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Comparison of sorption of Pb^{2+} and Cd^{2+} on Kaolinite clay and polyvinyl alcohol-modified Kaolinite clay

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Abstract Kaolinite clay obtained from Ubulu-Ukwu, Delta state in Nigeria was modified with polyvinyl alcohol (PVA) reagent to obtain PVA-modified Kaolinite clay adsorbent. Scanning Electron Microscopy (SEM) of the PVA-modified adsorbent suggests that Kaolinite clay particles were made more compact in nature with no definite structure. Modification of Kaolinite clay with PVA increased its adsorption capacity for 300 mg/L Pb^{2+} and Cd^{2+} by a factor of at least 6, i.e., from 4.5 mg/g to 36.23 mg/g and from 4.38 mg/g to 29.85 mg/g, respectively, at 298 K. Binary mixtures of Pb^{2+} and Cd^{2+} decreased the adsorption capacity of Unmodified Kaolinite clay for Pb^{2+} by 26.3% and for Cd^{2+} by 0.07%, respectively. In contrast, for PVA-modified Kaolinite clay, the reductions were up to 50.9% and 58.5% for Pb^{2+} and Cd^{2+}, respectively.

The adsorption data of Pb^{2+} and Cd^{2+} onto both Unmodified and PVA-modified Kaolinite clay adsorbents were found to fit the Pseudo-Second Order Kinetic model (PSOM), indicating that adsorption on both surfaces was mainly by chemisorption and is concentration dependent. However, kinetic adsorption data from both adsorbent generally failed the Pseudo-First order Kinetic model (PFOM) test.

Extents of desorption of 91% Pb^{2+} and 94% Cd^{2+} were obtained, using 0.1 M HCl, for the Unmodified Kaolinite clay adsorbent. It was found that 99% Pb^{2+} and 97% Cd^{2+}, were desorbed, for PVA-modified Kaolinite clay adsorbents within 3 min for 60 mg/L of the metal ions adsorbed by the adsorbents.

Keywords Adsorption · Desorption · Kaolinite · Kinetic · Model · Modified adsorbent

1 Introduction

In recent years, there has been a growing concern for the immobilization of metal ions introduced into water and wastewater bodies by the increasing human technological activities. It has been established beyond doubt that heavy metal ions in the environment (water, soil and air) pose a very serious threat to the health of man. In our world today, with the exponentially increasing population, the need for controlling heavy metal discharge into the environment is even more pronounced. This is best carried out at the source of the discharge, before toxic metal ions enter the complex ecosystem.

It is difficult to follow the fate of these metallic ions after they enter the ecosystem and pollute the ecosystem, as they move through from one ecological trophic layer to another (Volesky 2001). Through the food chain, they accumulate in living tissues of humans and animals which eventually lead to various health complications in man. The various health problems associated with the intake of these toxic metal ions

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by man is reflected in his total well being: his productivity being negatively affected. This results in a decline in national productivity. Thus, controlling heavy metal discharges into the environment and effectively removing these toxic metal ions from aqueous solutions has become a challenge to scientists in the 21st century.

Currently, there is a pronounced tendency to utilize mechanically stable synthetic or natural solid matrices in many applications, such as chemically bonded silica in chromatography, extraction of cations from aqueous and non-aqueous solvents, catalytic or ion-exchange reactions, electronics, ceramics and also in bioengineering. One of the important properties explored is related to the adsorption of significantly large concentrations of metal ions onto a solid surface from a complex mixture of the metal ions or single metal ion solutions.

The use of modified clay minerals for the adsorption of metal ions from aqueous solutions, for the purpose of water purification or industrial wastewater treatment, has been widely studied, as discussed below. These clay minerals, when used as colloids or powders, have been found to be equally as efficient as activated carbon but it is difficult to recover the adsorbent from filters after use. This further renders the regeneration and possible reuse of the clay adsorbent very difficult and the use of the adsorbent less cost effective.

The kinetics of the adsorption of these toxic metal ions is needful in order to predict the rate at which these toxic metal ions are being removed from the aqueous system so as to provide data for the design of appropriate treatment plants. Adsorption kinetics also provides us with an insight into the mechanism of adsorption (Ho and McKay 1999).

Although a number of kinetic investigations have been carried out on the adsorption of Pb^{2+} onto Peat (Ho et al. 2001), Pb^{2+} onto decaying leaves (Salim et al. 1994), Cd^{2+} onto hydrous Ferric oxide (Dzombak and Morel 1986), Cu^{2+} and Pb^{2+} onto polysulfone and algae complex (Ramelow et al. 1996), Cr(VI) onto Peat (Sharma and Forster 1994), Pb^{2+} on Palm kernel fibre (Ho and Ofomaja 2005), Pb^{2+} onto Orthophosphate modified Kaolinite clay (Unuabonah et al. 2007), Pb^{2+} and Cd^{2+} onto Tripolyphosphate-modified Kaolinite clay (Adebowale et al. 2008), to mention but a few. These adsorbents all showed good potential as low cost adsorbents in the adsorption of metal ions except that they exist in aqueous solution as either colloids or dispersed particles that are difficult to recover from filters. Besides, there is no report on the kinetics of the adsorption and desorption of Pb^{2+} and Cd^{2+} onto polyvinyl alcohol (PVA)-modified kaolinite adsorbent.

To address the problem of recovery of adsorbent/resins after use from filters, this study focuses on the production of a novel, water-stable and mechanically strong adsorbent from locally obtained Kaolinite clay using polyvinyl alcohol reagent. This is subsequently used for the adsorption of Pb^{2+} and Cd^{2+}.

This study further considers the kinetics of the adsorption of Pb^{2+} and Cd^{2+} onto Unmodified and PVA-modified kaolinite adsorbents. The effect of initial metal ion concentration, temperature and binary solutions of Pb^{2+} and Cd^{2+} on the initial sorption rate, the Pseudo-second order and Pseudo-first order rate constants and the adsorption capacity of the adsorbents are studied as well as the desorption kinetics for adsorbed Pb^{2+} and Cd^{2+} for both adsorbents. Kinetic adsorption and kinetic desorption data obtained are modeled against existing kinetic adsorption models and kinetic desorption models.

2 Materials and methods

Kaolinite was obtained from Ubulu-Ukwu, Delta State, Nigeria. On collection, stones and other heavy particles were removed from the sample. It was then sieved through a +220 µm mesh sieve to remove the larger non-clay fractions from the clay. A part of the raw Kaolinite was kept suspended in doubly deionized water in a 1 L beaker for several hours. It was further purified using the method of (Moore and Reynolds 1989). This involves the stirring of the mixture in small amount of 30% hydrogen peroxide solution till all effervescence has ceased. This treatment removes any organic substances remaining in the clay. The mixture was kept standing overnight. The supernatant was decanted and the Kaolinite washed thoroughly with deionized water to remove traces of hydrogen peroxide before being used. The suspended Kaolin was centrifuged and oven dried at 343 K to obtain the kaolin sample. Scanning Electron Microscopy (SEM) of both adsorbents was done with Philips EDAX microscopy machine using the Back Scattered Electron (BSE) detector.

3 Modification of clay sample

The kaolinite was acid treated with 2 M HNO_3 for 1 hour to oxidize the clay mineral. This was then centrifuged and washed several times with distilled-deionized water and the sample was dried in the oven at 373 K.

50 g of kaolinite sample was added to a certain amount of distilled-deionized water. This was heated to boiling, and then certain percentages of polyvinyl alcohol (PVA) and formaldehyde solution were added to the suspension. This was swiftly agitated until kaolinite-resin gel was formed. On formation of Kaolinite resin gel, 5% PVA was then added as coating. This was heated for a while. This step was repeated three times before the sample was washed thoroughly with distilled-deionized water and dried at 333 K in an oven. Once dried, the very hard kaolinite-resin was broken into

particles and sieved into desired particle size of +350 µm. This was the same particle size of the Unmodified kaolinite adsorbent used throughout the experiment.

4 Kinetics of adsorption

Stock solutions of 1000 mg/L Pb^{2+} and Cd^{2+} were prepared from the nitrates of both metal ions using distilled-deionized water. For the Unmodified kaolinite adsorbent, 300, 500, 1000 mg/L single metal ion solutions of Pb^{2+} and Cd^{2+} were prepared. For PVA-modified kaolinite adsorbent, 150, 300, 400 mg/L of single metal ion solutions of Pb^{2+} and Cd^{2+} were prepared and their pH adjusted to 5.5 ± 0.01 with either 0.1 M HCl or 0.1 M NaOH. 15 g/L and 5 g/L for Unmodified and PVA-modified kaolinite adsorbents, respectively, were used for kinetic measurements. A power stirrer was used to keep the adsorbents in constant contact with the aqueous metal ion solution at 150 rpm. 0.5 ml of samples were withdrawn at time intervals between 0 to 300 min and made to 5 ml. The samples collected were then analyzed for Pb^{2+} or Cd^{2+} using ICPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy) IRIS Advantage model (made by Thermo Fisher). The same procedure was carried out for samples at 298 K, 313 K and 323 K.

The effect of the simultaneous presence of Pb^{2+} and Cd^{2+} on the kinetics of the adsorption of both metal ions onto the various adsorbents was studied by mixing the exact weights required to prepare 500:500 mg/L, 100:500 mg/L and 500:100 mg/L Pb:Cd mixed metal ion solutions in 1 L solution of distilled-deionized water for Unmodified kaolinite adsorbent. In contrast, 60:60 mg/L, 150:60 mg/L and 60:150 mg/L Pb:Cd mixtures were used for PVA-modified kaolinite adsorbent. Their pHs were adjusted to 5.5 ± 0.01 using 0.1 M NaOH or 0.1 M HCl. Samples were treated as in the kinetic experiments above.

Blank samples containing lead and Cadmium ions without the adsorbent were also used in this study. The amounts of Lead and Cadmium ions adsorbed by the adsorbents were calculated by difference using the formula:

$$q_e(\text{mg/g}) = \frac{C_o - C_e(V/1000)\text{L}}{W(\text{g})} \tag{1}$$

5 Adsorption kinetic models

The Pseudo First Order Model (PFOM) is obtained as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

On rearrangement

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

which on integration under the boundary conditions of $t = 0$ to t, and $qt = 0$ to qt, gives a linear logarithmic expression,

$$-\ln(q_e - q_t) + \ln q_e = k_1 t \tag{3}$$

Rearranging (3) we have

$$1 - q_t/q_e = \exp(-k_1 t) \tag{4}$$

The non-linear form of (4) when q_t is made the subject of the formula is:

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{5}$$

The Pseudo Second Order Kinetic Model (PSOM) is obtained as follows:

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

On rearrangement and integration

$$\frac{1}{q_e - q_t} - \frac{1}{q_e} = k_2 t \tag{7}$$

When this is linearized, it gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where q_e is the amount of Pb^{2+} and Cd^{2+} adsorbed at equilibrium (mg/g), q_t is the amount of Pb^{2+} and Cd^{2+} adsorbed at time t (min) in mg/g and k_2 is the rate constant of the PSOM for sorption of both metal ions.

The initial sorption rate h, can be obtained by the following equation:

$$h = k_2 q_e^2 \tag{9}$$

where h is the initial sorption rate (mg/g min).

The non-linear form of the PSOM is written as follows:

$$q_t = \frac{t}{1/h + t/q_e} \tag{10}$$

6 Desorption kinetics

A 0.1 M HCl aqueous solution was used for desorption of the both metal ions from the Unmodified and PVA-modified kaolinite adsorbents. Prior to those tests, solutions containing 60 mg/L of Pb^{2+} and Cd^{2+} were adjusted to pH 5.5 ± 0.01 and were added to 15 g/L and 5 g/L of Unmodified and PVA-modified kaolinite adsorbents, respectively. During each test, 0.5 ml of samples were regularly withdrawn at 0 to 1,900 sec and diluted to 5 ml. Samples were then read for Pb^{2+} and Cd^{2+} using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES), as mentioned earlier.

For reuse of samples, the above weight-volume ratios of adsorbent-adsorbate ratio at 60 mg/L of adsorbate concentration were stirred for 300 min, after which the supernatant liquid was removed and the samples were air-dried at 298 K. Subsequently the air-dried samples were introduced into 1 L of 0.1 M HCl at 298 K and stirred (150 rpm) for 3 min. During those tests, 0.5 ml of samples were withdrawn and diluted to 5 ml. Samples were then read for Pb^{2+} and Cd^{2+} using ICPAES.

7 Results and discussions

7.1 Scanning electron microscopy

The Scanning Electron Microscopy (SEM) scans for both adsorbents are shown in Figs. 1a and 1b. When viewed under the Scanning Electron Microscope (SEM), the shapes

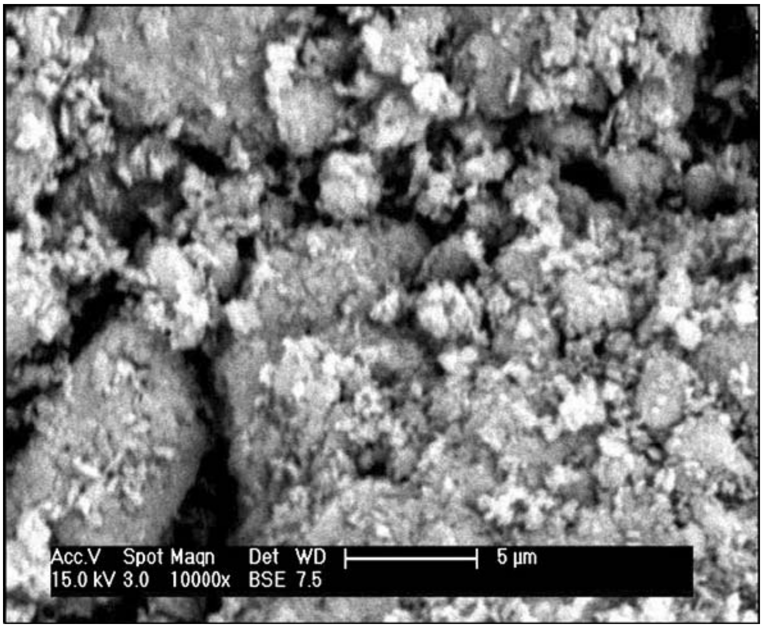


Fig. 1a Scanning electron microgram scan for Unmodified Kaolinite clay adsorbent particles

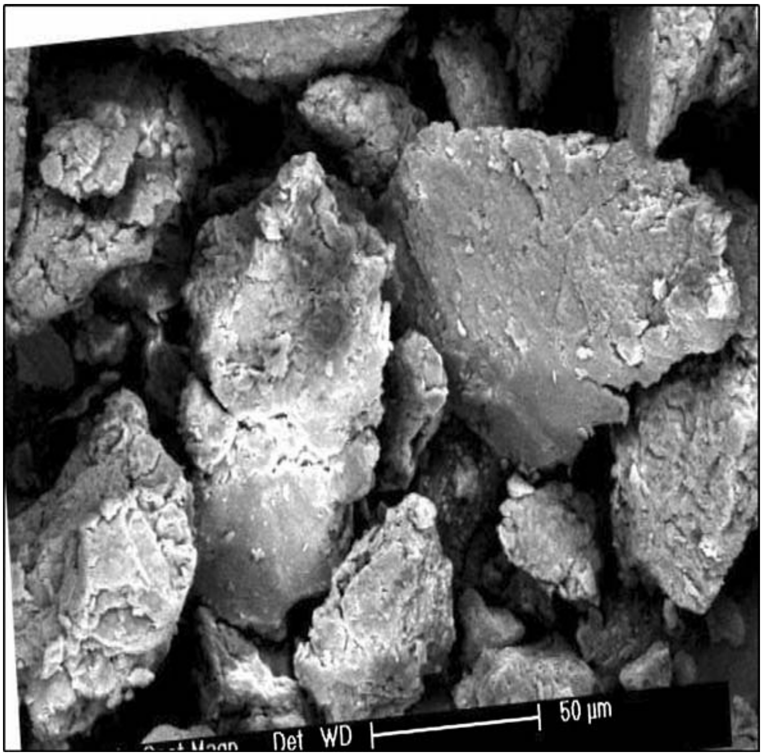


Fig. 1b Scanning electron microgram scan for PVA-modified Kaolinite clay adsorbent particles

of the Unmodified kaolinite clay adsorbent particles gave irregular structures (Fig. 1a). The unmodified kaolinite adsorbent showed some white particles on the surface of the mineral particles. These were likely to be non-clay minerals like Sodium, Potassium, Calcium, Iron and Magnesium oxides (Galan et al. 1996).

The particles of the PVA modified kaolinite adsorbent (Fig. 1b) gave a different structure. The PVA-modified Kaolinite adsorbent gave very compact particles together. These particles were amorphous and were found to be hard, water-stable and yet active even when left in aqueous solution for 5 hrs. The particles were an order of magnitude larger than those of the Unmodified Kaolinite adsorbent, i.e. from 5 µm for the Unmodified kaolinite particles to 50 µm for the PVA-modified particles at same magnification (Figs. 1a and 1b).

7.2 Kinetics of adsorption

The Pseudo-first order model rate (PFOM) constants were obtained using (3) to make linear plots. The PFOM could only be applied to the adsorption data in the first 20 min of adsorption for kinetic data obtained from the both the PVA-modified and Unmodified Kaolinite clay adsorbents. This is because beyond this time, the data showed large deviation from the model. Kalavathy et al. (2005) in their study of the kinetics of the adsorption of Cu^{2+} onto H_3PO_4-activated rubber wood sawdust observed that the PFOM fitted well to their adsorption data for the first 25 min. This implies that for the first 20 min, the adsorption of Pb^{2+} and Cd^{2+} onto the adsorbents was very rapid and not concentration dependent but film diffusion controlled. Subsequently, as shown below, the adsorption reaction is then controlled by the PSOM which supports strongly ion-exchange/chemical reaction mechanism of adsorption (Ho et al. 2001). Thus, the PFOM accurately represents the initial stages where rapid adsorption of Pb^{2+} and Cd^{2+} onto both adsorbents occurs, but it cannot be applied for the entire adsorption period.

When PFOM was applied to kinetic data obtained from both adsorbents within the first 20 min it was observed that kinetic data from PVA-modified Kaolinite clay gave PFOM rate constants that were approximately 1.5 times those from Unmodified Kaolinite clay adsorbent. Furthermore, adsorption capacity of PVA-modified Kaolinite clay adsorbent was higher than for Unmodified Kaolinite clay adsorbent at 300 mg/L at increasing initial metal ion concentration and temperature (Tables 1 and 2).

However, for the unmodified adsorbent, the PSOM rate constant, k_2, for the adsorption of Pb^{2+} was observed to have increased with temperature and decreased with increase in initial metal ion concentration (Tables 3 and 4). Ho and McKay (1999) also reported a similar trend with the PSOM when they studied the adsorption Pb^{2+} on Peat. The increase in the PSOM rate constant with increasing temperature may imply that increasing temperature may have increased the rate of adsorption at the solid-liquid interface. This is perceived to occur not by creating new adsorption sites on the adsorbent surface but by creating new adsorption pathways that increase only slightly the adsorption capacity of the adsorbent and possibly the rate of the adsorption of the metal ions (Tables 3 and 4).

The decrease in k_2, with increasing initial metal ion concentration may have resulted from a decrease in the number of active sites available as there could be increase in the rate of both adsorption and desorption of the metal ions occurring simultaneously on the surface of the adsorbent, which characterizes many adsorption mechanisms. For the adsorption of Cd^{2+} onto Unmodified kaolinite adsorbent, no particular trend was observed.

With PVA-modified kaolinite adsorbent the pseudo-second order rate decreased with both increasing temperature and initial metal ion concentration for the adsorption of both Pb^{2+} and Cd^{2+}.

Adsorption of 300 mg/L of Pb^{2+} and Cd^{2+} onto Unmodified kaolinite adsorbent gave PSOM rate constants higher than those for PVA-modified adsorbent at same concentration (Tables 3 and 4), although the initial sorption rates for the adsorption of both metal ions onto PVA-modified kaolinite adsorbent were quite higher than for those of the Unmodified kaolinite adsorbent. This may suggest that the equilibrium phase for the adsorption of Pb^{2+} and Cd^{2+} onto PVA-modified kaolinite adsorbent might be quite slower than for the Unmodified adsorbent especially with increasing initial metal ion concentration. This will thus result in a smaller overall PSOM rate constant for adsorption of the metal ion onto the PVA-modified adsorbent. Although this is a disadvantage in the use of the PVA-modified adsorbent for the adsorption of the metal ions, the higher adsorption capacity of PVA-modified adsorbent makes it a better adsorbent.

The linearity of the pseudo-second order plots, (not shown) and from the R^2 values in Tables 3 and 4, indicates that chemical reaction (ion-exchange reaction) is possibly the main adsorption mechanism by which both metal ions were adsorbed on both Unmodified and PVA-modified kaolinite adsorbents (Ho et al. 2001). However, the possibility of *physisorption* of the metal ions onto these adsorbents, along side the ion-exchange mechanism, cannot be completely ruled out.

It is possible that numerous chemical reactions and diffusion processes coexist in the adsorption of Pb^{2+} and Cd^{2+} onto both PVA-modified and Unmodified kaolinite adsorbents. Thus, the relative contributions of chemical and physical processes are difficult to isolate. Thus, the rate parameters obtained in this study are apparent ones. PSOM rate constants were obtained from linear plots of (8).

Table 1 Effects of temperature and initial metal ion concentration on PFOM parameters in the adsorption of Pb^{2+} and Cd^{2+} by PVA-modified Kaolinite clay for the first 20 min

	Lead			Cadmium		
	298 K	313 K	323 K	298 K	313 K	323 K
150 mg/L						
q_e	12.69	15.33	25.18	11.14	12.67	13.63
k_1	0.119	0.1046	0.1026	0.1099	0.0792	0.0939
R^2	0.9604	0.9529	0.9273	0.8929	0.9300	0.9538
300 mg/L						
q_e	22.13	25.18	24.07	14.72	19.22	19.44
k_1	0.1239	0.0834	0.0665	0.0970	0.1015	0.1011
R^2	0.9763	0.9832	0.9956	0.9565	0.9948	0.9685
400 mg/L						
q_e	29.66	28.64	21.37	19.63	26.17	13.26
k_1	0.0955	0.0787	0.0709	0.0831	0.1190	0.0980
R^2	0.9713	0.9746	0.9136	0.9728	0.9973	0.9747

$q_e = \mathrm{mg/g}$, $k_1 = \mathrm{min}^{-1}$

Table 2 Effects of temperature and initial metal ion concentration on PFOM parameters in the adsorption of Pb^{2+} and Cd^{2+} by Unmodified Kaolinite clay for the first 20 min

	Lead			Cadmium		
	298 K	313 K	323 K	298 K	313 K	323 K
300 mg/L						
q_e	4.10	3.98	3.94	3.82	3.90	4.00
k_1	0.087	0.073	0.079	0.047	0.047	0.044
R^2	0.9845	0.9196	0.8942	0.9781	0.9820	0.9790
500 mg/L						
q_e	4.80	4.36	3.70	3.34	3.40	3.43
k_1	0.078	0.074	0.063	0.084	0.069	0.07
R^2	0.9824	0.9268	0.9886	0.9790	0.9587	0.9306
1000 mg/L						
q_e	10.93	10.57	9.46	7.54	7.35	7.17
k_1	0.086	0.084	0.076	0.047	0.048	0.049
R^2	0.9634	0.9767	0.9344	0.9609	0.9473	0.9533

$q_e = \mathrm{mg/g}$, $k_1 = \mathrm{min}^{-1}$

The initial sorption rates of the metal ions onto the Unmodified adsorbent were quite lower than those of the PVA-modified adsorbent, which suggests that the modification of the adsorbent with Polyvinyl Alcohol reagent not only enhanced the adsorption capacity of the adsorbent for the adsorption of Pb^{2+} and Cd^{2+}, as seen from Tables 3 and 4, but also its initial sorption rates of adsorption for the metal ions. Initial sorption rates for Pb^{2+} and Cd^{2+} onto both adsorbents increased with increasing initial metal ion concentration.

The higher initial sorption rate, h, for the metal ions shown by PVA-modified adsorbent (Tables 3 and 4) could further suggest that the main mechanism for the adsorption of both metal ions onto this adsorbent (PVA-adsorbent) in the early stages of adsorption could be more of ion-exchange. This view was further strengthened by the large decrease in the pH of aqueous metal ion solution from 5.5 to 4.4 (up to 1.0 pH units). This decrease was observed in the first 4 min of the adsorption of both metal ions. The initial

Table 3 Effects of temperature and initial metal ion concentration on PSOM parameters in the adsorption of Pb^{2+} and Cd^{2+} by Unmodified-Kaolinite clay

	Lead			Cadmium		
	298 K	313 K	323 K	298 K	313 K	323 K
300 mg/L						
q_e	4.5	4.79	4.86	4.38	4.54	4.77
h	1.19	1.36	1.66	0.42	0.47	0.46
k_2	5.88×10^{-2}	5.93×10^{-2}	7.03×10^{-2}	2.19×10^{-2}	2.28×10^{-2}	2.02×10^{-2}
R^2	0.9939	0.9955	0.9963	0.9961	0.9968	0.9949
500 mg/L						
q_e	8.18	8.40	8.76	5.00	5.46	5.66
h	2.91	3.38	4.75	1.45	1.55	1.69
k_2	4.35×10^{-2}	4.79×10^{-2}	6.19×10^{-2}	5.80×10^{-2}	5.20×10^{-2}	5.28×10^{-2}
R^2	0.9997	0.9997	0.9999	0.9994	0.9994	0.9989
1000 mg/L						
q_e	16.31	16.75	16.84	12.32	12.38	12.39
h	3.96	4.33	5.03	2.19	2.43	2.60
k_2	1.49×10^{-2}	1.54×10^{-2}	1.77×10^{-2}	1.44×10^{-2}	1.59×10^{-2}	1.69×10^{-2}
R^2	0.9986	0.9984	0.9991	0.9980	0.9985	0.9986

$q_e = \mathrm{mg/g}$, $h = \mathrm{mg\,g^{-1}\,min^{-1}}$, $k_2 = \mathrm{g\,mg^{-1}\,min}$

Table 4 Effects of temperature and initial metal ion concentration on PSOM parameters in the adsorption of Pb^{2+} and Cd^{2+} by PVA-modified Kaolinite clay

	Lead			Cadmium		
	298 K	313 K	323 K	298 K	313 K	323 K
150 mg/L						
q_e	22.88	21.79	20.79	20.45	16.29	14.95
h	14.68	8.36	6.28	11.27	3.77	2.77
k_2	2.8×10^{-2}	1.76×10^{-2}	1.45×10^{-2}	2.69×10^{-2}	1.42×10^{-2}	1.24×10^{-2}
R^2	0.9994	0.9984	0.9966	0.9992	0.9957	0.9997
300 mg/L						
q_e	36.23	32.36	31.45	29.85	20.12	18.62
h	21.79	8.21	6.58	17.79	3.87	2.58
k_2	1.66×10^{-2}	7.84×10^{-3}	6.65×10^{-3}	2.00×10^{-2}	9.56×10^{-3}	7.44×10^{-3}
R^2	0.9993	0.9964	0.9947	0.9994	0.9929	0.9935
400 mg/L						
q_e	50.25	36.10	29.67	36.10	28.49	19.19
h	23.36	8.26	7.23	16.37	7.47	7.07
k_2	9.25×10^{-3}	6.34×10^{-3}	1.02×10^{-2}	1.26×10^{-2}	9.20×10^{-3}	1.92×10^{-2}
R^2	0.9991	0.9962	0.9963	0.9989	0.9968	0.9984

$q_e = \mathrm{mg/g}$, $h = \mathrm{mg\,g^{-1}\,min^{-1}}$, $k_2 = \mathrm{g\,mg^{-1}\,min}$

sorption rates of Pb^{2+} for both adsorbents were all higher than those for Cd^{2+}. This was also observed by Bunzl et al. (1976).

While the Unmodified adsorbent showed increasing initial sorption rates for the adsorption of both metal ions with increasing temperature, PVA-modified adsorbent showed a reverse trend (Tables 3 and 4). This suggests two things. First, that the adsorption of Pb^{2+} and Cd^{2+} onto PVA-modified and Unmodified kaolinite adsorbents are likely exothermic and endothermic in nature, respectively. This implies that increasing temperature above room temperature may not favor the adsorption of both metal ions onto PVA-modified kaolinite adsorbent and vice versa for the Unmodified kaolinite adsorbent. Secondly, it is possible that increasing temperature could have increased the mass transfer coefficients of the metal ions towards the active sites on Unmodified adsorbent, thereby reducing the time taken for the metal ions to react with the active sites on the Unmodified kaolinite adsorbent surface.

This difference in the quantity of Pb^{2+} and Cd^{2+} adsorbed onto both PVA-modified and Unmodified kaolinite may be attributable to the different affinities of the metal ions for the adsorbents surface and the type of surface complex that may have been formed between the adsorbent and the adsorbate.

The kinetic data obtained for the adsorption of Pb^{2+} and Cd^{2+} onto Unmodified and PVA-modified Kaolinite adsorbents were found to generally give better fit to the Pseudo-Second Order Kinetic model (PSOM) than the Pseudo-First Order Kinetic Model (PFOM). Kinetic data from both adsorbents failed the PFOM test. Plots of data and fits for both adsorbents using the PSOM kinetic model are shown in Figs. 2–5. The good fits of the kinetic data to PSOM shown by both adsorbents suggests that the main mechanism of adsorption of both metal ions onto the both adsorbents is chemisorption (ion-exchange mode) and some amount of Intraparticle/pore diffusion (Ho et al. 2001).

Although q_e is not a kinetic parameter but a thermodynamic parameter, q_e obtained from our kinetic plots were used in data fitting. This is because there was a good degree of agreement between the q_e obtained from kinetic test and q_{eq} from independent equilibrium tests, as can be seen from Table 7. This has also been observed in our previous study (Adebowale et al. 2008).

7.3 Kinetics of binary metal ion adsorption

The effects of the simultaneous presence of Pb^{2+} and Cd^{2+} on the kinetics of the adsorption of both metal ions onto PVA-modified and Unmodified kaolinite adsorbents are shown in Table 5.

There was an observed drop in the amount of Pb^{2+} adsorbed at equilibrium, q_e, onto the various adsorbents, when 500 mg/L of both Pb^{2+} and Cd^{2+} where present simultaneously in the aqueous solution. For example, the loading on Unmodified kaolinite adsorbent dropped about 26%, from 8.18 mg/g to 6.03 mg/g. Similarly, there was also a decrease in the amount of Cd^{2+} adsorbed at equilibrium of about 1.4%, from 5.00 mg/g to 4.93 mg/g. Thus, the decrease was more for the adsorption of Pb^{2+} than for Cd^{2+}. This could suggest that Cd^{2+} can compete effectively with Pb^{2+} for the adsorption sites on the surfaces of both adsorbents.

With changing ratios of the initial concentrations of both metal ions present in solutions, the Unmodified adsorbent tend to show stronger preference for Pb^{2+} than Cd^{2+} although its initial sorption rates for both metal ions was reduced for Pb:Cd ratios of 100:500 and 500:100 This is also the case with their respective overall kinetic rate constant,

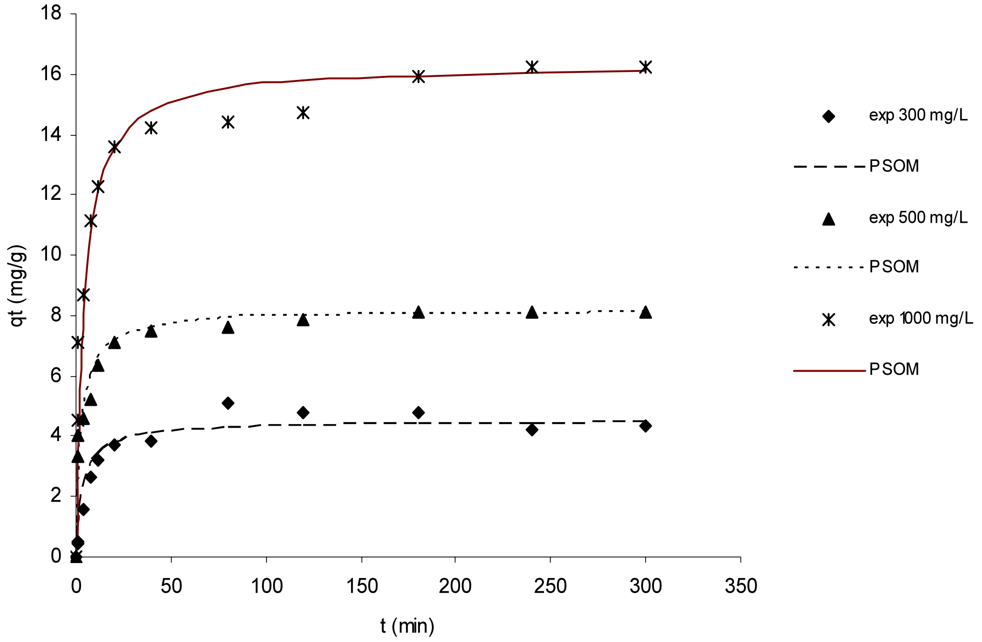


Fig. 2 Pseudo-second order kinetic model plot for adsorption of Pb^{2+} onto Unmodified Kaolinite clay

Fig. 3 Pseudo-second order kinetic model plot for adsorption of Cd^{2+} onto Unmodified Kaolinite clay

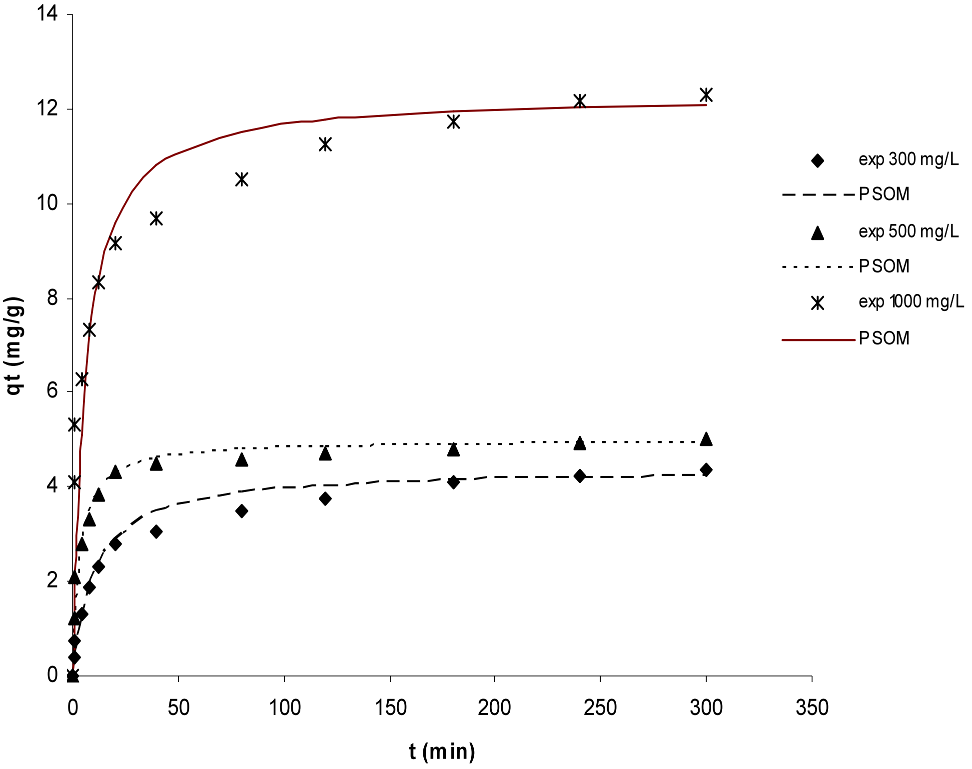
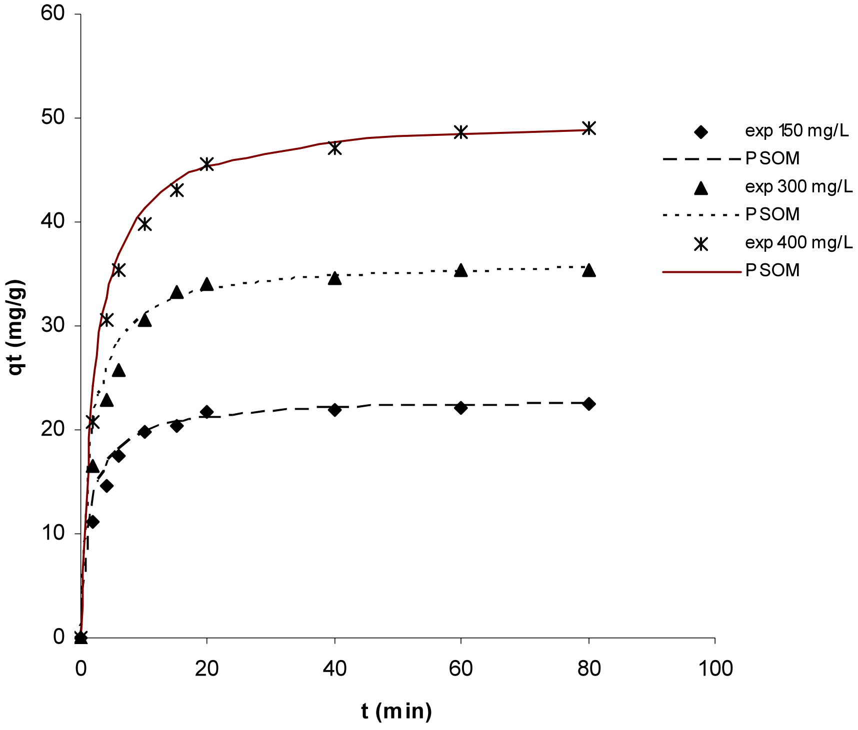


Fig. 4 Pseudo-second order kinetic model plot for adsorption of Pb^{2+} onto PVA-modified Kaolinite clay



k_3 (Table 5). However, at a Pb:Cd ratio of 100:500, the initial sorption rate of Cd^{2+} onto the unmodified adsorbent was higher than that for Pb^{2+}, even though the overall kinetic rate for the adsorption of Pb:Cd at this ratio was higher. This could suggest that in the early stages of the adsorption process Cd^{2+} competes with Pb^{2+} very strongly for adsorp-

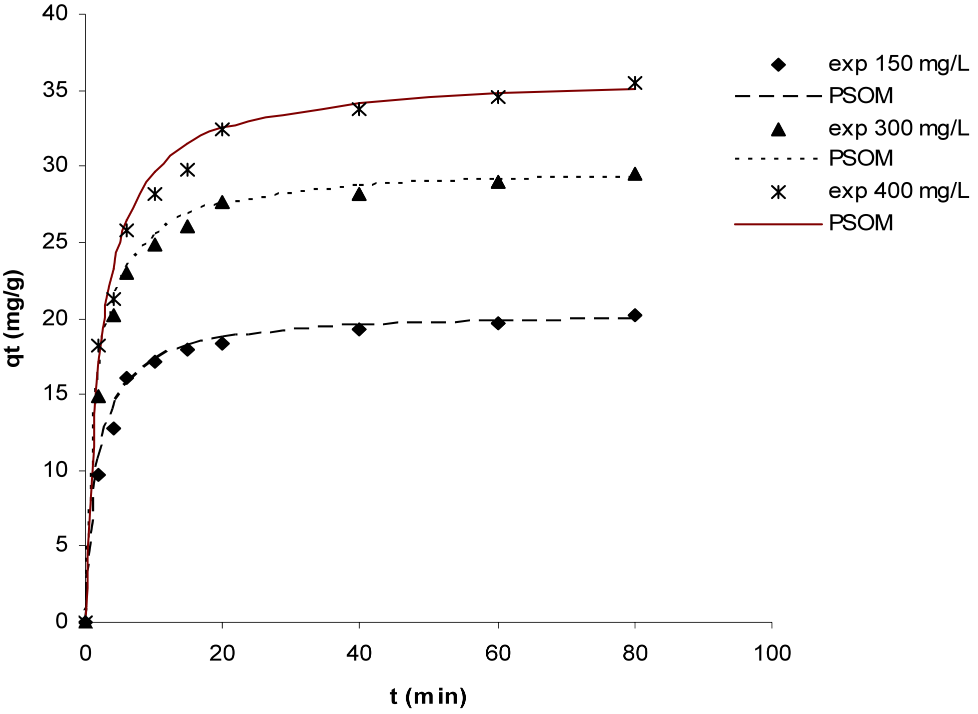


Fig. 5 Pseudo-second order kinetic model plot for adsorption of Cd^{2+} onto PVA-modified Kaolinite clay

Table 5 Effect of the adsorption of binary solutions of Pb^{2+} and Cd^{2+} on the PSOM parameters (Unmodified adsorbent)

Kinetic parameters	Lead			Cadmium		
	500:500*	500:100*	100:500*	500:500*	500:100*	100:500*
q_e	6.03 (26.3%↓)	6.46 (21.0%↓)	1.43 (20.6%↓)	4.93 (0.07%↓)	0.97 (13.4%↓)	4.50 (5.5%↓)
h	1.53	2.20	0.53	1.03	0.18	1.36
k_3	4.21×10^{-2}	5.28×10^{-2}	2.59×10^{-1}	4.25×10^{-2}	1.93×10^{-1}	3.22×10^{-2}
R^2	0.9997	0.9997	0.9998	0.9994	0.9991	0.9993

$q_e = \text{mg/g}$, $h = \text{mg g}^{-1}\text{ min}^{-1}$, $k_3 = \text{g mg}^{-1}\text{ min}$; *Pb:Cd ratio in mg/L; ↓= percentage decrease in adsorption capacity

tion sites on the Unmodified kaolinite adsorbent in an aqueous solution containing same concentration of both metal ions, as mentioned above.

As the adsorption reaction progressed in the binary metal ion solutions, the overall PSOM kinetic rate constant k_3, in which the subscript 3 is used to differentiate it from k_2, which is the rate constant for the uptake version of the PSOM in a single metal ion solution, increased for Pb^{2+} adsorption.

The results above suggest a higher affinity for Pb^{2+} than for Cd^{2+}, by Unmodified Kaolinite adsorbent, even in a binary solution of Pb^{2+} and Cd^{2+}. This observation appears to be true, despite the larger ionic size of Pb^{2+} compared with that of Cd^{2+}, and despite the strong competition from Cd^{2+} for adsorption sites on the Unmodified kaolinite adsorbent in the initial stages of the adsorption reaction.

Srivastava et al. (2005), showed that metal ions that form hydrolysis products more readily (Pb^{2+} and Cu^{2+}), adsorb to variable charge surfaces from about pH 5.0 and above. Due to its tendency to form hydrolysis products, Pb^{2+} does not compete effectively for permanent charge surfaces, and so its adsorption is more restricted to variable charged sites; hence, we see an increased overall uptake rate of Pb^{2+} as against Cd^{2+}, at these sites. The Unmodified kaolinite adsorbent is known to possess more variable charged sites than permanent charged sites (Spark et al. 1995; Ikhsan et al. 1999; Srivastava et al. 2005). Thus, Pb^{2+} would tend to be adsorbed more on the variable charged sites than Cd^{2+} when both are simultaneously present in the solution. This could have suppressed the adsorption of Cd^{2+} onto such sites and subsequently reduce the overall adsorption capacity of the Unmodified adsorbent for Cd^{2+}.

During preliminary investigations on the adsorptive properties of the PVA-modified Kaolinite adsorbent (only one data point for each metal), it was observed that, in 2 min, the uptakes of single metal ion solutions of 60 mg/L Pb^{2+}

Table 6 Effect of the adsorption of binary solutions of Pb^{2+} and Cd^{2+} on the PSOM parameters (PVA-modified adsorbent)

Kinetic parameters	Lead		Cadmium	
	60:60*	150:60*	60:60*	150:60*
q_e	12 (ND)	11.24 (50.9%↓)	10.87 (27.5%↓)	8.48 (58.5%↓)
h	–	26.46	5.83	8.22
k_3	–	2.10×10^{-1}	4.94×10^{-2}	1.14×10^{-1}
R^2	–	1.0000	0.9983	0.9992

$q_e = \text{mg/g}$, $h = \text{mg g}^{-1}\text{ min}^{-1}$, $k_3 = \text{g mg}^{-1}\text{ min}$; *Pb:Cd ratio in mg/L; ND = not detected, ↓= percentage decrease in adsorption capacity

Table 7 q_e obtained from kinetic test and q_{eq} from equilibrium test for adsorption of 300 mg/L Pb^{2+}

	Lead			Cadmium		
	298 K	313 K	323 K	298 K	313 K	323 K
Unmod	4.46(4.50)	4.77(4.79)	4.89(4.86)	4.39(4.38)	4.49(4.54)	4.65(4.77)
PVA-Mod	35.98(36.23)	31.25(32.36)	30.88(31.45)	29.70(29.85)	20.46(20.12)	18.64(18.62)

Note: Values in bracket are q_e obtained from kinetics at same 300 mg/L of metal ions for equilibrium test

and Cd^{2+} were complete with no detectable amount of either metal ion. Further study is necessary, and additional work is forthcoming. However, in binary solutions of both metal ions, there was a decrease in the amount of both metal ions adsorbed, except for the adsorption of Pb^{2+} onto PVA-modified kaolinite adsorbent in a binary mixture of 60:60 mg/L Pb:Cd, where there was no detectable amount of Pb^{2+}. For PVA-modified adsorbent, Table 6 suggests that adsorption of Pb^{2+} at 60:60 Pb:Cd ratio was ≈100%, while some small amounts of Cd^{2+} were still found in the equilibrium solution (Table 6). Both initial sorption rate and overall kinetic rate for the adsorption of Pb^{2+} onto PVA-modified adsorbent were higher than those for Cd^{2+}. This may indicate that the rate adsorption of Pb^{2+} onto PVA-modified Kaolinite clay adsorbent from binary solutions of Pb:Cd at ratios of 60:60 mg/L and 150:60 mg/L is higher than for Cd^{2+} onto the same adsorbent.

8 Desorption kinetics

Approximately 95% and 99% desorption of 60 mg/L of both metals from both Unmodified and PVA-modified Kaolinite adsorbents, respectively, were achieved within 3 min. PVA-modified adsorbent gave the best desorption efficiency of 99% for both metal ions. On using the recovered adsorbent for adsorption of metal ions, only 80% of the metal ions were adsorbed on the Unmodified Kaolinite adsorbent, but as much as 95% for the PVA-modified Kaolinite adsorbent. This might be due to the fact that the acid used for desorption may have negatively affected some adsorption sites available for the adsorption of these metal ions in the Unmodified Kaolinite adsorbent. Figure 6 depicts desorption kinetics plots for both adsorbents.

9 Conclusions

- Modification of Kaolinite clay with Polyvinyl Alcohol reagent made the Kaolinite particles water-stable and active for adsorption of Pb^{2+} and Cd^{2+} from aqueous solution.
- Modification of Kaolinite clay with PVA increased its adsorption capacity by at least 6-fold for 300 mg/L Pb^{2+} and Cd^{2+}, from 4.5 mg/g to 36.23 mg/g and from 4.38 mg/g to 29.85 mg/g, respectively, at 298 K.
- The PSOM rate constants for the adsorption of both Pb^{2+} and Cd^{2+} onto Kaolinite clay adsorbent were observed to decrease when it was modified with Polyvinyl Alcohol reagent.
- Kinetic data showed a better fit to the PSOM than to the PFOM. The kinetic data failed the PFOM test after 20 min.
- Binary mixtures of Pb^{2+} and Cd^{2+} decreased the adsorption capacity of both Unmodified and PVA-modified Kaolinite adsorbents.
- 95% and 99% desorption of 60 mg/L of both Pb^{2+} and Cd^{2+} from both Unmodified and PVA-modified Kaolinite adsorbents, respectively, were achieved within 3 min.
- Although the single cycle of adsorption-desorption equilibrium studies as used in this study is not enough to sufficiently assess the desorption capacity of a desorption reagent, this desorption study has demonstrated that

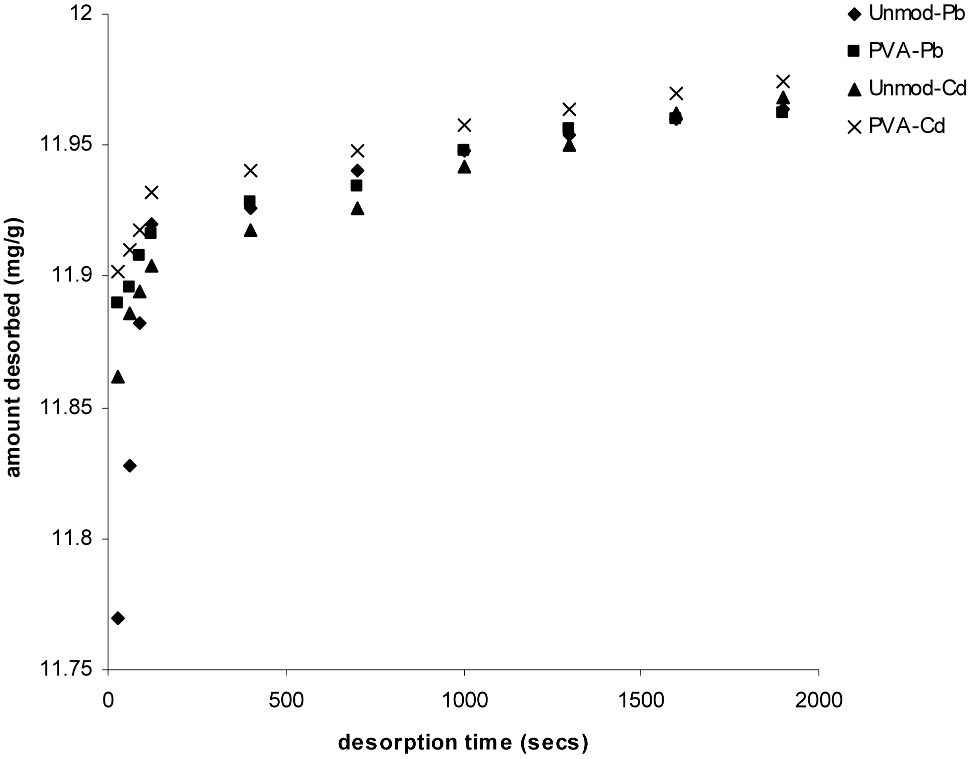


Fig. 6 Desorption kinetics for Unmodified and PVA-modified Kaolinite clay adsorbents

both Unmodified and PVA-modified Kaolinite adsorbents could be reused for adsorption of metal Pb^{2+} and Cd^{2+} from waste streams especially with the PVA-modified Kaolinite adsorbent. The results of this investigation are quite useful for further research. The study could be beneficial to small and medium scale industries.

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