo-second order kinetics.

3.4.3. Elovich Model

The Elovich equation is commonly used to describe the kinetics of gas chemisorption on solids [42]. The model assumes that the active sites on the adsorbent are heterogeneous and thus their activation energies for chemisorption varies [41]. The simplified linear form of the Elovich equation is represented as [43]:

$$q_t = \frac{2.303}{b} \log(ab) + \frac{2.303}{b} \log t$$

where q_t (mg/g) is the adsorption capacity at time t , a (mg/g min) is the initial adsorption rate and b (g/mg) represents the extent of surface coverage and activation energy for chemisorption interaction between adsorbate and adsorbent [35]. The values of the constants, a and b , can be obtained

from the slope and intercept of the linear plot of q_t vs. $\log t$. The plot will be found to be linear if the interaction between adsorbate and adsorbent follows the Elovich model.

Figure 8c shows the plot of the experimental data fitted to the Elovich equation. The fitting gave lower values of coefficient of determination (R^2) for both metal ions (0.7453 for Pb(II) and 0.4947 for Cd(II) ions), suggesting that the adsorption process did not fit the Elovich model.

3.4.4. Intra-particle Diffusion Model

The Weber – Morris model is often used in adsorption studies to investigate the possibility of diffusion of adsorbate species into the interior of the pores of the adsorbent [34, 44]. The intra-particle diffusion model is represented as

$$q_t = k_i t^{1/2}$$

where k_i is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$). If the plot of q_t vs. $t^{1/2}$ yields straight line that passes through the origin, the intra-particle diffusion plays a significant role in controlling the kinetics of the adsorption process with the slope giving the rate constant, k_i [44]. As shown in Figure 8d, the plot of the intra-particle diffusion is not linear with R^2 values of 0.485 for Pb(II) and 0.2570 for Cd(II). This also suggests that the model did not fit the adsorption process studied in this work.

4. Conclusion

Herein, the natural clay obtained from Goronyo Local Government area of Sokoto state, Nigeria was investigated

as adsorbent for the removal of Pb(II) and Cd(II) ions from aqueous solution. Batch adsorption studies indicated that the solution pH, initial metal ion concentration, contact time and adsorbent dose have significant effect on Pb(II) and Cd(II) ions adsorption on the GN clay. Kinetic analysis showed that the sorption process followed the pseudo-second order kinetic model. The Langmuir and Freundlich isotherms provided the best fit to the adsorption data, which indicated that the interaction was mainly chemical in nature but the adsorption sites were heterogeneous. The high adsorption capacity obtained for both ions indicated that the GN clay can be utilized as an alternative adsorbent for metal ions removal in water since it is cheap and in large abundance.

It is recommended that further research should be carried out on the reusability of the clay, its affinity for other metals and also its performance in actual contaminated water.

Acknowledgements

The authors would like to thank the Tertiary Education Trust Fund (Tetfund) for research grant (IBR 2019) through Kebbi State University of Science and Technology, Aliero.

References

- [1] Ali, M. M., Ali, M. L., Islam, M. S., & Rahman, M. Z., (2016). Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh, *Environmental Nanotechnology, Monitoring & Management*, 5, 27–35. doi: <https://doi.org/10.1016/j.enmm.2016.01.002>
- [2] Liu, J., Zhang, X.-H., Tran, H., Wang, D.-Q., & Zhu, Y.-N., (2011). Heavy metal contamination and risk assessment in water, paddy soil, and rice around an electroplating plant, *Environmental Science and Pollution Research*, 18, (9), 1623. doi: 10.1007/s11356-011-0523-3.
- [3] Kobielska, P. A., Howarth, A. J., Farha, O. K., & Nayak, S., (2018). Metal–organic frameworks for heavy metal removal from water, *Coordination Chemistry Reviews*, 358, 92–107. doi: 10.1016/j.ccr.2017.12.010.
- [4] Bradl, H. B., (2005). Chapter 1 Sources and origins of heavy metals, H. B. B. T.-I. S. and T. Bradl (Ed.), *Heavy Metals in the Environment: Origin, Interaction and Remediation* (Vol. 6), Elsevier, 1–27. doi: [https://doi.org/10.1016/S1573-4285\(05\)80020-1](https://doi.org/10.1016/S1573-4285(05)80020-1)
- [5] Fu, F., & Wang, Q., (2011). Removal of heavy metal ions from wastewaters: A review, *Journal of Environmental Management*, 92, (3), 407–418. doi: <https://doi.org/10.1016/j.jenvman.2010.11.011>
- [6] Rehman, Z. U., Khan, S., Brusseau, M. L., & Shah, M. T., (2017). Lead and cadmium contamination and exposure risk assessment via consumption of vegetables grown in agricultural soils of five-selected regions of Pakistan, *Chemosphere*, 168, 1589–1596. doi: 10.1016/j.chemosphere.2016.11.152.
- [7] Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J., (2012). Molecular, Clinical and Environmental Toxicology, 101, 1–30. doi: 10.1007/978-3-7643-8340-4.
- [8] Khan, T. A., & Singh, V. V., (2010). Removal of cadmium(II), lead(II), and chromium(VI) ions from aqueous solution using clay, *Toxicological & Environmental Chemistry*, 92, (8), 1435–1446. doi: 10.1080/02772241003592930.
- [9] Walcarius, A., & Mercier, L., (2010). Mesoporous organosilica adsorbents: nanoengineered materials for removal of organic and inorganic pollutants, *Journal of Materials Chemistry*, 20, (22), 4478–4511. doi: 10.1039/B924316J.
- [10] Gupta, V. K., Moradi, O., Tyagi, I., Agarwal, S., Sadegh, H., Shahryari-Ghoshekandi, R., et al., (2016). Study on the removal of heavy metal ions from industry waste by carbon nanotubes: Effect of the surface modification: a review, *Critical Reviews in Environmental Science and Technology*, 46, (2), 93–118. doi: 10.1080/10643389.2015.1061874.
- [11] Rao, R. A. K., & Kashifuddin, M., (2016). Adsorption studies of Cd(II) on ball clay: Comparison with other natural clays, *Arabian Journal of Chemistry*, 9, S1233–S1241. doi: <https://doi.org/10.1016/j.arabjc.2012.01.010>
- [12] Uddin, M. K., (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade, *Chemical Engineering Journal*, 308, 438–462. doi: <https://doi.org/10.1016/j.cej.2016.09.029>
- [13] Kubilay, Ş., Gürkan, R., Savran, A., & Şahan, T., (2007). Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite, *Adsorption*, 13, (1), 41–51. doi: 10.1007/s10450-007-9003-y.
- [14] Sdiri, A., Khairy, M., Bouaziz, S., & El-Safty, S., (2016). A natural clayey adsorbent for selective removal of lead from aqueous solutions, *Applied Clay Science*, 126, 89–97. doi: 10.1016/j.clay.2016.03.003.
- [15] Lorentz, B., Shanahan, N., Stetsko, Y. P., & Zayed, A., (2018). Characterization of Florida kaolin clays using multiple-technique approach, *Applied Clay Science*, 161, (May), 326–333. doi: 10.1016/j.clay.2018.05.001.
- [16] Madejová, J., Gates, W. P., & Petit, S., (2017). *IR Spectra of Clay Minerals, Developments in Clay Science* (Vol. 8). doi: 10.1016/B978-0-08-100355-8.00005-9.
- [17] Jiang, M. qin, Jin, X. ying, Lu, X. Q., & Chen, Z. liang, (2010). Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay, *Desalination*, 252, (1–3), 33–39. doi: 10.1016/j.desal.2009.11.005.
- [18] Sdiri, A. T., Higashi, T., & Jamoussi, F., (2014). Adsorption of copper and zinc onto natural clay in single and binary systems, *International Journal of Environmental Science and Technology*, 11, (4), 1081–1092. doi: 10.1007/s13762-013-0305-1.
- [19] Gorzin, F., & Bahri Rasht Abadi, M. M., (2018). Adsorption of Cr(VI) from aqueous solution by adsorbent prepared from paper mill sludge: Kinetics and thermodynamics studies, *Adsorption Science and Technology*, 36, (1–2), 149–169. doi: 10.1177/0263617416686976.
- [20] Algothmi, W. M., Bandaru, N. M., Yu, Y., Shapter, J. G., & Ellis, A. V., (2013). Alginate–graphene oxide hybrid gel beads: An efficient copper adsorbent material, *Journal of Colloid and Interface Science*, 397, 32–38. doi: <https://doi.org/10.1016/j.jcis.2013.01.051>
- [21] Bhattacharyya, K. G., & Sen Gupta, S., (2006). Pb(II) uptake by kaolinite and montmorillonite in aqueous medium: Influence of acid activation of the clays, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 277, (1–3), 191–200. doi: 10.1016/j.colsurfa.2005.11.060.

- [22] Unuabonah, E. I., Olu-Owolabi, B. I., Adebowale, K. O., & Ofomaja, A. E., (2007). Adsorption of lead and cadmium ions from aqueous solutions by tripolyphosphate-impregnated Kaolinite clay, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 292, (2), 202–211. doi: <https://doi.org/10.1016/j.colsurfa.2006.06.024>
- [23] Chaari, I., Fakhfakh, E., Chakroun, S., Bouzid, J., & Boujelben, N., (2008). Lead removal from aqueous solutions by a Tunisian smectitic clay, 156, 545–551. doi: [10.1016/j.jhazmat.2007.12.080](https://doi.org/10.1016/j.jhazmat.2007.12.080).
- [24] Wang, J., & Guo, X., (2020). Adsorption isotherm models: Classification, physical meaning, application and solving method, *Chemosphere*, 258, 127279. doi: <https://doi.org/10.1016/j.chemosphere.2020.127279>
- [25] Febrianto, J., Natasia, A., Sunarso, J., Ju, Y., Indraswati, N., & Ismadji, S., (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, 162, 616–645. doi: [10.1016/j.jhazmat.2008.06.042](https://doi.org/10.1016/j.jhazmat.2008.06.042).
- [26] Togue Kanga, F., (2019). Modeling adsorption mechanism of paraquat onto Ayous (*Triplochiton scleroxylon*) wood sawdust, *Applied Water Science*, 9, (1), 1–7. doi: [10.1007/s13201-018-0879-3](https://doi.org/10.1007/s13201-018-0879-3).
- [27] Jiang, M., Jin, X., Lu, X., & Chen, Z., (2010). Adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay, *DES*, 252, (1–3), 33–39. doi: [10.1016/j.desal.2009.11.005](https://doi.org/10.1016/j.desal.2009.11.005).
- [28] Adebowale, K. O., Unuabonah, I. E., & Olu-Owolabi, B. I., (2005). Adsorption of some heavy metal ions on sulfate- and phosphate-modified kaolin, *Applied Clay Science*, 29, (2), 145–148. doi: [10.1016/j.clay.2004.10.003](https://doi.org/10.1016/j.clay.2004.10.003).
- [29] Sdiri, A., & Jamoussi, F., (2014). Adsorption of copper and zinc onto natural clay in single and binary systems, (May). doi: [10.1007/s13762-013-0305-1](https://doi.org/10.1007/s13762-013-0305-1).
- [30] Al-Ghouti, M. A., & Da'ana, D. A., (2020). Guidelines for the use and interpretation of adsorption isotherm models: A review, *Journal of Hazardous Materials*, Elsevier B. V., 122383. doi: [10.1016/j.jhazmat.2020.122383](https://doi.org/10.1016/j.jhazmat.2020.122383).
- [31] Kecili, R., & Hussain, C. M., (2018). *Chapter 4 - Mechanism of Adsorption on Nanomaterials*, *Nanomaterials in Chromatography*, Elsevier Inc. doi: [10.1016/B978-0-12-812792-6/00004-2](https://doi.org/10.1016/B978-0-12-812792-6/00004-2).
- [32] Sarma, G. K., SenGupta, S., & Bhattacharyya, K. G., (2018). Adsorption of Monoazo Dyes (Crocein Orange G and Procion Red MX5B) from Water Using Raw and Acid-Treated Montmorillonite K10: Insight into Kinetics, Isotherm, and Thermodynamic Parameters, *Water, Air, and Soil Pollution*, 229, (10). doi: [10.1007/s11270-018-3971-2](https://doi.org/10.1007/s11270-018-3971-2).
- [33] Shikuku, V. O., Zanella, R., Kowenje, C. O., Donato, F. F., Bandeira, N. M. G., & Prestes, O. D., (2018). Single and binary adsorption of sulfonamide antibiotics onto iron-modified clay: linear and nonlinear isotherms, kinetics, thermodynamics, and mechanistic studies, *Applied Water Science*, 8, (6), 1–12. doi: [10.1007/s13201-018-0825-4](https://doi.org/10.1007/s13201-018-0825-4).
- [34] Ahmad, A., Rafatullah, M., Sulaiman, O., Ibrahim, M. H., & Hashim, R., (2009). Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution, *Journal of Hazardous Materials*, 170, (1), 357–365. doi: [10.1016/j.jhazmat.2009.04.087](https://doi.org/10.1016/j.jhazmat.2009.04.087).
- [35] Sathishkumar, P., Arulkumar, M., Ashokkumar, V., Mohd Yusoff, A. R., Murugesan, K., Palvannan, T., et al., (2015). Modified phyto-waste Terminalia catappa fruit shells: a reusable adsorbent for the removal of micropollutant diclofenac, *RSC Advances*, 5, (39), 30950–30962. doi: [10.1039/C4RA11786G](https://doi.org/10.1039/C4RA11786G).
- [36] Sarma, G. K., & Bhattacharyya, S. S. G. K. G., (2019). Removal of hazardous basic dyes from aqueous solution by adsorption onto kaolinite and acid - treated kaolinite: kinetics, isotherm and mechanistic study, *SN Applied Sciences*, 1, (3), 1–15. doi: [10.1007/s42452-019-0216-y](https://doi.org/10.1007/s42452-019-0216-y).
- [37] Fu, C., Zhu, X., Dong, X., Zhao, P., & Wang, Z., (2021). Study of adsorption property and mechanism of lead (II) and cadmium (II) onto sulphydryl modified attapulgite, *Arabian Journal of Chemistry*, 14, (2), 102960. doi: [10.1016/j.arabjc.2020.102960](https://doi.org/10.1016/j.arabjc.2020.102960).
- [38] Qiu, H., Lv, L., Pan, B. C., Zhang, Q. J., Zhang, W. M., & Zhang, Q. X., (2009). Critical review in adsorption kinetic models, *Journal of Zhejiang University: Science A*, 10, (5), 716–724. doi: [10.1631/jzus.A0820524](https://doi.org/10.1631/jzus.A0820524).
- [39] Ho, Y. S., & McKay, G., (1999). Pseudo-second order model for sorption processes, *Process Biochemistry*, 34, (5), 451–465. doi: [https://doi.org/10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5)
- [40] Qin, S., & Guo, W., (2008). Adsorption behavior of Pb (II) on montmorillonite, 320, 92–97. doi: [10.1016/j.colsurfa.2008.01.038](https://doi.org/10.1016/j.colsurfa.2008.01.038).
- [41] Pérez-Marín, A. B., Zapata, V. M., Ortuño, J. F., Aguilar, M., Sáez, J., & Lloréns, M., (2007). Removal of cadmium from aqueous solutions by adsorption onto orange waste, *Journal of Hazardous Materials*, 139, (1), 122–131. doi: [10.1016/j.jhazmat.2006.06.008](https://doi.org/10.1016/j.jhazmat.2006.06.008).
- [42] Cheung, C. W., Porter, J. F., & McKay, G., (2001). Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char, *Water Research*, 35, (3), 605–612. doi: [https://doi.org/10.1016/S0043-1354\(00\)00306-7](https://doi.org/10.1016/S0043-1354(00)00306-7)
- [43] Wu, F.-C., Tseng, R.-L., & Juang, R.-S., (2009). Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems, *Chemical Engineering Journal*, 150, (2), 366–373. doi: <https://doi.org/10.1016/j.cej.2009.01.014>
- [44] Zhang, S. Q., & Hou, W. G., (2008). Adsorption behavior of Pb(II) on montmorillonite, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 320, (1), 92–97. doi: <https://doi.org/10.1016/j.colsurfa.2008.01.038>