

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

CM Kede^{1,2}, MA Etoh², PP Ndibewu¹, HM Ngomo³, PM Ghogomu³

¹*Department of Chemistry, Tshwane University of Technology, P. O. Box 56208, 0007 Arcadia, Pretoria, Republic of South Africa,* ²*Department of Chemistry, Faculty of Science, University of Douala, PO Box 24175 Douala, Cameroon*

³*Department of Chemistry, Faculty of Science, University of Yaoundé I, PO Box 812 Yaoundé, Cameroon.*

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: conc 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 and non-linear isotherm models. The adsorption behavior was well described by the non-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.

1. Introduction

Persistent heavy metal ions in trace quantities are difficult to remove from aqueous solution. 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 (Mohanty et al., 2006; Zhu et al., 2008). 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 (Mohan et al., 2001; Gupta et al., 2003; Chiron et al., 2003; Peric et al., 2004; 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. 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. Strawn et al. (2004) reported the adsorption of Cu (II) by smectites (montmorillonite and beidellite) as a function of ionic strength and pH.

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 (Weiss and Amstutz, 1966). 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 $< 2 \mu\text{m}$.

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. 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 H_2O_2 (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).

2.3.3. Characterization of the materials

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 $0.03^\circ/5$ s. The XRD patterns were collected using a $\text{Cu K}\alpha$ 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 mm^2 , 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

The sorption equilibrium data of Cd^{2+} on clay was analyzed using Freundlich and Langmuir isotherm models (Foo and Hameed, 2011). 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 and C_e are the equilibrium concentrations of Cd^{2+} in the adsorbed and liquid phases in mg/g. 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 (Lagergren, 1998) (3):

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

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 slope and intercept of plot of $\log(q_e - q_t)$ versus t (Fig. 9) were used to determine the first-order rate constant k_1 . In many cases, the first-order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (Ho and McKay, 2000). Kinetic data were further treated with the pseudo-second-order kinetic model (Ho and Wang, 2004). The pseudo-second-order equation is also based on the sorption capacity of the solid phase. Contrary to the other model, it predicts the behaviour over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step. The differential equation is the following:

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

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):

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

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

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

The slope and intercept of plot of t/q_t versus t (Fig. 10) were used to calculate the second-order rate constant k_2 . It is more likely to predict the behaviour over the whole range of adsorption and is in agreement with the chemisorption mechanism being the rate controlling step (McKay, 2000).

2.6. Adsorption mechanism

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber and Morris's intraparticle diffusion model (Weber and Morris., 1963), in which the rate of intraparticle diffusion is a function of $t^{1/2}$ and can be defined 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 Kw intraparticle diffusion rate. k_w values can be obtained by linearizing the curve $q = f(t^{1/2})$. Such types of plots may present a multi-linearity, implying that the overall adsorption process may be controlled by one or more steps, such as film or external diffusion, intraparticle diffusion and a chemical reaction on the pore surface, or a combination of more than one step. (Weber and Morris, 1963) reported that if intraparticle diffusion was involved in the adsorption process, then a plot of the square root of time versus the adsorption amount would result in a linear relationship, and that the intraparticle diffusion would be the controlling step if this line passes through the origin.

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, $2\theta = 62.589^\circ$).

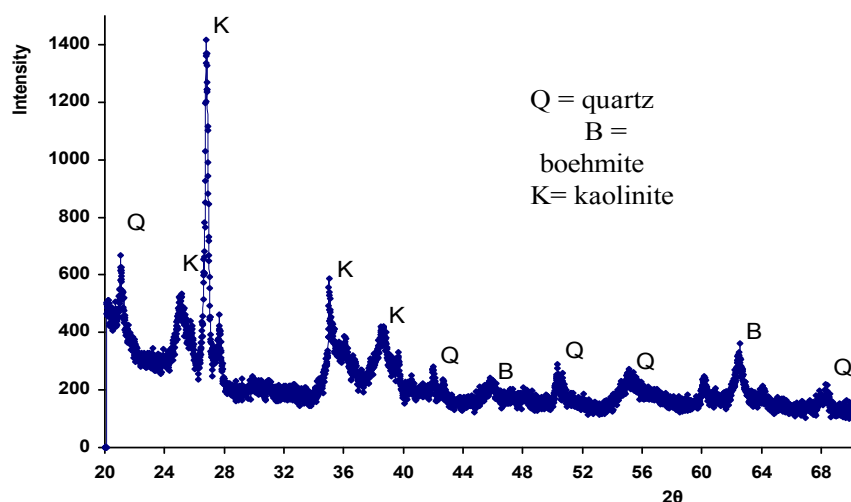


Fig.1. X-ray diffraction patterns of the natural clay.

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 $540.\text{ cm}^{-1}$ can be attributed to vibrations due to deformation of Si-O and Si-O-Al bonds, respectively (Sayilkan et al., 2004).

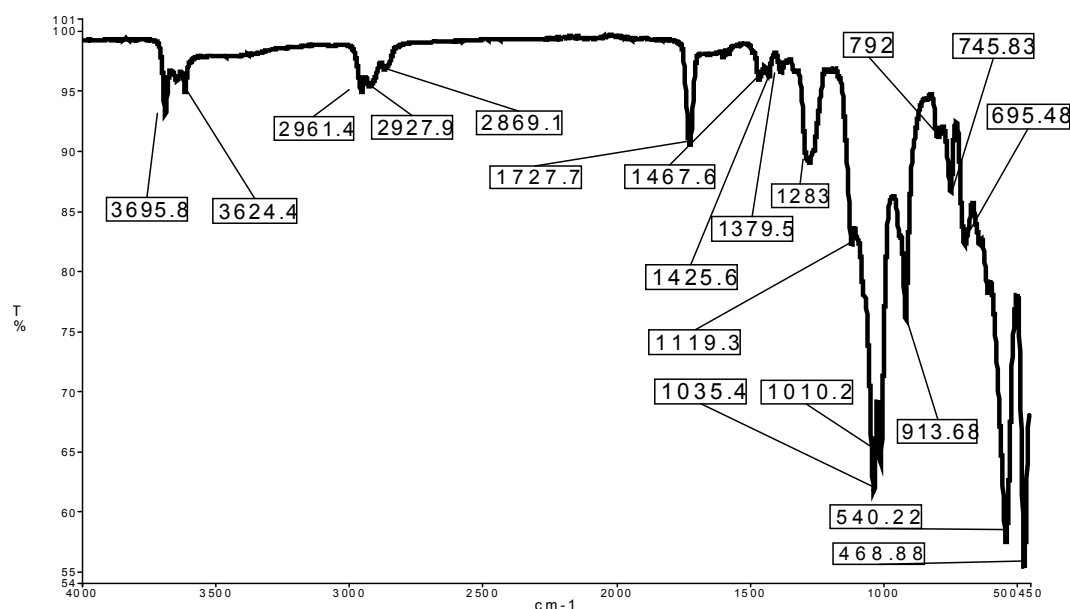


Fig. 2. FTIR spectrum of a sample clay studied (MARV4)

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, titane, silicium zinc, copper and iron (Table 1).

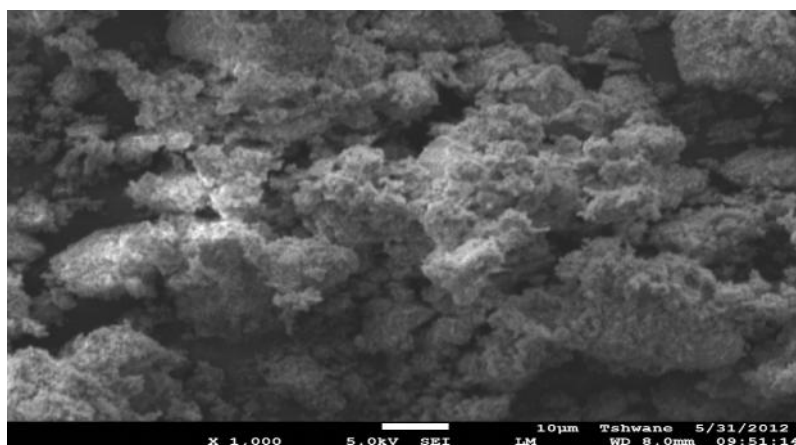


Fig.3. SEM photographs of a sample clay sample (MARV4)

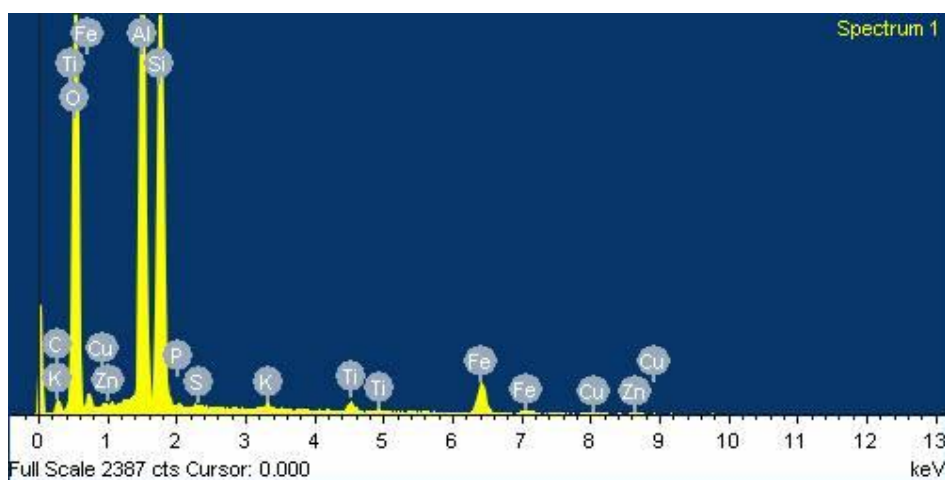


Fig. 4. EDX of a sample clay sample MARV4 showing abundance of certain metals (Al and Si are typically present in clay minerals of this type)

Table 1. Elemental analysis of clay

elements	C	O	Al	Si	P	S	K	Ti	Cu	Fe	Zn
Weight%	104.70	1505.47	336.37	348.39	4.17	0.49	3.69	12.58	5.99	74.79	13.14
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+}

Fig. 9 shows the effect of contact time on removal of Cd^{2+} . Experimental studies were carried out with varying initial metal ion concentrations of Cd^{2+} ranging from 10 – 60 ppm using 0.2 g of adsorbent. Equilibrium adsorption was established within 30 min for the metal ion. It is very clear from these results that the agitation time required for maximum uptake of metal ions by clay was dependent on the initial metal ion concentration. 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.

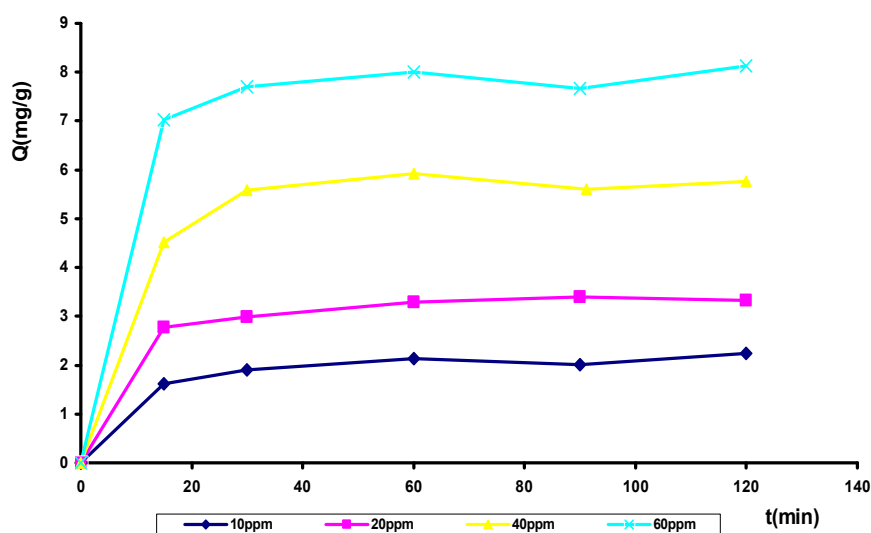


Fig.5. Effect of agitation time and initial concentration of Cd^{2+} on the adsorption of Cd^{2+} (conditions: carbon concentration, 0.2g/50 mL.)

3.4. Equilibria isotherms

Adsorption isotherms provide qualitative information on the nature of the solute–surface interaction, as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. The equilibrium experiment was studied room temperature, adsorbent mass: 0.2g, C_0 : 10 – 60 ppm. In order to

understand the adsorption mechanisms of Cd^{2+} onto the clay, two adsorption isotherm models, Langmuir and Freundlich, were used to fit the experimental data. For determining the isotherm parameters (Table 2) by using non-linear regression, Origin version 7.0, a window based statistical software, was used. Different adsorption isotherms obtained at clay are illustrated in Fig.6 and 7. The values of the parameters and the correlation coefficients obtained at clay are listed in Table 2. It is well known that the Langmuir model is usually used with an ideal assumption of a monolayer adsorption surface (Langmuir, 1918). The value of correlation coefficients (R^2) for the two models at different concentration shows that the goodness-of-fit of the models is Freundlich.

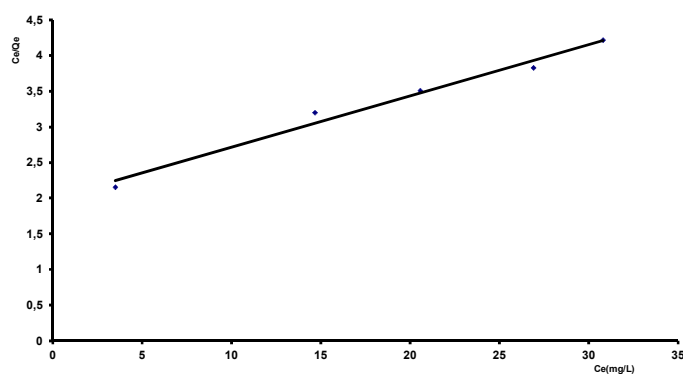


Fig 6. Langmuir isotherm for cadmium adsorption onto clay at room temperature

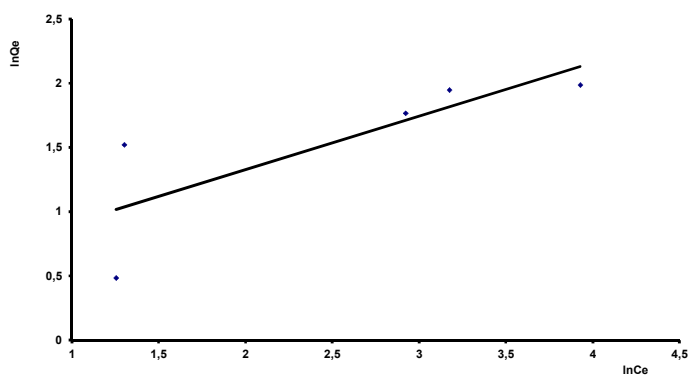


Fig 7. Freundlich isotherm for cadmium adsorption onto clay at room temperature

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

3.5. 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 were used. The values of the parameters and the correlation coefficients obtained using non-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.8-9. 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 the activated carbon.

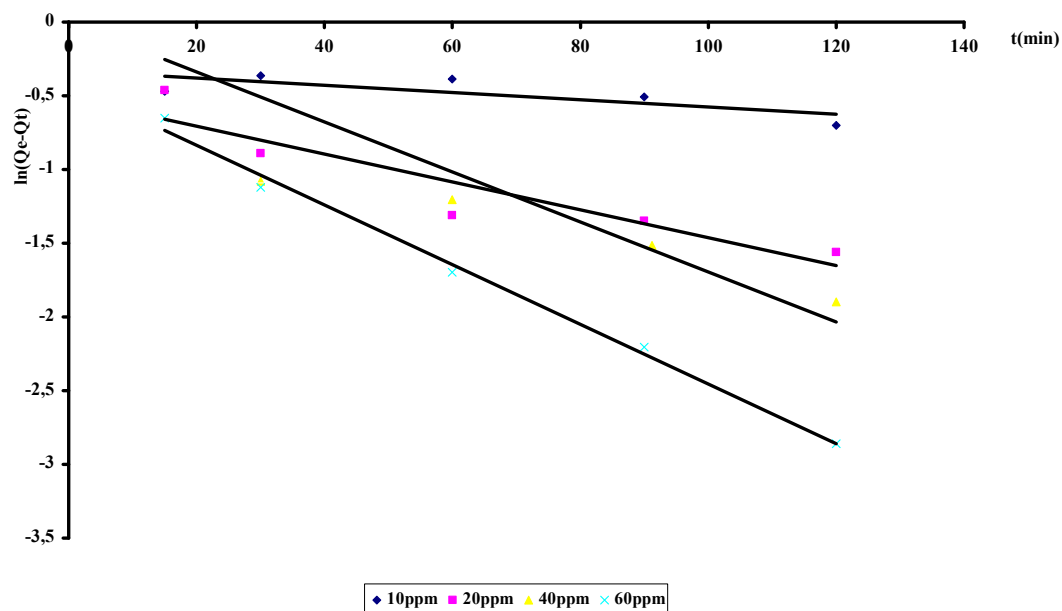


Fig.8. Pseudo-first-order kinetics for adsorption of Cd^{2+} onto clay

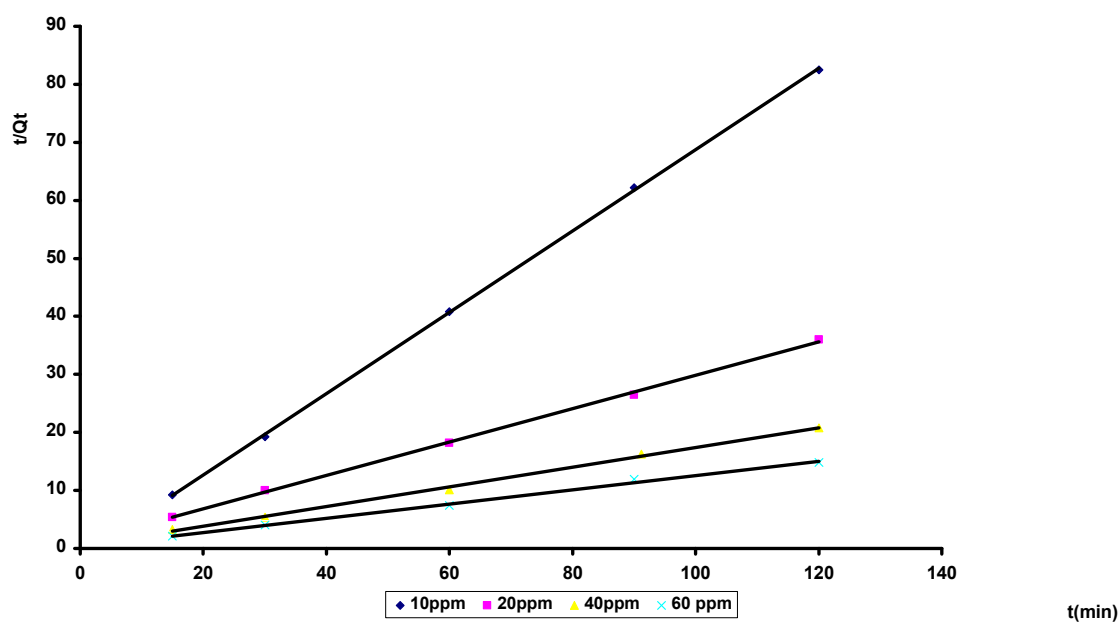


Fig.9. Pseudo-second-order kinetics for adsorption of Cd^{2+} onto clay

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

Model	Lagergren		2 nd order			Intraparticulaire diffusion		
	K_1 (min^{-1})	R^2	$K_{2\text{app}}$ ($\text{g} \cdot \text{ng}^{-1} \cdot \text{min}^{-1}$)	R^2	$h(\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	K_w	R^2	I
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) but its predicted q_e values are overestimated as compared to the experimentally observed values, especially at high cadmium concentration. However, q_e values estimated from the pseudo-second-order model are an extrapolation outside the time period that was experimentally investigated, the fact still remains that the model accurately predicts the adsorption kinetics throughout the period of experiments. 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.

3.6. Adsorption mechanism

Fig. 10 shows the intraparticle diffusion plot of the adsorption of Cd^{2+} on the clay at four concentrations. As it can be seen from this figure (Fig. 10), the plots of clay show similar features that have two linear segments followed by a plateau. In the first 15 min, the first linear portion passed through the origin, implying that the intraparticle diffusion played an important role and controlled the rate of the adsorption. In the 60 min. that followed, the regression was nearly linear but did not pass through the origin, suggesting that the intraparticle diffusion was not the sole rate-controlling step in this stage. The K_w value evaluated from the first linear parts of these curves at 10, 20, 40 and 60 ppm was 0.106, 0.099, 0.088 and 0.028, respectively. The I-value decreased with the increasing concentration of Cd^{2+} , which showed that the adsorption rate increased with the increasing concentration. Comparing to the plots of 10 ppm, 20 ppm, 40 ppm and 60 ppm, the plot of 60 ppm had an added curved portion in the first 5 min, showing that film diffusion played an important pole in this stage (Weber and Morris, 1963).

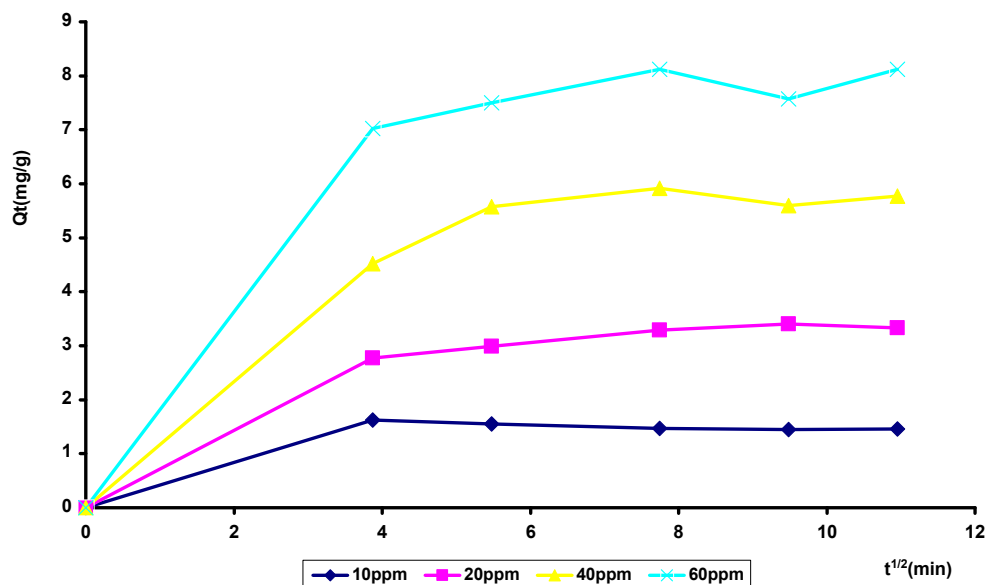


Fig.10. Plot of intraparticle diffusion model for adsorption of Cd^{2+} on clay

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 for initial Cd^{2+} conc. (60 ppm) 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.

Acknowledgements

This research was supported by the Universities of Yaoundé I and Douala, both in Cameroon. Appreciation is expressed to the Academy of Sciences for the Developing World (TWAS) in Trieste, Italy, for financial assistance to the main author to travel to the host institution, the Tshwane University of Technology (TUT), in Pretoria, South Africa working under Profs RI McCrindle & PP Ndibewu. Finally, the National Research Foundation (NRF) of South Africa is acknowledged for having provided funds to the host institution (TUT) necessary for the procurement of chemicals used throughout the entire project.

References

Mohanty, K., Das, D., Biswas, M.N., (2006). Preparation and characterization of activated carbons from *Sterculia alata* nutshell by chemical activation with zinc chloride to remove phenol from wastewater. *Adsorption* 12, 119–132.

Zhu, S., H. Hou.,Xue, Y., (2008). Retracted: Kinetic and isothermal studies of lead ion adsorption onto bentonite. *Applied Clay Sci.*, 40: 171-178.

Mohan, D., Gupta, V.K., Srivastava, S.K., Chander, S., (2001). Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste. *Colloids Surf. A: Physico chem. Eng. Asp.* 177, 169–181.

Gupta, V.K., Jain, C.K., Ali, I., Sharma, M., Saini, V.K., (2003). Removal of cadmium and nickel from wastewater using bagasse fly ash — a sugar industry waste. *Water Res.* 37, 4038–4044.

Chiron, N., Guilet, R., Deydier, E., (2003). Adsorption of Cu (II) and Pb (II) onto a grafted silica: isotherms and kinetic models. *Water Res.* 37, 3079–3086.

Peric, J., Trgo, M., Medvidovic, N.V., (2004). Removal of zinc, copper and lead by natural zeolites a comparison of adsorption isotherms. *Water Res.* 38, 1893–1899.

Alvarez-Ayuso, E., Nugteren, H.W., (2005). Purification of chromium (VI) finishing wastewaters using calcined and uncalcined Mg–Al– CO₃–hydrotalcite. *Water Res.* 39, 2535–2542.

Weiss, A., Amstutz, G.C., (1966). Ion-Exchange Reactions on Clay Minerals and Cation Selective Membrane Properties as Possible Mechanisms of Economic Metal Concentrations. *Mineralium Deposita*. 1, 60-66.

Ndibewu, P.P., Mgangira, M.B., Cingo, N., McCrindle, R.I., (2010). Metal and anion composition of two biopolymeric chemical stabilizers and toxicity risk implication for the environment. *Journal of Toxicology and Environmental Health, Part A*, 73(4), 261-271.

Pedra, F., Polo, A., Ribeiro, A., Domingues, H. (2007). Effects of municipal solid waste compost and sewage sludge on mineralization of soil organic matter. *Soil Biology and Biochemistry*. 39(6)1375–1382.

Mellah, A., Chegrouche, S., (1997). The removal of zinc from aqueous solutions by natural bentonites. *Water Res.* 31, 621–629.

Tanabe, K., (1981). Catalysis—science and technology. In: Anderson, J.R., Boudart, M. (Eds.), Springer - Verlag, New York, p. 231.

Sanchez, A.G., Ayuso, E.A., De, B.O.J., (1999). Sorption of heavy metals from industrial wastewater by low cost mineral silicates. *Clay Miner.* 34, 469–477.

Alvarez-Ayuso, E., Garcia-Sanchez, A., (2003). Removal of heavy metals from waste waters by natural and Na-exchanged bentonites. *Clays Clay Miner.* 51, 475–480.

Khan, S.A., Rehman, R., Khan, M.A., (1995). Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite. *Waste Manag.* 15, 271–282.

Strawn, D.G., Palmer, N.E., Furnare, L.J., Goodell, C., Amonette, J.E., Kukkadapu, R.K., (2004). Copper sorption mechanisms on smectites. *Clays Clay Miner.* 52, 321–333.

Foo, K.Y., Hameed, B.H., (2011). Preparation of activated carbon from date stones by microwave induced chemical activation: application for methylene blue adsorption. *Chem. Eng. J.* 170 (1), 338–341.

Lagergren, S., (1998). About the theory of so-called adsorption of soluble substances. *K. Sven. Vetenskapsakad. Handl.* 24, 1–39.

Ho, Y.S., McKay, G., (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* 34, 735–742.

Ho. Y.S, Wang. C.C., (2004). Pseudo-isotherms for the Sorption of Cadmium ion onto Tree fern, *Process. Biochem.* 39 ,759–763.

Weber. W.J, Morris. J.C, (1963). 'Kinetics of Adsorption of Carbon from Solutions', *J, Sanit, Eng, Div, Amer, Soc, Civ, Eng*, 89, 31-63.

Farmer V.C.,(1974). The Layer Silicates: The Infrared Spectra of Minerals. In: V.C. Farmer (Ed.), *Mineralogical Society, London*, 4, 331–363.

Bouras.O., (2003). Propriétés Adsorbantes d'Argiles Pontées Organophiles : Synthèse et Caractérisation.

Amritphale S.S., Bhasin S., Chandra N. (2005). Energy Efficient Process for Making Pyrophyllite-based Ceramic Tiles Using Phosphoric Acid and Mineralizers. *Ceramics International, Article in press.*

Sayilkan. H., Erdemoglu. S. , Sener.S., Sayilkan.F., Akarsu. M., Erdemoglu. M., (2004). Surface Modification of Pyrophyllite with Amino Silane Coupling Agent for the Removal of 4-Nitrophenol from Aqueous Solutions. *Journal of Colloid and Interface Science*, 275, 530–538.

Kadirvelu. K, Namasivayam. C., (2003). *Adv. Environ. Res.* 7,471.

Langmuir. I., (1916). The Constitution and Fundamental Properties of Solids and Liquids, *J. Am. Chem. Soc.*, 38, 2221–2295