



Comparison of two-stage sorption design models for the removal of lead ions by polyvinyl-modified Kaolinite clay

E.I. Unuabonah^{a,*}, B.I. Olu-owolabi^b, D. Okoro^c, K.O. Adebowale^b

^a Department of Chemical Sciences, College of Natural Sciences, Redeemer's University, Km 46, Lagos-Ibadan Expressway, Redemption City, Ogun State, Nigeria

^b Faculty of Science, Department of Chemistry, University of Ibadan, Ibadan, Nigeria

^c College of Sciences, Department of Chemistry, Federal University of Petroleum Resources, Effurun, Nigeria

ARTICLE INFO

Article history:

Received 13 January 2009

Received in revised form 26 May 2009

Accepted 27 May 2009

Available online 6 June 2009

Keywords:

Optimization

Clay

Two-stage

Kaolinite clay

Models

Batch adsorption

ABSTRACT

Kaolinite clay obtained from Ubulu-Ukwu, Delta State in Nigeria was modified with polyvinyl-alcohol (PVA) reagent to obtain PVA-modified Kaolinite clay. Kinetic and equilibrium data were obtained for the batch adsorption of Pb²⁺ onto PVA-modified Kaolinite clay.

Time-dependent Langmuir and pseudo-second order kinetic models (TDLM and PSOM) were developed to predict the optimized minimum operating time for the adsorption of Pb²⁺ onto PVA-modified Kaolinite clay in a two-stage batch adsorber system. Results obtained suggest that the two-stage batch adsorber process leads to improved contact time and increased percentage Pb²⁺ removal.

Data from both models (TDLM and PSOM) were compared using *t*-test and *F*-test and were found to be precise enough for use in the optimization of kinetic data for a two-stage adsorption of Pb²⁺ ions from aqueous solution.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Contamination of water with heavy metal ions from aqueous waste streams of industries such as metal plating, mining operations, tanneries, smelting, etc., has become a serious threat to both the environment and health of man and animals. Increased concern about the environment and the health of man has led to various national and international regulations on water pollution. In recent years, scientists have been involved in research to find cheap alternative source of adsorbents and cost-effective technologies for the removal of heavy metal ions from water and wastewater solutions.

Information on the adsorption kinetics and equilibrium is needed for adsorbent evaluation and process design and optimization. Such information is usually obtained from experimental studies. Mathematical models are then developed and validated based on this information.

Batch adsorption process has over the years gained wide acceptability because unlike fixed adsorption process, there is little or no pressure drop as a result of particle size of adsorbent. Besides, agitation improves the adsorption better than fixed bed method because of reduced mass transfer resistance at the adsorbate–adsorbent interface.

Previous optimization models for batch adsorbers were based on minimizing the mass of the adsorbent required to remove certain concentration of metal ion from a fixed volume of wastewater. This optimized parameter becomes critical when expensive adsorbents such as activated carbon and zeolites are involved [1].

Using cheaper adsorbents and minimizing contact time required to achieve a desired percentage removal of the metal ion with a fixed adsorbent dose will enable the treatment of more batches of polluted wastewater per day. This will lead to reduction in process plant equipment size and ultimately a decrease in capital cost of treatment [1].

Clay minerals usually referred to as phyllosilicates, have been found to be effective adsorbents for metal ions. However, there is the problem of their recovery from filters after use which makes them less attractive as adsorbents when compared with activated carbon.

Previous articles have discussed the use of the pseudo-second order kinetic model for the optimization of minimum contact time in a two-stage batch adsorption process [2–4]. In same vein, there are only two articles (Ho and McKay [1] and Unuabonah et al. [5]) on the use of the time-dependent Langmuir model for the optimization of minimum contact time in a two-stage batch adsorption process using equilibrium data. However, comparison of data from both two-stage pseudo-second order kinetic and two-stage time-dependent Langmuir have not being made to ascertain how reliable either model could be for use on kinetic or equilibrium data obtained from a one-stage batch adsorption process.

* Corresponding author. Tel.: +234 805 3175 971.

E-mail address: iyaemma@yahoo.com (E.I. Unuabonah).

This paper therefore, reports the optimization of equilibrium and kinetic data obtained for the adsorption of Pb^{2+} onto a new adsorbent called polyvinyl-modified Kaolinite clay adsorbent (PVA-modified Kaolinite clay adsorbent) which is water-stable and quite efficient in the removal of Pb^{2+} from aqueous solution [6]. This was achieved using two-stage adsorber design models- two-stage time-dependent Langmuir model and two-stage pseudo-second order kinetic model initially developed by Ho and McKay [1,7] respectively. The principle behind the models is based on predicting the minimum contact time required to adsorb a fixed percentage of adsorbate from a given volume of wastewater effluent of specified adsorbate concentration, using a fixed mass of the adsorbent. This minimum contact time enables the minimum size of the batch adsorption equipment to be specified and therefore minimize capital investment costs.

Data from both models were further compared statistically to determine the suitability of either model for optimizing kinetic and equilibrium data for minimum contact time in a two-stage batch adsorption process.

Data used for the model analysis were kinetic and equilibrium data for the adsorption of Pb^{2+} onto PVA-modified Kaolinite clay.

2. Materials and methods

Kaolinite clay used in this study 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. It was further purified by method described in our previous work [8].

2.1. Modification of clay sample

The Kaolinite was acid treated with 2 M HNO_3 for 1 h 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 220 μm . This was the same particle size of the Unmodified Kaolinite adsorbent used throughout the experiment.

2.2. Adsorption equilibrium study

The pH of the metal ion solutions for polyvinyl alcohol modified adsorbent (PVA-modified kaolinite clay sample) were adjusted to 5.5 ± 0.05 . Batch adsorption experiments were performed at room temperature ($28.0 \pm 2^\circ\text{C}$) on a rotary shaker at 100 rpm, using 120 mL capped polyethylene bottles containing 20 mL of 60–400 mg/L of Pb^{2+} solutions and 0.1 g of PVA-modified kaolinite clay adsorbents for 5 h. After agitation, the suspensions were centrifuged at 1500 rpm for 15 min and supernatant kept for Pb^{2+} analysis.

2.3. Kinetics of adsorption

The points of zero charge (PZC) of the unmodified and PVA-modified kaolinite clay adsorbents were found to be 4.40 and

4.25, respectively. A series of adsorption experiments were carried within a pH range of 4.0–7.0 and it was observed that adsorption of Pb^{2+} increased with increasing pH. It was observed that at pH 5.0 the percentage Pb^{2+} precipitated from 300 mg/L Pb^{2+} solution was 4.5% while at 6.0 it was 8.75%. It increased up 27.5% at pH 7.0. Using the information from both PZC and percentage precipitation it was decided that the adsorption reaction in this research work be carried out at pH 5.5 [6].

A stock solution of 1000 mg/L Pb^{2+} was prepared from its nitrate using distilled-deionized water. 150, 300, 400 mg/L of metal ion solutions of Pb^{2+} was prepared and their pH adjusted to 5.5 ± 0.01 with either 0.1 M HCl or 0.1 M NaOH. For kinetic measurements, 5 g in 1 L of the PVA-modified Kaolinite adsorbent was used. A power stirrer with impeller blades 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 and 80 min, filtered through a 0.45 μm millipore filter paper and made up to 5 mL. The samples collected were then analyzed for Pb^{2+} using ICPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy) IRIS Advantage model (made by Thermo Fisher). This procedure was carried out for samples at 298, 313 and 323 K.

The amounts of lead ions adsorbed by the adsorbent were calculated by difference using the formula:

$$q_e = (C_o - C_e) \times V/W \quad (1)$$

where C_o is the initial concentration of metal ion (mg/L), C_e the equilibrium concentration of metal ion (mg/L), V is the volume of metal ion (mL), W is the weight of adsorbent used (g) and q_e is the amount of metal ion adsorbed (mg/g).

2.4. Adsorption kinetic models

The pseudo-second order kinetic model (PSOM) is obtained as follows:

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

On rearrangement and integration

$$\frac{1}{q_e - q_t} - \frac{1}{q_e} = kt \quad (3)$$

When this is linearized, it gives

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (4)$$

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

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

$$h = kq_e^2 \quad (5)$$

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

The non-linear form Eq. (8) is:

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \quad (6)$$

3. Results and discussions

3.1. Physicochemical properties

In our previous study it was observed that the adsorption capacity of PVA-clay Kaolinite clay adsorbent was over 8 times that of Unmodified Kaolinite clay for the adsorption of Pb^{2+} . The Scanning Electron Microscopy of PVA-modified Kaolinite clay adsorbent has

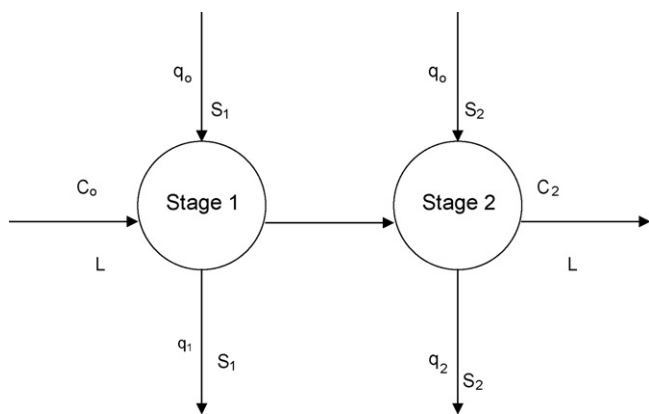


Fig. 1. Schematic diagram for a two-stage countercurrent batch adsorption process.

been presented in our previous works [9,10]. The specific surface area (SSA) of PVA-clay was $7.92 \text{ m}^2 \text{ g}^{-1}$ while the SSA of Unmodified Kaolinite clay adsorbent was $10.56 \text{ m}^2 \text{ g}^{-1}$. The observed decrease in SSA did not in any way affect the efficiency of the PVA-modified Kaolinite clay adsorbent as it was more efficient than the unmodified adsorbent in the adsorption of Pb^{2+} . This is because the decrease in surface area was well compensated for by the increase in active sites available for the adsorption of metal ions, on the surface of the modified adsorbent [5].

The point of zero charge (the pH at which the sum total of the charges on the surface an adsorbent is zero) of both Unmodified and PVA-modified Kaolinite clay adsorbents were found to be 4.40 and 4.25 respectively. This implies that at pH values above the PZC of the adsorbent (4.25) the surface of the PVA-modified Kaolinite clay adsorbent will possess increasing amount of negative charges while below this charges will be positive. The cation exchange capacity (CEC) of PVA-modified Kaolinite clay adsorbent was determined to be 51.04 meq/100 g adsorbent [5] while that for the Unmodified Kaolinite clay was 7.81 meq/100 g adsorbent [7].

3.2. Batch adsorber analysis

3.2.1. Two-stage pseudo-second order model

Kinetic equations can be used to predict the design of two-stage crosscurrent batch adsorption systems [2,3,6,11,12]. The basis of this model is now discussed. A schematic diagram for a two-stage adsorption system is shown in Fig. 1.

The solution to be treated contains $L \text{ (dm}^3\text{)}$ solution and the Pb^{2+} concentration is reduced for each stage from C_0 to C_1 (mg/dm^3). The amount of adsorbent added is S (g) with solid-phase Pb^{2+} concentration on the PVA-modified Kaolinite clay adsorbent q_0 (mg/g). Thus, Pb^{2+} concentration on the adsorbent increases from q_0 to q_1 (mg/g) adsorbent. The mass balance equation gives [8].

$$L(C_{n-1} - C_n) = S(q_{t,n} - q_0) \quad (7)$$

If at each stage certain amount of the adsorbent is used for the adsorption, the pseudo-second order equation can then be used to describe the equilibrium in the two-stage adsorption system. Thus the mass balance equation can be obtained by combining Eqs. (6) and (7):

$$C_n = C_{n-1} - \frac{Skq_{e,n}^2 t}{L(1 + kq_{e,n}t)} \quad (8)$$

The total amount of Pb^{2+} removal can be calculated analytically as follows.

$$\sum_{n=1}^N C_{n-1} - C_n = \sum_{n=1}^N \frac{100Skq_{e,n}^2 t}{LC_0(1 + kq_{e,n}t)} \quad (9)$$

where n is the adsorption system number ($n = 1, 2, 3, 4, \dots, N$).

The Pb^{2+} removal, R_n , in each stage can be evaluated from the equation as follows:

$$R_n = \frac{100(C_{n-1} - C_n)}{C_0} = \frac{100Skq_{e,n}^2 t}{LC_0(1 + kq_{e,n}t)} \quad (10)$$

The total removal of Pb^{2+} can be calculated analytically as follows:

$$\sum_{n=1}^N R_n = \frac{100S}{LC_0} \sum_{n=1}^N \frac{kq_{e,n}^2 t}{1 + kq_{e,n}t} \quad (11)$$

The corresponding linear plots of the values of q_e and k against initial Pb^{2+} concentrations C_0 were regressed to obtain expressions for these values in terms of the initial Pb^{2+} concentration [4]. High correlation coefficients were obtained as shown in Table 1. Therefore it is useful for process design purposes if q_e and k can be expressed as a function of C_0 for adsorption of metal ion onto PVA-modified Kaolinite clay as follows:

$$q_e = X_{q_e} C_0^{Y_{q_e}} \quad (12)$$

$$k = X_k C_0^{Y_k} \quad (13)$$

Substituting the values of q_e and k from Eqs. (12) and (13) into Eqs. (10) and (11), gives:

$$R_n = \frac{100S(X_k C_{n-1}^{Y_k})(X_{q_e} C_{n-1}^{Y_{q_e}})^2 t}{LC_0[1 + (X_k C_{n-1}^{Y_k})(X_{q_e} C_{n-1}^{Y_{q_e}})t]} \quad (14)$$

$$\sum_{n=1}^N R_n = \frac{100S}{LC_0} \sum_{n=1}^N \frac{(X_k C_{n-1}^{Y_k})(X_{q_e} C_{n-1}^{Y_{q_e}})^2 t}{[1 + (X_k C_{n-1}^{Y_k})(X_{q_e} C_{n-1}^{Y_{q_e}})t]} \quad (15)$$

Eqs. (7)–(15) were developed by Ho and McKay [4]. Eqs. (14) and (15) can be used to predict the removal of Pb^{2+} at any given initial Pb^{2+} concentration and the reaction time for any multi-stage system.

When q_e and k against initial Pb^{2+} concentration were regressed, the following equations were obtained:

$$q = 0.4592C_0^{0.7765} \quad r^2 = 0.9813 \quad (16)$$

$$k = 5.96C_0^{-1.0601} \quad r^2 = 0.9306 \quad (17)$$

When these were

$$\sum_{n=1}^N R_n = \frac{100S}{LC_0} \sum_{n=1}^N \frac{(5.96C_{n-1}^{-1.0601})(0.4592C_{n-1}^{0.7765})^2 t}{[1 + (5.96C_{n-1}^{-1.0601})(0.4592C_{n-1}^{0.7765})t]} \quad (18)$$

3.2.2. Two-stage time-dependent Langmuir model

Batch adsorption equilibrium can be represented by the Langmuir isotherm as derived and applied by Ho and McKay [1]:

$$q_e = \frac{Q_{m,e} b_{L,e} C_e}{1 + b_{L,e} C_e} \quad (19)$$

where q_e = the sorption capacity at the equilibrium of solute concentration C_e ($\text{mg metal ion g}^{-1}$ adsorbent); C_e = the concentration of adsorbate in solution ($\text{mg metal ion L}^{-1}$); $Q_{m,e}$ = the maximum adsorption capacity corresponding to complete monolayer coverage ($\text{mg metal ion g}^{-1}$ adsorbent); $b_{L,e}$ = Langmuir constant related to the energy of sorption ($\text{L}^{-1} \text{ mg}^{-1}$).

This is for a single batch adsorber system and does not incorporate the time factor. The parameters C_e and q_e are equilibrium values and such single batch adsorber system require long contact times for the sorption system to reach complete equilibrium saturation which invariably leads to unreasonably long hold-up times. To circumvent this problem, it is therefore better to replace these values by more realistic time-dependent liquid phase concentrations, $C_{e,t}$,

Table 1
Adsorption times (min) for the adsorption of various percentage removal of Pb²⁺ for a series of two-stage batch adsorption systems using PSOM.

System no.	Stage 1	Stage 2			
	Contact time	95% Removal time (min)	90% Removal time (min)	85% Removal time (min)	80% Removal time (min)
1	2	35.5	33.7	31.8	29.9
2	4	27.0	25.6	24.2	22.7
3	6	24.2	22.9	21.6	20.4
4	8	22.8	21.6	20.4	19.2
5	10	21.9	20.7	19.6	18.5
6	12	21.3	20.2	19.1	18.0
7	14	20.9	19.8	18.7	17.6
8	16	20.6	19.5	18.5	17.4
9	18	20.4	19.3	18.2	17.2
10	20	20.2	19.1	18.1	17.0
11	22	20.1	19.0	17.9	16.9
12	24	19.9	18.9	17.8	16.8
13	26	19.8	18.8	17.7	16.7
14	28	19.7	18.7	17.6	16.6
15	30	19.6	18.6	17.6	16.5

and adsorbed phase concentrations, $q_{e,t}$. Nevertheless, for a multi-stage adsorber, the question of how the mass balance equation can be solved and optimized to minimize total batch contact time arises. To provide solutions to these questions the time-dependent Langmuir type equation was developed.

$$q_{e,t} = \frac{Q_{m,t} b_{L,t} C_t}{1 + b_{L,t} C_t} \quad (20)$$

The values of twelve sample times from 2 to 30 min for Pb²⁺ are given in Table 1 with their various effective time dependent Langmuir equation parameters for the different fixed contact times. The correlation coefficients are in the range of 0.9840–0.9950. Linear plots of $Q_{m,t}$ and $b_{L,t}$ against time were made and their values were regressed to obtain expressions of $Q_{m,t}$ and $b_{L,t}$ as a function of time.

For the adsorption of Pb²⁺ ions onto PVA-modified Kaolinite clay adsorbent

$$Q_{m,t} = \frac{t}{1.60 \times 10^{-2} t + 0.0237} \quad r^2 = 0.9988 \quad (21)$$

$$b_{L,t} = \frac{t}{64.034t + 120.15} \quad r^2 = 0.9532 \quad (22)$$

$$q_{e,t} = \frac{(t/(1.60 \times 10^{-2} t + 0.0237))(t/(64.034t + 120.15))C_{e,t}}{1 + (t/(64.034t + 120.15))C_{e,t}} \quad (23)$$

where $Q_{m,t}$ and $b_{L,t}$ are time dependent equilibrium adsorption capacity and time dependent Langmuir constant related to the energy of adsorption. Eq. (23) can be used to predict the amount of Pb²⁺ adsorbed for any sorption contact time.

The mass balance equation for the use of fresh adsorbent at each stage ($q_0 = 0 \text{ mg g}^{-1}$) using the time-dependent Langmuir expression of Eq. (23) to describe the amount of metal ion adsorbed at

Table 2
Fixed time dependent langmuir equation parameters for the adsorption of Pb²⁺ onto PVA-modified Kaolinite clay adsorbent.

Time (min)	$Q_{m,t}$ (mg/g)	b (g mg ⁻¹ min)	r^2
2	30.96	5.86×10^{-3}	0.9815
4	49.50	5.35×10^{-3}	0.9744
6	45.87	9.85×10^{-3}	0.9321
10	51.55	1.22×10^{-3}	0.9669
15	61.35	1.03×10^{-3}	0.9825
20	57.47	1.44×10^{-3}	0.9564
40	60.24	1.40×10^{-3}	0.9511
60	62.50	1.39×10^{-3}	0.9458
80	60.24	1.59×10^{-3}	0.9386

final state in a multi-stage sorption system is:

$$C_n = C_{n-1} - \frac{(t/(1.60 \times 10^{-2} t + 0.0237))(t/(64.034t + 120.15))C_{e,t}}{1 + (t/(64.034t + 120.15))C_{e,t}} \quad (24)$$

The total amount of Pb²⁺ adsorbed onto PVA-modified Kaolinite clay adsorbent can be calculated analytically from the equations below

$$\sum_{n=1}^N C_{n-1} - C_n = \sum_{n=1}^N \frac{S(t/(1.6 \times 10^{-2} t + 0.0237))(t/(64.034t + 120.15))C_n}{L[1 + (t/(64.034t + 120.15))C_n]} \quad (25)$$

where n is the adsorption system number ($n = 1, 2, 3, 4, \dots, N$). S and L are the weight adsorbent (g) and volume of adsorbate (L).

The percentage Pb²⁺ removal, R_n , in each stage can be evaluated from the equation below.

$$R_n = \frac{100(C_{n-1} - C_n)}{C_0} = \frac{S(t/(1.60 \times 10^{-2} t + 0.0237))(t/(64.034t + 120.15))C_n}{L[1 + (t/(64.034t + 120.15))C_n]} \quad (26)$$

The total metal ion adsorbed can be determined analytically from the following equation

$$\sum_{n=1}^N R_n = \frac{100S}{LC_0} \sum_{n=1}^N \frac{(t/(1.60 \times 10^{-2} t + 0.0237))(t/(64.034t + 120.15))C_n}{[1 + (t/(64.034t + 120.15))C_n]} \quad (27)$$

Let us consider a two-stage sorption system where 2 kg of PVA-modified Kaolinite clay is used to treat 2.5 m³ of wastewater containing 300 mg/L of Pb²⁺. Figs. 2 and 4 show the reaction time for a set of 15 two-stage sorption systems in series for each individual stage and for the combined total of the two-stages. Each of the 15 systems representing the x -axes in Figs. 2 and 4 was based on a 2 min contact time interval in the first adsorber starting with system 1 at 2 min. A series of contact times from 2 min up to 30 min in a 2 min increment has been considered in stage one of a two-stage sorption system for the sorption of Pb²⁺. In the first adsorber, for example, system number 10 implies that the first adsorber contact time is 2 min + (10 – 1)2 min = 20 min since system number 1 represents 2 min contact time in adsorber number 1. Thus, the contact

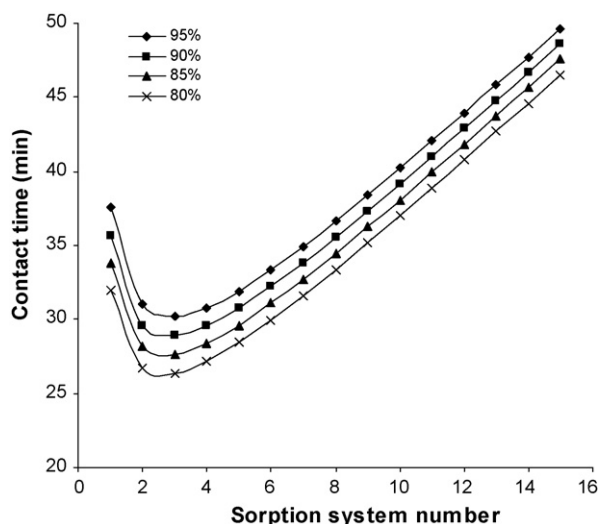


Fig. 2. Minimum contact time for the various percentage Pb²⁺ removal in a two-stage adsorption process using PSOM.

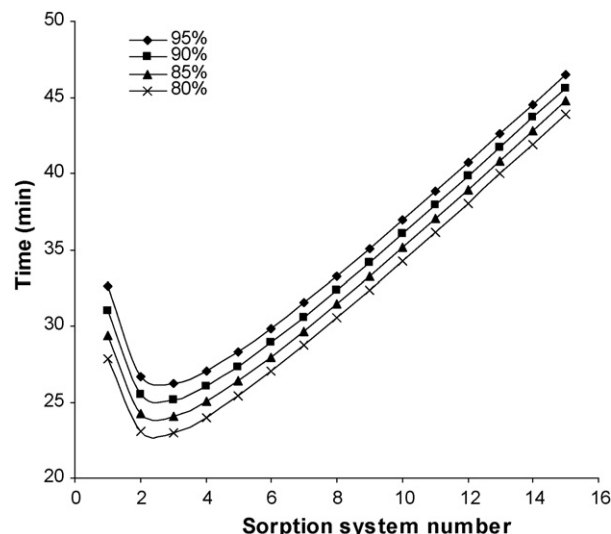


Fig. 3. Minimum contact time for the various percentages of Pb²⁺ removal in a two-stage adsorption process using TDLM.

time in the second adsorber, t_2 , is the time required, T (min), to achieve a fixed total percentage of Pb²⁺ removal minus the contact time in the first adsorber stage t_1 , therefore:

$$T = t_1 + t_2$$

For N systems, t_1 , becomes

$$t_1 = 2 + (N - 1)2 \dots \text{min}$$

The total batch contact time, T , is

$$T = 2 + (N - 1)2 + t_2$$

The total contact time for each system number is calculated based on the fixed t_1 values for a particular percentage removal of the metal ion. The plots of T vs system number are shown in Figs. 3 and 5. Tables 2 and 3 shows a series of sorption system $N=1-15$ and the contact times for each stage at a particular percentage removal. Figs. 2 and 3 shows the minimum contact time for the various percentages of Pb²⁺ adsorbed onto PVA-modified Kaolinite clay adsorbent. The minimum total contact time for the

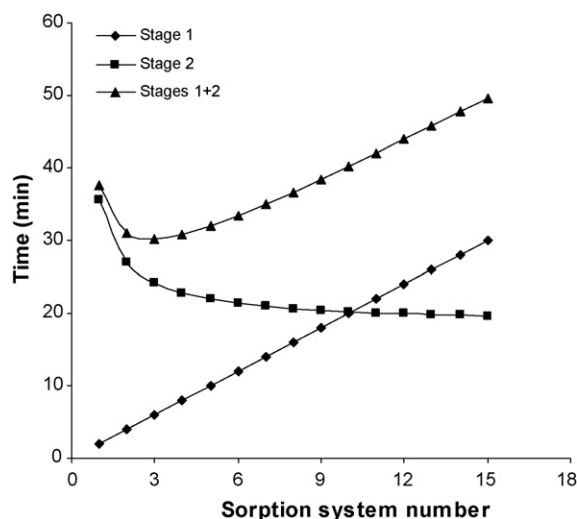


Fig. 4. Comparison of 95% Pb²⁺ ion adsorption time by PVA-modified Kaolinite clay for each stage in a two-stage batch adsorption process using PSOM.

Table 3

Adsorption times (min) for the adsorption of various percentage removal of Pb²⁺ for a series of two-stage batch adsorption systems using TDLM.

System no.	Stage 1	Stage 2			
	Contact time	95% Removal time (min)	90% Removal time (min)	85% Removal time (min)	80% Removal time (min)
1	2	30.6	29.0	27.4	25.8
2	4	22.7	21.5	20.3	19.1
3	6	20.2	19.1	18.1	17.0
4	8	19.0	18.0	17.0	16.0
5	10	18.3	17.3	16.4	15.4
6	12	17.8	16.9	16.0	15.0
7	14	17.5	16.7	15.7	14.7
8	16	17.3	16.3	15.4	14.5
9	18	17.1	16.2	15.3	14.4
10	20	16.9	16.0	15.1	14.2
11	22	16.8	15.9	15.0	14.1
12	24	16.7	15.8	14.9	14.1
13	26	16.6	15.7	14.9	14.0
14	28	16.5	15.7	14.8	13.9
15	30	16.5	15.6	14.7	13.9

Table 4
Minimum adsorption times (min) to achieve various percentage of Pb²⁺ removals for a series of two-stage adsorption system using PVA-modified Kaolinite clay.

%Removal	System no.	Stage 1 (min)	Stage 2 (min)	Total (min)
PSOM				
95	3	6	24.2	30.2
90	3	6	22.1	28.1
85	3	6	21.6	27.6
80	3	6	20.4	26.4
TDLM				
95	3	6	20.2	26.2
90	3	6	19.1	25.1
85	3	6	18.1	24.1
80	3	6	17.0	23.0

various percentages of Pb²⁺ removals in the two-stage crosscurrent batch sorption process is calculated using Eqs. (18) and (27).

The various minimum total contact times for a two-stage crosscurrent batch adsorption of Pb²⁺ onto PVA-modified Kaolinite clay adsorbent are shown in Table 4 for both PSOM and TDLM. The minimum contact time for 95% Pb²⁺ removal is 30.2 min for PSOM and 26.2 min for TDLM for same system number.

It was observed for both models that increasing percentage removal of Pb²⁺ required increasing minimum contact time (Table 4). The time required to treat effluent in the second-stage decreased with increasing first-stage contact time. The system numbers for each percentage removal were all the same for both models. This might suggest that the reaction reaches equilibrium at approximately the same time for any percentage removal of Pb²⁺ with either model. However, for all our sorption reaction in the one-stage sorption process of Pb²⁺, using PVA-modified Kaolinite clay, equilibrium was observed to set in from 70th minute of sorption to achieve 59% removal of Pb²⁺ from 300 mg/L of Pb²⁺. This may suggest that sorption by a two-stage process leads to improved contact time and increased percentage metal ion removal which is of benefit to the industry in their clean-up of metals from waste streams.

When the data for the two models were compared, it was observed that they showed very high correlation values within range of 0.9962–0.9978 (Table 5). Data showed that increasing percentage removal increased correlation values.

A very good way of testing the validity of a new or existing model is by comparing them with those obtained by using a second or perhaps a reference model. The null hypothesis that the two models give the same results is

$$H_0: \mu_1 = \mu_2,$$

Table 5
t-Test table for TDLM and PSOM data.

	<i>t</i> -Test					
	95% Removal		90% Removal		80% Removal	
	TDLM	PSOM	TDLM	PSOM	TDLM	PSOM
Mean	34.70	38.28	33.71	37.10	31.74	34.76
Variance	45.18	41.34	46.33	42.50	48.85	45.11
Observations	15	15	15	15	15	15
Pooled variance	43.26	–	44.41	–	46.98	–
Hypothesized mean difference	0	–	0	–	0	–
Degree of freedom	28	–	28	–	28	–
<i>t</i> = stat	–1.49	–	–1.49	–	–1.20	–
<i>P</i> (<i>T</i> ≤ <i>t</i>) one tail	0.07	–	0.07	–	0.12	–
<i>t</i> Critical one tail	1.70	–	1.70	–	1.70	–
<i>P</i> (<i>T</i> ≤ <i>t</i>) two tail	0.15	–	0.15	–	0.24	–
<i>t</i> critical two tail	2.05	–	2.05	–	2.05	–
<i>r</i> ²	0.9962	–	0.9962	–	0.9978	–

Table 6
F-test table for TDLM and PSOM data.

	<i>F</i> -test					
	95% Removal		90% Removal		80% Removal	
	TDLM	PSOM	TDLM	PSOM	TDLM	PSOM
Mean	34.70	38.28	33.71	37.10	31.74	34.76
Variance	45.18	41.34	46.33	42.50	48.85	45.11
Observations	15	15	15	15	15	15
df	14	14	14	14	14	14
<i>F</i> -test	1.09	–	1.09	–	1.08	–
<i>P</i> (<i>F</i> ≤ <i>f</i>) one tail	0.44	–	0.44	–	0.44	–
<i>F</i> -Critical one tail	2.48	–	2.48	–	2.48	–

Hence, we need to test whether the difference between the means of data from both models differs significantly from zero. Since an unequal variance was assumed, a pooled estimate of the standard deviation was calculated from the two individual standard deviations of the data from both models. The output of the *t*-test analysis for 95%, 90% and 80% removal using Microsoft excel 2007[®] is given in Table 5.

Since the assumption of an increase or a decrease in the variances is not necessary, the two-tailed *t*-test was adopted. For all three different percentage removals, the calculated experimental value of $|t|$ (absolute value of the statistical *t* regardless of the sign) is less than the critical values; hence the null hypothesis is retained. This shows that [*P*($|t| > t$) = 0.15 at 90% removal; 0.17 at 90% removal and 0.24 at 80% removal] whose probabilities are greater than 0.05, which indicates that the result is not significant at the 5% level. The TDLM is as good as the PSOM.

The *F*-test was used for further comparison by comparing the standard deviations of the two models with the use of the data analysis options of the Microsoft Excel 2007 add-Ins. The *F*-test may be used to decide the precision of two models and the difference in the precision of the two models.

The *F*-test in this study was used to determine whether the TDLM differ significantly from the PSOM. Considering the null hypothesis that the two sample variances are equal using one-tailed *F*-test, *F* was calculated and were observed to be greater than or equal to one. Differences from one can occur because of random variations. The output of the *F*-test is shown in Table 6 representing values for 95%, 90% and 80% removal. Since the calculated *F*-values are close to one, then the null hypothesis is true—there is no significant difference between the models. Moreover, it follows that since the calculated *F*-values are lower than the critical *F*-values at 5% probability levels, the null hypothesis is retained. The two models are equally very good for the optimization of minimum contact time in the design

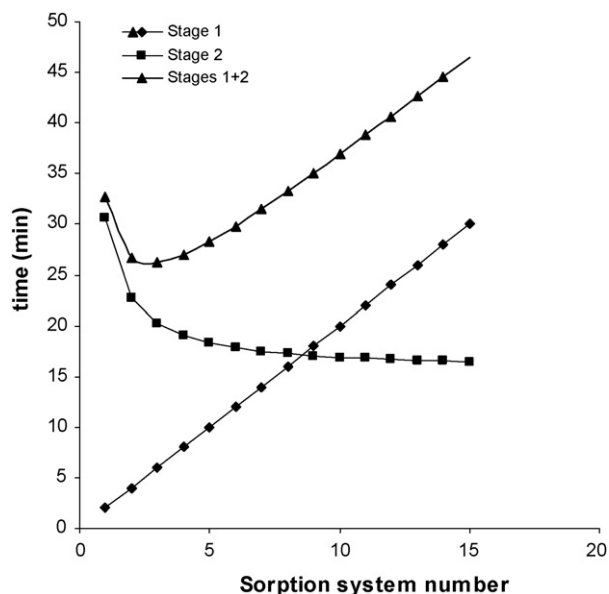


Fig. 5. Comparison of 95% Pb²⁺ ion adsorption time by PVA-modified Kaolinite clay for each stage in a two-stage adsorption process using TDLM.

of adsorber for the adsorption of Pb²⁺ from aqueous solution using PVA-modified Kaolinite clay adsorbent.

3.2.3. Mechanism of adsorption

One of the modes of adsorption of metal ions onto the surface of the adsorbent is:



where S is used to represent the surface of adsorbent.

To support the above equation there was an observed drop in pH of equilibrium solutions of Pb²⁺ from 5.50 to between 3.87 and 3.98 for both adsorbents during the adsorption process which has also been observed by Singh et al. [13]. Eq. (28) was further confirmed from the Infra-red spectrograph which suggests that the main functional group present on the PVA-modified Kaolinite clay adsorbent is the –OH group [10].

On the PVA-modified Kaolinite clay adsorbent, the active sites are perhaps weakly acidic in nature. Thus, with increasing pH, they are gradually deprotonated making available, more and more sites for metal ion uptake. In acidic medium, the adsorbent surface acquires a net positive charge as follows:



This surface reduces the adsorption capacities of the adsorbent for the metal ion at low pH. As pH increases towards the alkaline region, the adsorbent surface becomes negatively charged favoring the uptake of the metal ions by the adsorbents:



where “S” represents the adsorbent’s surface and “M” represent a metal.

Our findings from modeling equilibrium data obtained in our previous study [10] suggest that the Diffuse Layer Model (DLM) supports the adsorption of Pb²⁺ onto PVA-modified Kaolinite clay adsorbent.

4. Conclusion

Optimization models developed for the sorption of Pb²⁺ from aqueous solution in a two-stage adsorber system suggests that both contact time and efficiency of adsorbent were improved by two-stage sorption onto PVA-modified Kaolinite clay. The use of PSOM and TDLM for optimization of both kinetic and equilibrium data gave results with good agreement. When data from both models were subjected to *t*-test and *F*-test they were observed not to be significantly different. Both models were observed to be precise enough for use in the optimization of kinetic data for a two-stage sorption of Pb²⁺ from aqueous solution.

Acknowledgement

The authors wish to acknowledge the Chinese Academy of Sciences (CAS) and Academy of Sciences for the Third World (TWAS) for the fellowship granted E.I. Unuabonah to do some aspects of this work.

References

- [1] Y.S. Ho, G. McKay, Batch sorber design using equilibrium and contact time data for the removal of lead, *Water, Air, Soil Pollut.* 124 (2000) 141–153.
- [2] Y.S. Ho, G. McKay, A two-stage batch sorption optimized design for dye removal to minimize contact time, *Trans. IChemE* 76B (1998) 313–318.
- [3] M. Özacar, I.A. Sengil, Equilibrium two-stage batch sorber design using second-order kinetic model for the sorption of metal complex dyes onto pine sawdust, *Biochem. Eng. J.* 21 (2004) 39–45.
- [4] Y.S. Ho, G. McKay, A two-stage batch sorption optimised design for dye removal to minimum contact time, *Process Saf. Environ. Prot.* 76 (1998) 313–318.
- [5] E.I. Unuabonah, K.O. Adebowale, A.E. Ofomaja, Two-stage batch adsorber design: a time-dependent Langmuir model for adsorption of Pb²⁺ and Cd²⁺ onto modified Kaolinite clay, *Water, Air, Soil Pollut.* (2008), doi:10.1007/s11270-008-9899-1.
- [6] K.O. Adebowale, E.I. Unuabonah, B.I. Olu-Owolabi, The effect of some operating variables on the adsorption of lead and cadmium ions on Kaolinite clay, *J. Hazard. Mater.* B134 (2006) 130–139.
- [7] E.I. Unuabonah, Kinetic and thermodynamics of the sorption of some heavy metal ions onto modified Kaolinite clay, PhD Thesis, University of Ibadan, Nigeria, 2007.
- [8] Y.S. Ho, G. McKay, A multi-stage batch sorption design with experimental data, *Adsorpt. Sci. Technol.* 17 (1999) 233–243.
- [9] E.I. Unuabonah, K.O. Adebowale, B.I. Olu-Owolabi, L.Z. Yang, Comparison of sorption of Pb²⁺ and Cd²⁺ on Kaolinite clay and polyvinyl alcohol-modified Kaolinite clay, *Adsorption* 14 (2008) 791–803.
- [10] E.I. Unuabonah, B.I. Olu-Owolabi, K.O. Adebowale, L.Z. Yang, Removal of lead and cadmium ions from aqueous solution by polyvinyl alcohol-modified Kaolinite clay: a novel clay adsorbent, *Adsorpt. Sci. Technol.* 26 (2008) 383–405.
- [11] R.E. Treybal, *Mass Transfer Operations*, 3rd edition, McGraw-Hill, New York, 1981, p. 125.
- [12] M. Özacar, I.A. Sengil, A two stage batch adsorber design for methylene blue removal to minimize contact time, *J. Environ. Manag.* 80 (2006) 372–379.
- [13] S.P. Singh, L.Q. Ma, G.W. Harris, Heavy metal interactions with phosphatic clay: sorption and desorption behavior, *J. Environ. Quality* 30 (2001) 1961–1968.