

Equilibria and kinetic studies on the adsorption of
Cadmium onto Cameroonian wetland clays

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Authors' contributions

This work was carried out in collaboration between all authors. Author CM K designed the study, wrote the first draft and managed the literature searches. Authors PP N and HM N managed all the analysis of the study and corrected the first manuscript. Authors MA E and PMG also corrected the manuscript. All authors read and approved the final manuscript.

Abstract

The possible use of clay ($\text{Al}_2\text{Si}_3\text{O}_5(\text{OH})_4$), locally mined (Makepe, Cameroon), as an adsorbent, for the removal of cadmium from wastewater was investigated. Spectroscopic studies including FTIR, porosity, elemental analysis (EA), XRPD, and SEM were used for its characterization. The effect of different variables, namely: concentration of metal ions and time of interaction were studied. The adsorptive property of clay was tested using Cd(II) as the model adsorbate. Equilibrium data was examined using a comparison of linear **linear** isotherm models. The adsorption behavior was well described by the **linear** Langmuir isotherm model, showing a monolayer adsorption capacity for Cd. The kinetic rates were modeled by using the Lagergren-first-order, pseudo-second-order and intraparticle model. The pseudo-second-order model was found to explain the adsorption kinetics most effectively. It was also found that the pore diffusion played an important role in the adsorption and intraparticle diffusion was the rate-limiting step during the first 30 min. of interaction.

Keywords: Adsorption; Kinetic; Equilibrium; wetland clays; **Cadmium**

1. Introduction

Persistent heavy metal ions in trace quantities are difficult to remove from aqueous solution (**Krishna G. Bhattacharyya and Susmita Sen Gupta, 2007**). Adsorption is a promising technique for regulating mobility of chemical species and their geochemical cycles in the environment. The process has the additional advantages of applicability at very low concentrations, suitable for both batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse, and low capital cost (**Yavuz, O et al 2003; Saleh Kaoser et al., 2005**). Thus, adsorption is

continuously becoming a preferred method for removal, recovery and recycling of toxic heavy metals from wastewaters. Different types of adsorbents are used for removing metal ions from aqueous solutions (Alvarez- Ayuso and Nugteren, 2005), each presenting some limitations that may include either cost of the materials or complex chemistry hindering recovery.

Clay minerals are important constituents of soil and they play the role of a natural scavenger for metals as water flows over soils or penetrate underground (Krishna G. Bhattacharyya and Susmita Sen Gupta, 2007). By clay standards, kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), are the principal constituent of soil nanostructure (up to 40% minerals in sedimentary rocks), (Ndibewu et al., 2010; Pedra et al., 2007). The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), Brönsted and Lewis acidity, etc., have made the clay minerals excellent materials for adsorption (Tanabe., 1981). Mellah and Chegrouche (1997) had used bentonite for removing Zn(II) from aqueous solution with Langmuir monolayer capacity of 52.91 mg g^{-1} at 293 K. The adsorption of Cd (II), Cu (II) and Zn(II) on sepiolite has also been reported (Sanchez et al., 1999). Original and Na exchanged bentonites have been used for the removal of Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from aqueous solution (Alvarez-Ayuso and Garcia-Sanchez, 2003) with maximum adsorption capacity of up to 49.8, 24.2, 23.1, 30.0 and 26.2 mg g^{-1} , respectively. The removal of Cr (III), Cr (VI) and Ag(I) from water by bentonite has also been reported (Khan et al., 1995) where Cr(III)-bentonite and Ag(I)-bentonite interactions were found to be exothermic while Cr(VI)-bentonite interactions was endothermic.

The present study investigates the adsorption of clay, in batch experiments, for the removal of Cd^{2+} metal ions from aqueous solutions.

2. Materials and methods

2.1. Chemicals

All the chemicals used were of analytical reagent grade. Deionised doubly distilled (DDD) water was used throughout the experimental studies. Working standards were prepared by progressive dilution of stock cadmium solutions (1000 ppm) using the DDD water.

2.2. Materials

The natural clays used in this study was mined from a subtropical wetland soil in Cameroon ((Littoral Region), West Africa. For this type of clay material, the cation exchange capacity (CEC) = 12.04 meq/100 g was considered. The clays were washed several times with distilled and deionized water after which they were completely dispersed in water. After 17 h at rest, the dispersed particles were centrifuged for one hour at 2400 rpm. The size of the clay particles obtained was $0.5 < r < 2 \text{ }\mu\text{m}$.

These clay particles were dispersed in water and heated at 75°C in the presence of a solution of sodium bicarbonate salts (1.0 M), citrate (0.3 M), and chloride (2.0 M). The purpose of this treatment was to eliminate inorganic and organic compounds, aluminium found in the inter-layer spaces and various free cations (Bouras, 2003; *Khalaf et al.*, 1997). Carbonates were removed by treatment with HCl (0.5 M) and chloride was eliminated after several washings. The organic matter was eliminated completely by treatment with H₂O₂ (30% v/v) at 70°C. The purified clay was dried at 110°C, then saturated with sodium (Na⁺). To ensure complete transformation into the sodium form, all samples were washed several times with a NaOH solution (1.0 M).

2.3. Characterization of the materials

The pH at the potential of zero charge of the clay was measured using the pH drift method. The pH of the solution was adjusted by using 0.01 M sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 250C to remove the dissolved carbon dioxide. Activated carbon 50 mg was added to 50 ml of the solution. After stabilization, the final pH was recorded. The graphs of final pH versus initial pH used to determine the zero point charge of the clay (Lopez-Ramon et coll., 1999).

The purity of the activated natural clay samples was tested by IR spectral analysis. An IR transmittance spectrum of the ground samples was obtained in the 4000 to 400 cm⁻¹ range on a PerkinElmer Spectrum Two spectrometer (UK).

To confirm the purity of the activated natural clay samples, x-ray diffraction (XRD) spectra were obtained. Analysis involved the identification and semi quantification of the characteristic peaks of the minerals present. The XRD diffractograms presented in this study were recorded using a Bruker D8 Discover X-Ray diffractometer (XRD) (UK) from Bruker (Germany) with a D5000 Ni-filtered CuK and an α radiation of 1, 5406 Å. Scans of natural clay samples with both randomly and preferred orientation were taken over a range from $2\theta = 10^\circ$ to 100° at scanning speeds of 0.0375 s. The XRD patterns were collected using a Cu K α radiation (1, 5406 Å) source (40 keV, 40 mA). The scans were performed at room temperature in 2θ steps of 0.02° , using open sample holders. The phases were identified using Bruker Diffract Plus evaluation software, distributed by the International Centre for Diffraction Data (ICDD).

A field emission scanning electron microscopy (FE-SEM) and energy-dispersive x-ray (EDX) was employed to observe the surface morphology of the clay samples. The instrument used to obtain SEM images and EDX spectra is a JEOL JSM-7600F Field Emission Scanning Electron Microscope, 800 mm², X-Max coupled to a silicon drift energy dispersive X-ray detector (SDD) (Oxford Instruments Ltd, UK).

The samples were gold coated to improve its conductivity so as to obtain good images. Additionally, EDX elemental spectra of a few spots on the samples were taken for determining the surface elemental compositions. Representative images and spectra of the samples are presented in Figs. 3 and 4.

For elemental analysis (EA), the percentage (%) carbon (C), nitrogen (N), oxygen (O) and sulphur (S) of the various samples was equally observed with the EDX spectra, although not very accurate for organic elements..

2.4. Equilibrium adsorption studies

A constant mass of adsorbent (0.2g) was weighed into 250 ml glass bottles and contacted with 50 ml of Cd^{2+} solutions of different initial concentration. The bottles were sealed and placed in a shaker until equilibrium is reached. Upon equilibration, samples of 4–5 ml were then withdrawn from the flasks and the adsorbents were separated from the solution by centrifugation (REMI make) at 2000rpm for 10 minutes, and analyzed to determine the residual equilibrium liquid-phase Cd^{2+} concentration. The sorption equilibrium data of Cd^{2+} on clay was analyzed using Freundlich and Langmuir isotherm models. Freundlich isotherm equation $x/m = k_f C_e^{1/n}$ can be written in the linear form as given below (1).

$$\log\left(\frac{x}{m}\right) = \log K_F + \frac{1}{n} \log C_e \quad (1)$$

Where x/m (mg/g) and C_e (mg/L) are the equilibrium concentrations of Cd^{2+} in the adsorbed and liquid phases. K_F and n are the Freundlich constants that are related to the sorption capacity and intensity, respectively. Freundlich constants K_F and n can be calculated from the slope and intercept of the

linear plot, with $\log (x/m)$ versus $\log C_e$. The Langmuir sorption isotherm equation $\frac{x}{m} = \frac{Q_{\max} K_L C_e}{1 + K_L C_e}$ on

linearization becomes (2):

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{\max}} + \frac{1}{Q_{\max}} C_e \quad (2)$$

Where $Q_{\max}$ is the adsorption capacity (mg/g) when all adsorption sites are occupied, C_e is the equilibrium concentration of cadmium, and the Langmuir constant K_L (L/mg) is derived from the ratio of the adsorption rate constant to the desorption rate constant.

2.5. Kinetic studies

Kinetic adsorption data were analyzed following pseudo-first-order kinetic model:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Where q_e and q_t refer to the amount of cadmium adsorbed (mg/g) at equilibrium and at any time, t (h), respectively, and k_1 is the equilibrium rate constant of pseudo-first-order sorption (1/h). Integration of Eq. (3) for the boundary conditions $t=0$ to t and $q_t=0$ to q_t , gives

$$\log \frac{q_e}{(q_e - q_t)} = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

Eq. (4) can be rearranged to give (5)

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

The pseudo second-order model was well-fitted to the Cd^{2+} sorption data on the minerals. The rate equation for the second-order model can be expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

Where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg min). Integrating Eq. (6) for the boundary condition $t=0$ to t and $q_t=0$ to q_t , gives (7):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_t} + k_2 \cdot t \quad (7)$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (7) can be rearranged to obtain a linear form (8):

$$\left(\frac{t}{q_t} \right) = \left(\frac{t}{q_e} \right) + \left[\left(\frac{1}{k_2 \cdot q_e^2} \right) \right] \quad (8)$$

where, q_t and q_e (mg/g) are the amount of Cd sorbed on the mineral at time t and at equilibrium, respectively and k_2 (g.mg⁻¹.min⁻¹) is the second-order rate constant.

2.6. Adsorption mechanism

In the model developed by Weber and Morris, the rate of intra-particle diffusion is a function of $t^{1/2}$ and can be defined by Eq. (9) as follows:

$$q = f\left(\frac{D_t}{r_p^2}\right)^{1/2} = k_w t^{1/2} \quad (9)$$

Where r_p is particle radius, D_t is the effective diffusivity of solutes within the particle, and K_w intraparticle diffusion rate. k_w values can be obtained by linearizing the curve $q = f(t^{1/2})$.

3. Results and discussions

3.1. Characterisation of clay

3.1.1. XRD analysis

Results of the X-ray diffraction analysis for clay are shown in Figure 1. Shows that the d spacing of clay, which could be attributed to the activated clay. Quartz (reflection at 4.226 Å, $2\theta = 21.061^\circ$; 2.336 Å, $2\theta = 38.523^\circ$; 1.822 Å, $2\theta = 50.339^\circ$; 1.673 Å, $2\theta = 55.118^\circ$ and 1.377 Å, $2\theta = 68.314^\circ$). The purified sample with Na-exchange shows the position of the 001 (reflection at 3.558 Å, $2\theta = 24.973^\circ$; 3.424 Å, $2\theta = 26.775^\circ$; 3.24 Å, $2\theta = 27.676^\circ$; and 2.56 Å, $2\theta = 35.021^\circ$) characteristic of Kaolinite and Boehmite (reflection at $d = 1.971$ Å, $2\theta = 45.835^\circ$ and $d = 1.474$ Å, $2\theta = 62.589^\circ$).

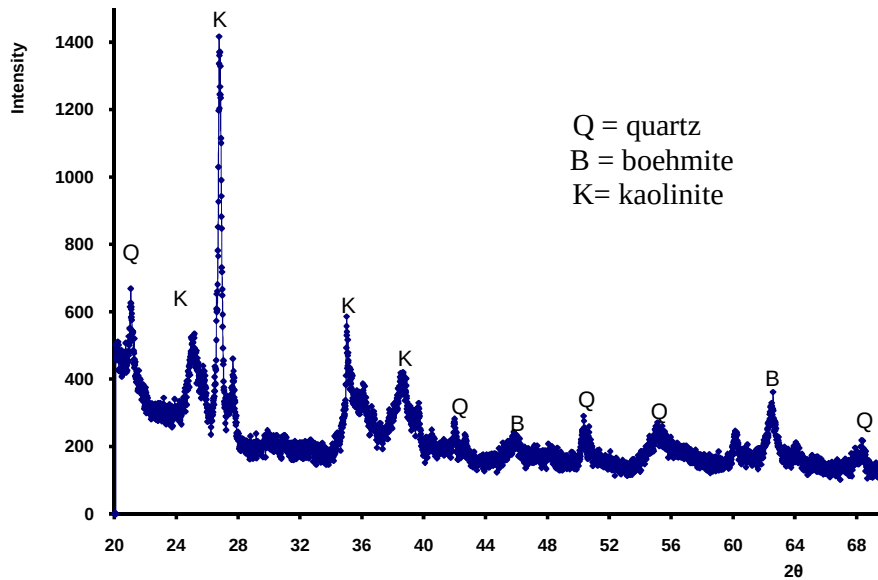


Fig.1. X-ray diffraction patterns of the natural clay.

3.1.2. Fourier transform-infrared spectroscopy (FTIR)

The FTIR spectrum of the clay is shown in Fig. 2. The frequency absorption band at 3695.8 cm^{-1} (OH-Al out-of-plane), 3624.4 cm^{-1} (OH-Al in-plane) and 913.68 cm^{-1} indicate the presence of OH-Al groups (Farmer, 1974).

- On one hand, peaks appearing at 2961.4 , 2927.9 and 2869.1 cm^{-1} between (2700 and 3150 cm^{-1}) and (1400 and 1500 cm^{-1}) depicts the presence of alkyl groups ($\text{CH}_2\text{-CH}_3$ and CH_3 (Bouras, 2003).
- The bands appearing at 1020 and 1120 cm^{-1} are ascribed to the formation of Si - O bond, characteristic of aluminosilicate (Amritphale et al., 2005). The additional peak at 695.45 cm^{-1} indicates the presence of Al-OH and Si-O (Amritphale et al., 2005).
- The bands observed at 468.88 and 540.22 cm^{-1} can be attributed to vibrations due to deformation of Si-O and Si-O-Al bonds, respectively (Sayilkan et al., 2004).

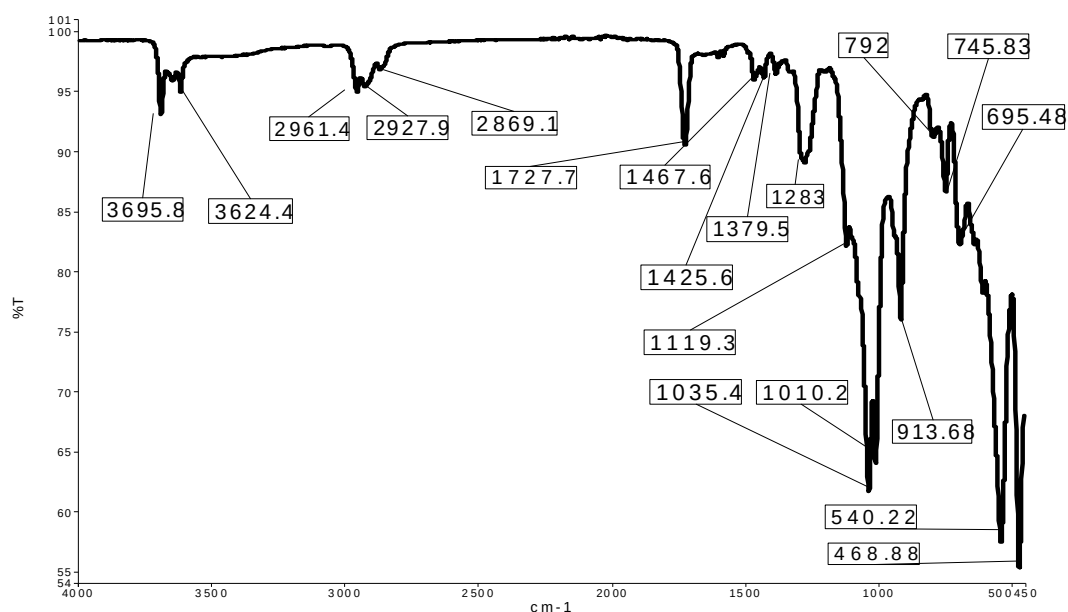


Fig. 2. FTIR spectrum of a sample clay studied (MARV4)

3.1.3. SEM and EDX

To observe the morphology of the clay sample, an example of a scanning electron microscopy (SEM) image is shown in Fig.3. The image displays the SEM micrographs of functionalized clay. In this case, the particles are apparently smaller in size than natural clay sample and are composed of disordered thin sheet particles aggregates. One can conclude that functionalization promotes the formation of disordered and less cohesive aggregates, probably due to a reduction of the edge-to-edge and face-to-face interactions. Unlike the hydrophilic end, which formed large size aggregates after drying of the clay sample became hardened and dispersed in water (hydrophobic) while easily kept as a loose powder after drying. This change constitutes an important advantage considering the product

application in commercial units. The EDX plot (Fig. 4) of clay shows the presence of carbon, oxygen, and inorganic elements like aluminium, titanium, silicon, zinc, copper and iron (Table 1).

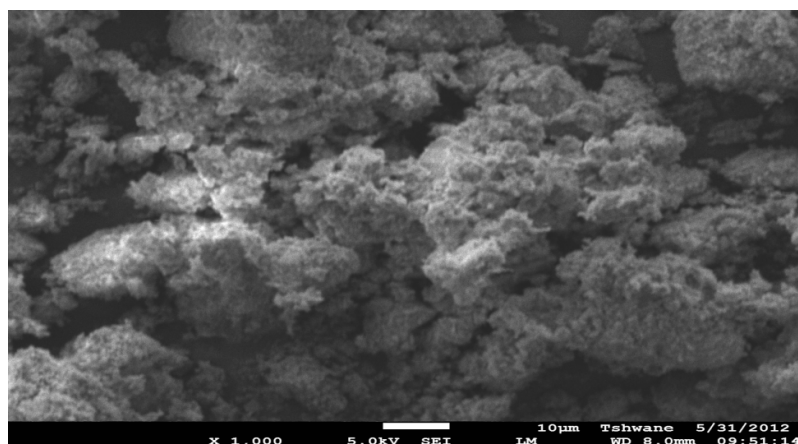


Fig.3. SEM photographs of a sample clay sample (MARV4)

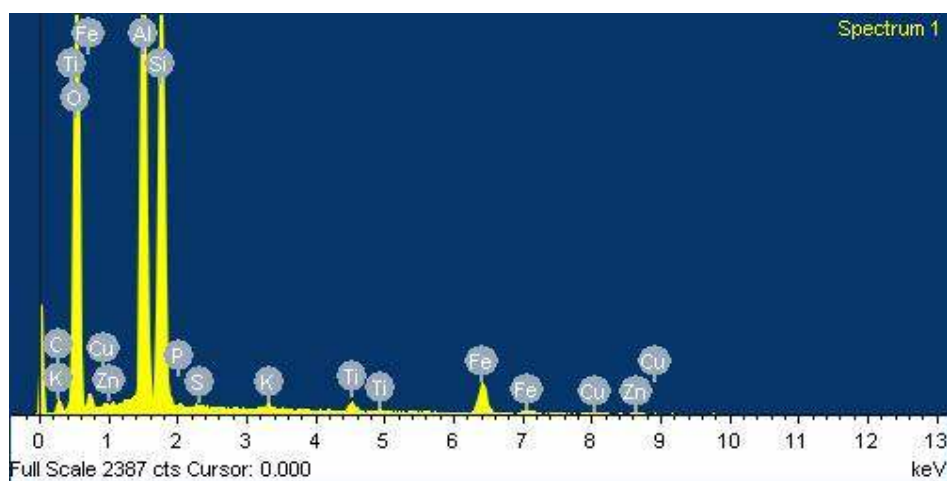


Fig. 4. EDX of a sample clay sample MARV4 showing abundance of certain metals (Al and Si are typically present in clay minerals of this type)

Table 1. Elemental analysis of clay

elements	C	O	Al	Si	P	S	K	Ti	Cu	Fe	Zn
Weight%	4.36	62.27	14.01	14.51	0.17	0.01	0.15	0.52	0.24	3.11	0.55
Atomic%	6.70	72.49	9.60	9.56	0.10	0.01	0.07	0.20	0.07	1.03	0.15

3.2. Effects of contact time and initial concentration of Cd^{2+}

The effect of contact time on batch adsorption of initial Cd^{2+} concentration ranged from 10 to 60 ppm at room temperature was shown in Fig 5. The amount of adsorption increases rapidly in the beginning and then gradually increases to reach an equilibrium value in 60 minutes. The increase in uptake capacity of the adsorbent with increasing Cd^{2+} concentration may be due to higher probability of collision between Cd^{2+} ions and adsorbent particles. The variation in the extent of adsorption may also be due to the fact that initially all sites on the surface of adsorbent were vacant and the solute concentration gradient was relatively high. Consequently, the extent of Cd^{2+} uptake decreases significantly with the increase of contact time, which is depending on the decrease in the number of vacant sites on the surface. This data is important because equilibrium time is one of the parameters for economic feasibility studies for in wastewater treatment plant application (Kadirvelu and Namasivayam, 2003). According to these results, the agitation time was fixed at 2h for the rest of the batch experiments to make sure that equilibrium was attained.

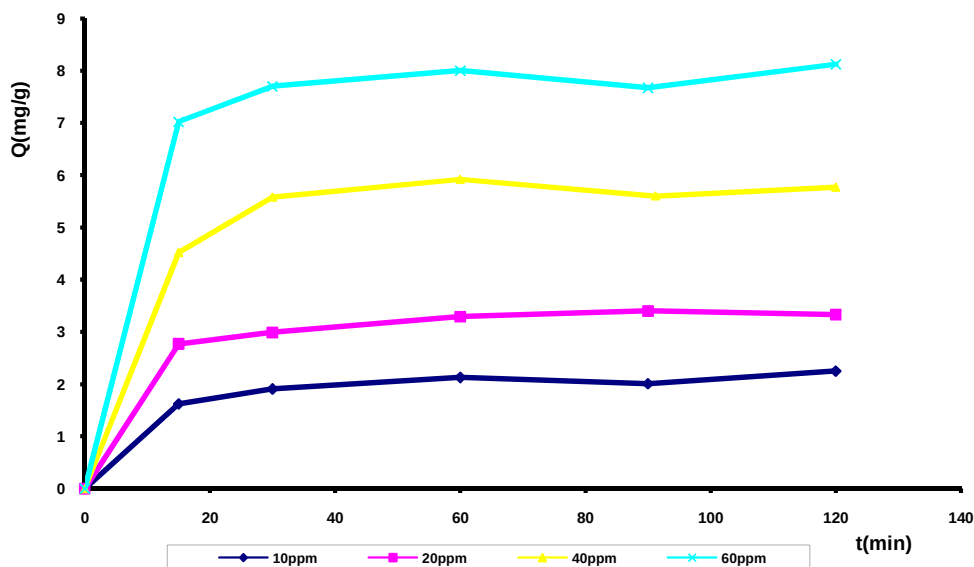


Fig.5. Effect of agitation time and initial concentration of Cd^{2+} on the adsorption of Cd^{2+} (conditions: clay concentration, 0.2g/50 mL.)

3.3. Effect of pH

The pH of the aqueous solution is an important parameter which controls the sorption process (Elliot and Huang, 1981) and metal removal typically increases with increasing pH values (Leinonen, H., J. Lehto., 2001). The pH may affect the ionization degree of the sorbate and the surface property of the sorbent (Motsi, T., 2009). Chemically, the solution pH influences metal speciation. For instance, heavy metal ions may form complexes with inorganic ligands such as OH. The extent of the complex

formation varies with pH, the ionic composition and the particular metal concerned. Exposure of clay surface to water causes the ionization of surface hydroxyl groups (OH-Al, Si-O, Si-O-Al). The degree of ionization depends on pH, and the acid/base reaction occurring at the hydroxyl groups may results in surface charge development (Hui, K.S al., 2005). Clays are not only influenced by pH but in turn are capable of affecting solution pH especially in batch system (Lin, C.Y., Yang, D.H., 2002) and clays tend to have a higher internal pH. In addition, the clay surface may be influenced by the ambient pH which is not equal to the external solution pH value and precipitation within the channels of clay and at the surface of clay may occur. The effect of the solution pH on the removal of Cd^{2+} ions by clay was examined. Based on the solubility product of metal hydroxides (Covarrubias, C., R et al., 2005) the pH of precipitation at the tested concentration was plotted as illustrated in Fig.6, the pH values were varied from 2 to 12 through this experiment. The maximum adsorption for Cd^{2+} was found at pH of 6.7. It is clear from the presented figure that the removal of metal ions is a pH dependent process. The adsorption mechanism on clay surfaces reflected the nature of the physicochemical interaction of the metal ions in solution and the active sites of clay (Misaelides, P., 2011). The low acidity (pH bellow 4) may collapse clay structure, especially that with low Si/Al ratio, but the destruction will be more at pH below 3. Biskup and Subotic 2004, stated that pH below 4.5 is not recommended for clay. Therefore, the decrease in removal capacity at low pH can be attributed to the collapse of clay structure. Out of these reasons and depending on the results of Fig. 6 an optimum pH of 6.7 was suggested to carry out the adsorption experiments.

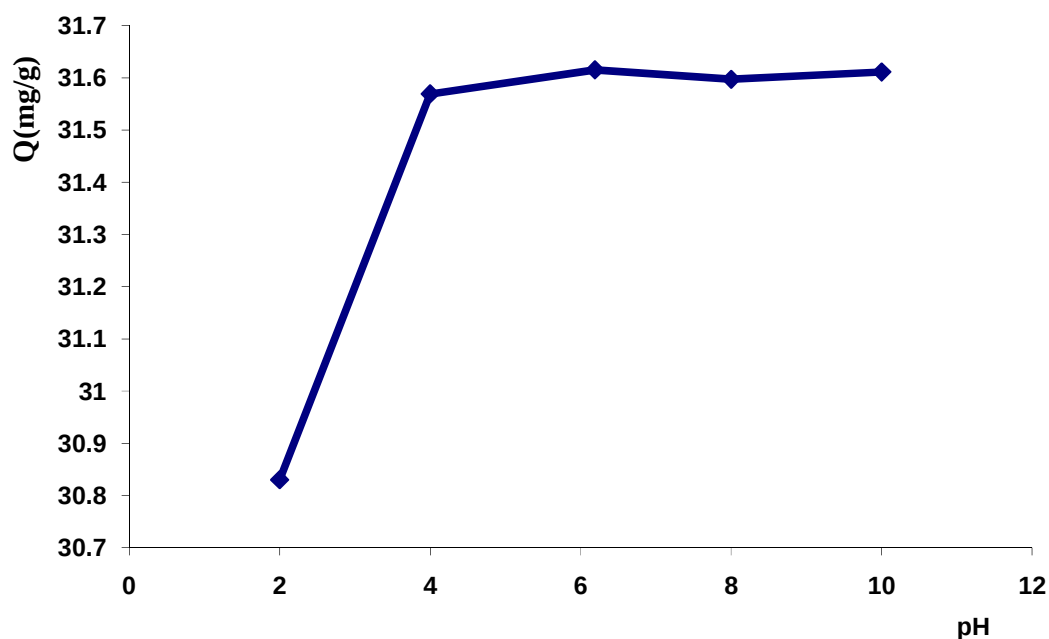


Fig. 6. Effect of pH on removal of cadmium (initial concentration 10 mg/l; contact time 120 min).

3.3. Equilibria isotherms

The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for designing purposes. The sorption data was analysed in terms of Freundlich and Langmuir isotherm models. The fitted constants for Freundlich and Langmuir models along with regression coefficients are summarised in Table 2. The Freundlich and Langmuir isotherms are shown graphically in Figs. 7 and 8. The values of the parameters and the correlation coefficients obtained at clay are listed in Table 2. As can be seen from isotherms and regression coefficients, the fit is better with Langmuir model than with Freundlich model. The Langmuir constants Q_m and K_L were 13.869 mg/g and 0.036 for cadmium. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which

is defined as
$$R_L = \frac{1}{1 + K_L C_0}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of Cd^{2+} . The R_L value indicates the shape of the isotherm as follows.

$R_L > 1$ Unfavourable

$R_L = 1$ Linear

$0 < R_L < 1$ Favourable

$R_L = 0$ Irreversible

According to McKay et al., 1982. R_L values between 0 and 1 indicate favourable adsorption. The R_L value for cadmium was 0.31, for concentration of 60 ppm. Hence, the adsorption of the metal ions on clay seems to be favourable. The Freundlich constants K_F and n were 1.647, 2.411 for cadmium, respectively. It has been shown that 'n' values between 1 and 10 represent beneficial adsorption. It is well known that the Langmuir model is usually used with an ideal assumption of a monolayer adsorption surface (Langmuir, 1918).

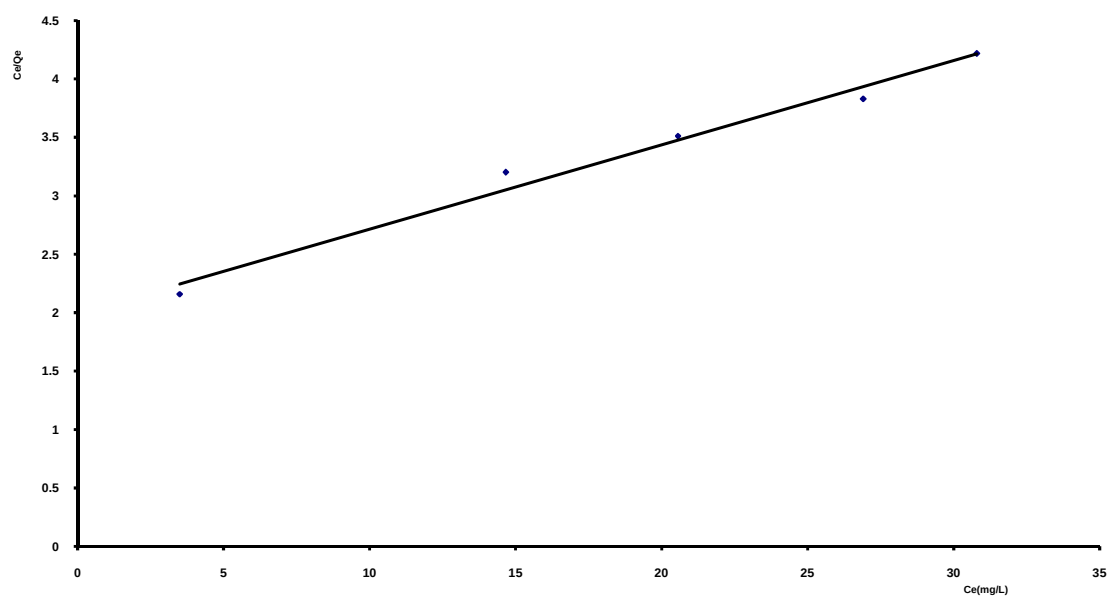


Fig 7. Langmuir isotherm for cadmium adsorption onto clay at room temperature

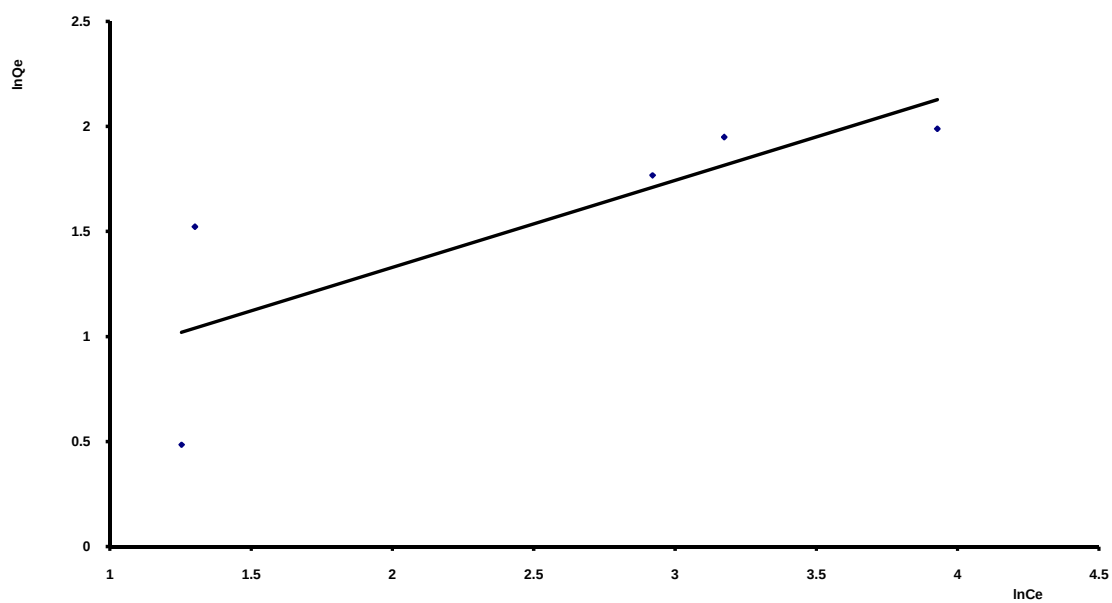


Fig 8. Freundlich isotherm for cadmium adsorption onto clay at room temperature

Table 2. Isotherm parameters for cadmium adsorption onto clay

Langmuir	$Q_{\max}(\text{mg/g})$	$K_L(\text{L/mg})$	R^2
	13.869	0.036	0.982
Freundlich	$K_f(\text{mg/g})$	n	R^2
	1.647	2.411	0.634

3.4. Kinetic studies

In order to investigate the kinetics of adsorption of Cd^{2+} , the Lagergren-first-order model and Ho's pseudo-second-order model (Ho Y.S., McKay G. 2000; Wu et al., 2009; Zhau et al., 2011) were used. The values of the parameters and the correlation coefficients obtained using linear regression by origin version 7.0 at four concentrations are listed in Table 3. Adsorption equation obtained and the fitting of the kinetic models are illustrated in Fig.9-10. It was found that the fitting to Ho's pseudo-second-order model gave the highest values of correlation coefficients more accurately than the other two models investigated. Therefore, Ho's pseudo-second-order model could be used for the prediction of the kinetics of adsorption of Cd^{2+} on clay.

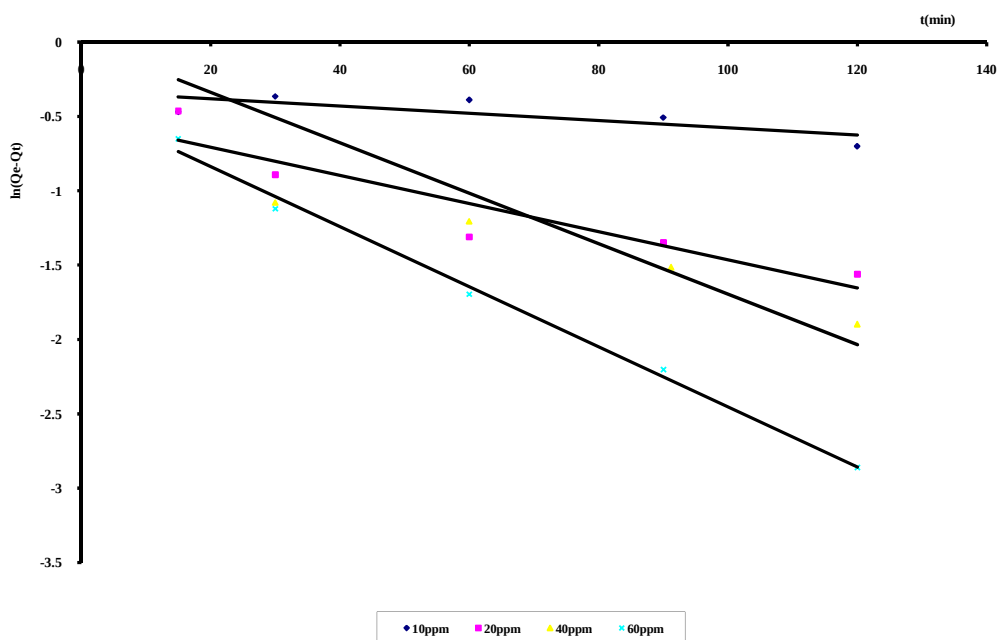


Fig.9. Pseudo-first-order kinetics for adsorption of Cd^{2+} onto clay

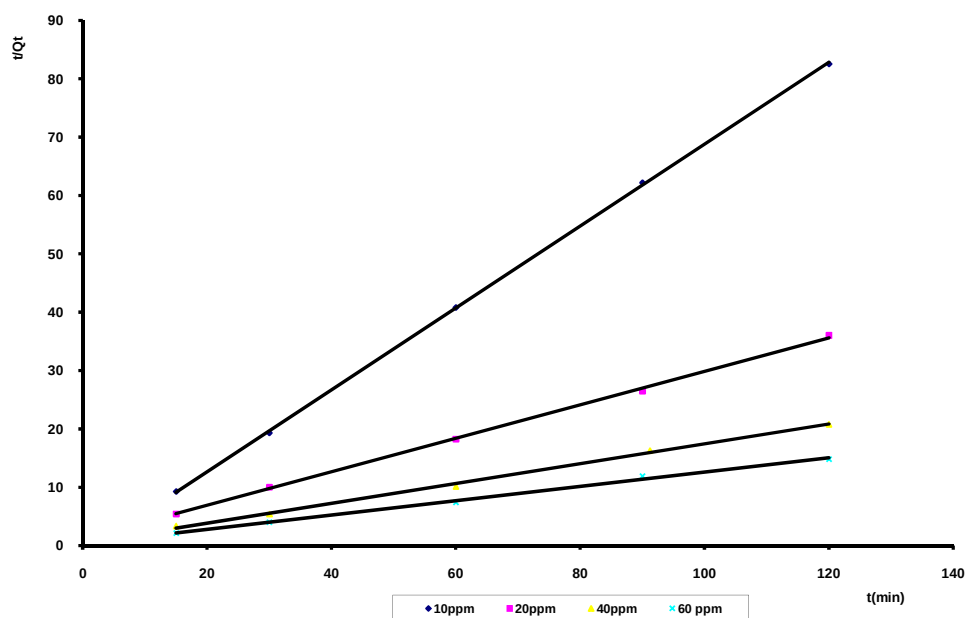


Fig.10. Pseudo-second-order kinetics for adsorption of Cd^{2+} onto clay

Table.3. Kinetic parameters for Cd^{2+} adsorption onto clay

Model	Lagergren		2 nd order			Intraparticulaire diffusion		
	K_1 (min^{-1})	R^2	K_{2app} ($\text{g.mg}^{-1}.\text{min}^{-1}$)	R^2	$h(\text{mg.g}^{-1}.\text{min}^{-1})$	K_w	R^2	t
10 ppm	0.002	0.611	0.111	0.999	0.350	0.106	0.240	2.019
20 ppm	0.009	0.861	0.074	0.999	0.894	0.099	0.856	1.299
40 ppm	0.017	0.748	0.064	0.997	2.240	0.088	0.607	0.790
60 ppm	0.020	0.994	0.113	0.996	6.635	0.028	0.946	0.366

The fittings of the experimental kinetic results to the two models are shown in Figs. 8-9 and the estimated parameters values are presented in Table 3. It can be seen from the R^2 values that the pseudo-second-order model gives the best fit (R^2 : 0.996–0.999). The values of the initial adsorption rate, h , were found to increase from 0.350 to 6.635 for increase in the initial Cd^{2+} ion concentration from 10 to 60 mgL^{-1} . Therefore, the pseudo-second-order model could be used for the prediction of the kinetics of adsorption of Cd^{2+} on clay. As for the other two models, it is not clear that there is a second

best; Lagergren's model performs reasonably well at high Cd^{2+} concentration and the goodness of fit deteriorates.

3.5. Adsorption mechanism

The intra-particle diffusion rates (K_w) were determined using linear regression. If intra-particle diffusion is a rate controlling step, then the plots should be linear and pass through the origin. In most cases these plots give general features of three stages; initial curved portion, followed by an intermediate linear portion and a plateau. The initial portion due to external mass transfer, the intermediate linear part is due to intra-particle diffusion and the plateau to the equilibrium stage where intraparticle diffusion starts to lowdown due to extremely low solute concentrations in the solution. A plot of the quantity of the cation adsorbed against 15min is shown in Fig. 11. It can be observed that the plots are not linear over the whole time range and the graphs of this figure reflect a dual nature, with initial linear portion followed by plateau. This implies that the external surface adsorption (stage 1) is absent and the stage of intra-particle diffusion (stage 2) is attained and continued to 90 min. Finally, equilibrium adsorption (stage 3) starts after 90 min. The cations are slowly transported via intra-particle diffusion into the particles and are finally retained in the pores. Similar dual nature of intraparticle diffusion curve with initial linear portion was found for adsorption of phosphorus onto calcined alunite (Ozacar M., 2003; Daifullah et al., 2007). The rates constants of intra-particle diffusion were calculated using linear regression and were found to be 0.106, 0.099, 0.088 and 0.028 mg/g.min for Cd^{2+} . However, the linear portion of the curve does not pass the origin and the latter stage of cadmium adsorption does not obey Weber–Morris equation. It may be concluded that the adsorption mechanism of this cation from aqueous solution is rather complex process and the intra-particle diffusion was not the only rate-controlling step.

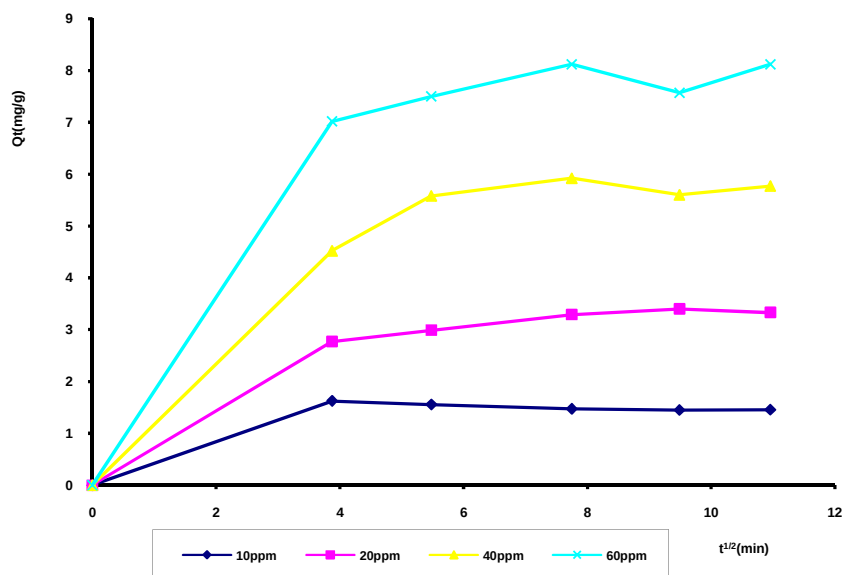


Fig.11. Plot of intraparticle diffusion model for adsorption of Cd^{2+} on clay

4. Conclusions

The present investigation showed that the clay used as an adsorbent can be effective for the removal of Cd^{2+} from dilute aqueous solution. The surface area of the clay was relatively low with large pore volume and was found to be microporous. The adsorption amount increased with increasing concentration. The maximum adsorption capacity was found to be 13.869 mg/g of clay. The Langmuir and Freundlich isotherm equations were used to interpret the adsorption phenomenon of the adsorbate, and the Langmuir isotherm was found to best describe the experimental data. There are several factors affecting the adsorption of metal ions onto clay. The kinetic rates were modelled using the Lagergren-first-order and pseudo-second-order equations, and the pseudo-second-order equation was found to explain the adsorption kinetics most effectively. It was also found that the pore diffusion played an important role in the adsorption. From an analytical point of view, spectroscopic techniques (XRD and FT-IR) and electron microscopy coupled to x-ray dispersive elemental surface analysis (SEM/EDs) were found to be powerful tools for the characterization of clay materials.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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