

## Modeling of fixed-bed column studies for the adsorption of cadmium onto novel polymer–clay composite adsorbent

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### ABSTRACT

Kaolinite clay was treated with polyvinyl alcohol to produce a novel water-stable composite called polymer–clay composite adsorbent. The modified adsorbent was found to have a maximum adsorption capacity of  $20,400 \pm 13$  mg/L (1236 mg/g) and a maximum adsorption rate constant of  $\approx 7.45 \times 10^{-3} \pm 0.0002$  L/(min mg) at 50% breakthrough. Increase in bed height increased both the breakpoint and exhaustion point of the polymer–clay composite adsorbent. The time for the movement of the Mass Transfer Zone ( $\delta$ ) down the column was found to increase with increasing bed height. The presence of preadsorbed electrolyte and regeneration were found to reduce this time. Increased initial  $\text{Cd}^{2+}$  concentration, presence of preadsorbed electrolyte, and regeneration of polymer–clay composite adsorbent reduced the volume of effluent treated. Premodification of polymer–clay composite adsorbent with Ca- and Na-electrolytes reduced the rate of adsorption of  $\text{Cd}^{2+}$  onto polymer–clay composite and lowered the breakthrough time of the adsorbent. Regeneration and re-adsorption studies on the polymer–clay composite adsorbent presented a decrease in the bed volume treated at both the breakpoint and exhaustion points of the regenerated bed. Experimental data were observed to show stronger fits to the Bed Depth Service Time (BDST) model than the Thomas model.

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### 1. Introduction

The recent growth in industrial and technological advancement globally brought with it the introduction of pollutants of diverse nature into water bodies. Such pollutants include heavy metals, dyes and organic matters. Their presence in industrial effluents or drinking water is a public health problem, due to their adsorption and possible accumulation in organisms [1].

Prominent among these pollutants are Pb (II), Cd (II), Hg (II), Ni (II) and Cr (II) [2]. Adsorption, as a wastewater treatment process, exploits the ability of some solids to concentrate certain substances from solution onto their surface. Activated carbon has been the most favored adsorbent in an adsorption process, but the high cost and tedious procedure for its preparation and regeneration has prompted the search for low-cost potential adsorbent.

Clay minerals have been found to also perform this same function of adsorption but with less effectiveness. Some are more effective towards cations e.g. Montmorillite and others are more effective towards anions e.g. Kaolinite [3]. Kaolinite clay mineral

has been found in abundant quantities in Delta, Kaduna, Bauchi and several other States of Nigeria. Several methods have been employed to improve on the low Cation Exchange Capacity (CEC) of kaolinite clay. Some of these include activation (both physical and chemical methods), pillaring and chemical modification of the surface using inorganic complex forming ions or organic-based complex forming ions [4]. Recent research suggests that chemically modified clay minerals represent a new and promising class of adsorbents for water purification and industrial wastewater treatment [5].

Batch adsorption experiments are used easily in the laboratory for the treatment of small volume of effluents, but less convenient to use on industrial scale, where large volumes of wastewater are continuously generated. Batch adsorption provides certain preliminary information such as pH for maximum adsorption, maximum initial metal ion concentration, and particle size for optimum adsorption of metal ions, and approximate time for adsorption of metal ion as well as the adsorption capacity of the adsorbent. All these information are useful for fixed-bed studies.

In fixed bed, the adsorbate is continuously in contact with a given quantity of fresh adsorbent, thus providing the required concentration gradients between adsorbent and adsorbate for adsorption. Fixed-bed operations are widely used in pollution control processes such as for the removal of ions by an ion-exchange bed or removal of toxic organic compounds by carbon adsorp-

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## Nomenclature

$BV_b$	bed volume at breakpoint (ml)
$BV_e$	bed volume at exhaustion point (ml)
$C_o$	inlet concentration of cadmium ion (mg/L)
$C_t$	outlet concentration of cadmium ion at time $t$ (mg/L)
$f$	fractional capacity
$F_M$	flow rate (ml/min)
$k_{Th}$	Thomas model constant ( $1 \text{ mg}^{-1} \text{ min}^{-1}$ )
$K_a$	bed depth service model rate constant ( $1 \text{ mg}^{-1} \text{ min}^{-1}$ )
$L_0$	length of the column (cm)
$M$	adsorbent mass (g)
$N_o$	Bed Depth Service Time adsorption capacity (mg/L)
$t_f$	service time (min)
$t_x$	total taken for the MTZ to establish itself, move down the length of the column and out of the column (min)
$t_\delta$	time for the movement of the MTZ down the column (min)
$T_{b10}$	time for concentration at 10% breakthrough (min)
$T_{b50}$	time for concentration at 50% breakthrough (min)
$V$	linear velocity ( $\text{cm min}^{-1}$ )
$V_b$	throughput volume at breakpoint (ml)
$V_e$	throughput volume (L)
$V'_b$	volume per gram at breakpoint (ml/g)
$V'_e$	volume per gram at exhaustion point (ml/g)
$V_{eff}$	effluent volume (ml)
$Z$	bed height (cm)
$Z_o$	critical bed height (cm)

### Greek symbol

$\sigma$	length of MTZ (cm)
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tion [6]. Fixed-bed adsorption of pollutants involves percolation of wastewater through percolating material. During the flow of the wastewater through the percolator, the wastewater is purified by physicochemical processes. The design and theory of fixed-bed adsorption systems focuses on establishing the shape of the breakthrough curve and its velocity through the bed. Breakthrough and bed volumes are usually employed in the evaluation of the performance of a fixed-bed column [7]. The performance of packed beds is described through the concept of the breakthrough curve.

Clays, as adsorbents, show good potentials 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 fixed-bed studies on the adsorption of cadmium ions onto polyvinyl alcohol–clay adsorbent.

To address the problem of recovery of adsorbent/resins after use from filters, a novel, water-stable and mechanically strong adsorbent was prepared from locally obtained Kaolinite clay using polyvinyl alcohol reagent. This was subsequently used to study the adsorption of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in batch systems. The physical characteristics of this adsorbent have been previously reported [8]. Batch experiments indicated that the polymer–clay composite adsorbent was seven times more efficient in the adsorption of  $\text{Cd}^{2+}$  compare to the unmodified Kaolinite clay [8,9].

This paper, therefore investigated the adsorption of  $\text{Cd}^{2+}$  onto polymer–clay composite adsorbent in fixed-bed columns. Operating variables such as initial metal ion concentration, bed height, and preadsorbed  $\text{Na}^+$  and  $\text{Ca}^{2+}$  were considered. Regeneration studies were also carried on the adsorbents.

## 2. Materials and methods

### 2.1. Materials

Kaolinite clay was obtained from Ubulu-Ukwu, Delta State, Nigeria. On collection, stones and other heavy particles were removed from the sample. It was purified according to methods of [10]. Mineralogical and chemical characterization of the clay has been reported [9,11].

### 2.2. Modification of clay sample

The Kaolinite clay was acid-treated with 2 M  $\text{HNO}_3$ , stirring for one hour to oxidize the clay mineral. This was then centrifuged and washed several times with deionized water. The sample was centrifuged again, the supernatant poured off and the sample was subsequently oven dried at 373 K. The clay was modified according to method in [9].

### 2.3. The fixed-bed column

The polymer–clay composite adsorbent particles were sieved, using a standard laboratory sieve and particle size of  $350 \mu\text{m}$  was selected for the various adsorption studies. A glass column with internal diameter 16 mm with length of 56 cm was packed with the polymer–clay composite adsorbent.

### 2.4. Effects of operating variables

#### 2.4.1. Effects of bed height

The polymer–clay composite adsorbent of different weights (20, 25 and 30 g) was placed in separate glass columns as discussed in Section 2.3. The packed density ( $0.965 \text{ g/cm}^3$ ) was the same for the different columns while the bed heights differ from one column to another (10.3, 12.86 and 15.45 cm respectively). 500 mg/L working standard at  $\text{pH } 5.5 \pm 0.2$  was percolated through each of the column under gravity flow and the effluent from each column was collected at an interval of one hour and kept for metal ion analysis.

#### 2.4.2. Effects of initial metal ion concentration

Stock solution of 1000 mg/L of  $\text{Cd}^{2+}$  was prepared from its nitrate salt (Aldrich), using deionized water. From this stock solution, working standards of concentration 150, 300 and 500 mg/L were subsequently prepared and adjusted to  $\text{pH } 5.5 \pm 0.2$ , with either 0.1 M HCl or 0.1 M NaOH. Kinetic experiments were carried out by percolating the working standards through the polymer–clay composite adsorbent bed. 20 g of the polymer–clay composite adsorbent was placed in three separate glass columns as described above (Section 2.3).

The different working standards of  $\text{Cd}^{2+}$  were percolated through the different columns and the influent was allowed to flow through the adsorbent bed by gravity flow. The effluent from the column were collected at intervals of one hour and kept for metal ion analysis.

#### 2.4.3. Effects of Preadsorbed $\text{Na}^+$ and $\text{Ca}^{2+}$

0.1 M sodium and calcium electrolytes solutions were prepared from their nitrates salt (Aldrich) respectively. Two separate glass columns were packed with 20 g of the polymer–clay composite adsorbent adsorbent. Each of the columns was percolated with each electrolyte solution until the effluent from the columns was the same as the influent solution.

The columns were then rinsed several times with deionized water (to remove excess  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) until zero concentration of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  were achieved by constantly analyzing effluents with a flame photometer. 300 mg/L working standard of the metal solu-

tion at pH  $5.5 \pm 0.2$  was subsequently prepared from the stock solution and this was percolated through each of the glass columns and the effluent from each column was collected for metal ion analysis.

#### 2.4.4. Effects of regeneration of adsorbent bed

The bed used to run the 300 mg/L initial metal ion concentration was regenerated by running 0.1 M HCl solution through it and the effluent were collected at intervals of 1 h. The 0.1 M HCl solution was allowed to completely drain from the bed and the bed was then rinsed thoroughly with deionized water. The regenerated bed was then loaded again with 300 mg/L at pH  $5.5 \pm 0.2$  metal solution and the effluent were also collected at interval of 1 h. The effluent solutions from both desorption and readsorption studies were then taken for metal ion analysis.

The loading of the beds continued until the metal ion concentration in the effluent reached approximately 90% of the influent concentration which was regarded as the exhaustion point. All experiments were carried out in duplicates and the deviations were within 5%. For all graphical representations, the mean values were used. All statistical analyses were made using MICROSOFT EXCEL® 2003 software.  $Cd^{2+}$  concentrations in aqueous solutions were measured, using flame atomic absorption Spectrometer (FAAS), Computer-Aided Solar Series, Model 969. The absorption line used for  $Cd^{2+}$  is 228.3 nm. Air-acetylene flame was used. The amounts of  $Cd^{2+}$  adsorbed by the adsorbents were calculated by difference.

### 2.5. Theory of models for fixed-bed studies

#### 2.5.1. The Thomas model

This kinetic model was developed by Thomas [12]. The Thomas solution is one of the most general and widely used methods in column performance theory [13]. The expression by Thomas for an adsorption column is given as follows:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp[K_{TH}(q_0M - C_0V_{eff})V]} \quad (1)$$

The value of  $C_t/C_0$  is the ratio of the effluent and the influent metal ion concentrations. The value of  $t$  (min) is:

$$t = \frac{V_{eff}}{V} \quad (2)$$

The linearized form of Thomas model can be expressed as follows:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{TH}q_0M}{F_m} - k_{TH}C_0t \quad (3)$$

The kinetic coefficient  $k_{TH}$  and the adsorption capacity can be obtained from the plot of  $C_t/C_0$  against time  $t$  at a given flow rate using linear regression.

#### 2.5.2. The Bed Depth Service Time Model (BDST Model)

Boharts and Adam [14] proposed a relationship between the bed depth ( $Z$ ) and service time ( $t$ ) for a fixed-bed adsorber. Service time refers to the time utilized by the adsorption column to reach the breakthrough point with specific saturation percentage [15]. The service time was related to process conditions and operating parameters as

$$\ln\left(\frac{C_0}{C_t}\right) = \ln(e^{k_a N_0 Z/V} - 1) - K_a C_0 t \quad (4)$$

Thus, if  $\ln((C_0/C_t) - 1)$  is plotted against  $t$ , then the slope given by  $K_a C_0$  can be used to calculate  $K_a$ .

Hutchins [16] proposed a linear relationship to this equation, to become

$$t = \frac{N_0 Z}{C_0 V} - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_t} - 1\right) \quad (5)$$

where  $t$  is the service time.

In Eq. (5), the service time of the bed  $t$  and the bed height  $Z$  can be correlated with other process variables; initial metal ion concentration, solution flow rate and adsorption capacity.

A plot of time  $t$  versus bed depth  $Z$  should yield a straight line where  $N_0$  and  $k_a$ , the adsorption capacity and rate constant respectively can be calculated. The critical bed depth ( $Z_0$ ) which is defined as the theoretical depth of adsorbent sufficient to prevent the adsorbate concentration from exceeding breakthrough concentration ( $C_b$ ) at  $t=0$ , can be obtained from Eq. (5), when the service time is zero;

$$Z_0 = \frac{V}{K_a N_0} \ln\left(\frac{C_0}{C_b} - 1\right) \quad (6)$$

A simplified form of the BDST model is given as

$$t = aZ - b \quad (7)$$

where the slope of the equation is equal to  $a$  and is given by the expression below

$$a = \frac{N_0}{C_0 V} \quad (8)$$

and  $b$  is the intercept of the straight line graph given as

$$b = \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \quad (9)$$

If  $K_a$  is large, even a short bed will avoid breakthrough, but as  $K_a$  decreases, a progressively longer bed is required to avoid breakthrough [17]. The BDST model parameters can be helpful to scale up the process for other flow rates without further experimental run.

According to Goel et al. [18] and Othman et al. [19], the slope constant for a new flow rate can be directly calculated from Eq. (10) given below:

$$a' = \frac{aV}{V'} = \frac{aF_m}{F'_m} \quad (10)$$

where  $a$  and  $V$  are the previous slope and influent linear velocity respectively and  $a'$  and  $V'$  are the new slope and influent velocity.

If the column used in the experiment has the same diameter, the ratio of the original influent velocity ( $V$ ) to that of the new influent velocity ( $V'$ ) and the original flow rate ( $F_m$ ) to that of the new flow rate ( $F'_m$ ) is equal.

### 2.6. Estimation of operating parameters

The Mass Transfer Zone is assumed to have a constant length or depth,  $S$ . The total time taken ( $t_x$ ) for the MTZ to establish itself, move down the length of the fixed bed of the adsorbent and out of the fixed bed is defined as [18]:

$$t_x = \frac{V_e}{F_m} \quad (11)$$

Different workers have reported that the value of  $t_x$  vary with the bed height of the adsorbent. It was found to increase with increasing bed height which suggests that it takes a longer time for the MTZ to establish, move down the length of the bed and out of the bed in a higher bed height than in shorter bed heights.

The time require for the movement of the Mass Transfer Zone ( $t_\delta$ ) downward in the column is defined as:

$$t_\delta = \frac{V_e - V_b}{F_m} \quad (12)$$

The time required for the initial formation of MTZ can thus be obtained from the equation given below:

$$t_f = \frac{V_b}{F_m} \quad (13)$$

The fixed-bed height can thus be equated with the time ratio using the equation below:

$$\frac{\delta}{D} = \frac{t_{\delta}}{t_x - t_f} \quad (14)$$

The length or depth ( $\delta$ ) of the Mass Transfer Zone can then be obtained from the relationship expressed in the above equation.

The fractional capacity,  $f$ , of the adsorbent in the Mass Transfer Zone, at breakpoint, to continue to remove solute from solution under the limiting condition can be defined by the equation stated below:

$$f = \frac{1 - t_f}{t_{\delta}} \quad (1)$$

## 2.7. Modeling

It has been observed that the various forms of a linear equation do affect data analysis significantly, thus, introducing errors to data obtained calculated. The use of non-linear regression analysis is a way of reducing such errors to a minimum. In this paper, Root Mean Square Method of Error analysis (RMSE), which operates via the non-linear analysis mode, was used. This is to confirm the best fit isotherm for the adsorption of cadmium ion onto polymer–clay composite adsorbent [18].

$$\text{RMSE} = \left[ \frac{\sum_{j=1}^n (y_j^{\text{exp}} - y_j^{\text{cal}})^2}{N} \right]^{1/2} \quad (16)$$

where  $y^{\text{exp}}$  and  $y^{\text{cal}}$  are the experimental and calculated values of  $C_t/C_o$  respectively. According to the model,  $N$  is the number of the experimental point.

## 3. Results and discussion

### 3.1. Volume of adsorbate treated

#### 3.1.1. Effects of bed height

The results in Table 1 present some of the calculated operational characteristics of the polymer–clay adsorbent fixed-bed column at different bed heights. The table suggests that the volume of  $\text{Cd}^{2+}$  solution treated per unit weight of adsorbent, increased as bed height increased.

From Table 1, the volume of aqueous solution treated,  $V'_b$ , obtained for the three different bed heights at breakthrough point showed that the rate of movement of the adsorption zone was rapid for the smallest bed height. The movement of the adsorption zone became reduced when the bed height was increased. The volume of the  $\text{Cd}^{2+}$  solution treated per unit mass of the polymer–clay com-

posite adsorbent at exhaustion point ( $V'_e$ ) was largest (56.1 ml/g) for the highest bed height (15.45 cm) when compared with the values of  $V'_e$  (53.1 ml/g and 55.6 ml/g) obtained for the other bed heights (10.3 cm and 12.88 cm respectively). The bed volumes ( $BV_b$  and  $BV_e$ ) at both the breakthrough and exhaustion points also increased as bed height increased (Table 1).

#### 3.1.2. Effects of metal ion concentration

The results in Table 2 depict the effect of initial metal ion concentration on the operational characteristics of polymer–clay composite adsorbent in a fixed bed for the adsorption of  $\text{Cd}^{2+}$ . From Table 2, it was observed that the volume of the  $\text{Cd}^{2+}$  solution treated at both breakthrough and exhaustion points decreased with increase in the initial metal ion concentration. This is because the ability of an adsorbent to continue to remove an adsorbate from solution is limited with time due to decreasing adsorption sites. Therefore, the volume of effluent treated per mass of a given adsorbent is a function of the influent concentration.

The results obtained in this study showed that 414 ml, 408 ml, and 348 ml were the respective volumes of the different  $\text{Cd}^{2+}$  solutions (150, 300 and 500 mg/L) treated per gram of the polymer–clay composite adsorbent at 50% breakthrough point while 1212 ml, 1176 ml and 1062 ml were the respective volumes treated at exhaustion point. An increase in inlet metal ion concentration at constant flow rate decreased the throughput volume until breakthrough. This may have been caused by high metal ion concentration saturating the adsorbent more quickly, thereby decreasing the breakthrough time.

The volume of the  $\text{Cd}^{2+}$  solution treated per unit mass of the polymer–clay composite adsorbent at exhaustion point ( $V'_e$ ) was largest (20.70 ml/g) for the least initial metal ion concentration (150 mg/L), when compared with the values of  $V'_e$  (20.40 ml/g and 17.40 ml/g) for the other concentrations (300 mg/L and 500 mg/L). The bed volumes ( $BV_b$  and  $BV_e$ ), at both the breakthrough and exhaustion points decreased as the concentration of the metal ion solution increased.

#### 3.1.3. Effects of electrolyte

Calculated values for some operating characteristics of the polymer–clay composite adsorbent premodified with 0.1 M  $\text{NaNO}_3$  and 0.1 M  $\text{Ca}(\text{NO}_3)_2$  for the adsorption of  $\text{Cd}^{2+}$  are shown in Table 3. The table compared the characteristics of polymer–clay composite adsorbent to that premodified with electrolytes. The results showed that at the same initial  $\text{Cd}^{2+}$  concentration, polymer–clay composite adsorbent treated more volume of the metal ion solution at breakthrough than with polymer–clay composite adsorbents premodified with electrolytes. This observed decrease can be attributed to the competitive effect between the electrolyte cations ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) and the  $\text{Cd}^{2+}$  in solution, as

**Table 1**  
Data for the operating characteristics of the polymer–clay composite adsorbent at different bed heights.

Mass (g)	$V_b$ (ml)	$V_e$ (ml)	$V_e - V_b$ (ml)	$V'_b$ (ml/g)	$V'_e$ (ml/g)	$BV_b$ (ml)	$BV_e$ (ml)	$T_{b10}$ (min)	$T_{b50}$ (min)
20	348	1062	714	17.4	53.10	16.79	51.24	295 (5.54)	630 (0.82)
25	485	1390	905	19.41	55.60	18.73	53.65	422 (5.60)	850 (0.85)
30	584	1683	1099	19.47	56.10	18.79	54.14	515 (5.62)	970 (0.87)

Note: Values in bracket are critical bed height ( $Z_o$ ) values.

**Table 2**  
Data for operating characteristics of the polymer–clay composite adsorbent for initial metal ion concentrations.

$C_o$ (mg/L)	$V_b$ (ml)	$V_e$ (ml)	$V'_b$ (ml/g)	$V'_e$ (ml/g)	$V_e - V_b$ (ml)	$BV_b$ (ml)	$BV_e$ (ml)	$T_{b10}$ (min)	$T_{b50}$ (min)
150	414	1212	20.70	60.60	798	19.96	58.48	345 (5.54)	580 (0.82)
300	408	1176	20.40	58.80	768	19.69	56.74	339 (5.54)	710 (0.82)
500	348	1062	17.40	53.10	714	16.79	51.24	290 (5.54)	630 (0.82)

Note: Values in bracket are critical bed height ( $Z_o$ ) values

**Table 3**

Data for the operating characteristics of the polymer–clay composite with electrolytes.

Adsorbent	$V_b$ (ml)	$V_e$ (ml)	$V'_b$ (ml/g)	$V'_e$ (ml/g)	$V_e - V_b$ (ml)	BV <sub>b</sub> (ml)	BV <sub>e</sub> (ml)	$T_{b10}$ (min)	$T_{b50}$ (min)
PVA	408	1176	20.40	58.80	768	19.69	56.74	339(5.54)	710(0.82)
Na <sup>+</sup> premodified	349	1073	17.45	53.65	724	16.84	51.19	295(5.28)	645(0.78)
Ca <sup>2+</sup> premodified	280	1048	14.00	52.40	768	13.51	47.52	235(5.26)	605(0.76)
Re-AD	254	927	12.50	46.35	573	12.26	44.73	215	510

Note: Values in bracket are critical bed height ( $Z_c$ ) values. Re-AD: re-adsorption.

they were being desorbed from the adsorbent's surface by Cd<sup>2+</sup>. However, the polymer–clay composite adsorbent premodified with Na<sup>+</sup> electrolyte treated more volume than the adsorbent premodified with Ca<sup>2+</sup> electrolyte. The volumes treated at exhaustion also followed a similar trend. The effect is presumed to be more pronounced with Ca<sup>2+</sup> because of its divalent nature.

### 3.1.4. Effect of regeneration of adsorbent bed

Table 3 gives the results of some of the calculated values for the operating characteristics of the polymer–clay composite adsorbent on adsorption, regeneration of adsorbent and re-adsorption of Cd<sup>2+</sup> at same initial metal ion concentration on the fixed-bed column. The results indicated that at same initial metal ion concentration, the volume treated at breakthrough point  $V_b$  (254 ml) and exhaustion point  $V_e$  (927 ml) by the regenerated bed is reduced compared to the volume treated by the fresh adsorbent bed (408 ml and 1176 ml respectively). There was also a sharp decrease in the volume of Cd<sup>2+</sup> solution treated per unit mass of polymer–clay composite adsorbent at exhaustion  $V'_e$  (from 58.80 to 46.35 ml/g) as well as at breakthrough  $V'_b$  (from 20.40 to 12.50 ml/g). These results may imply that on regeneration of the adsorbent bed, some of the previously vacant sites may have fixed some Cd<sup>2+</sup> after the first adsorption process. It is also possible that the regenerating reagent may have had a negative impact on the number of active sites present on the adsorbent.

### 3.2. Mass Transfer Zone (MTZ) of the polymer–clay composite adsorbent

The total time taken for the Mass Transfer Zone (MTZ) to establish itself, move down the length of the fixed bed of the polymer–clay composite adsorbent and out of the bed at different bed heights,  $t_x$  (Table 4) increased with increasing bed height. This may suggest that it takes a longer time for the MTZ to establish itself, move down the length of the polymer–clay composite adsorbent in the column and out of the column with higher bed heights than with shorter bed heights. The time required for the movement of the Mass Transfer Zone (MTZ) downward in the column  $t_\sigma$  for the different bed heights also followed similar trend. However, the length of the Mass Transfer Zone ( $\delta$ ) was found to increase with increasing bed height. The fractional capacity,  $f$ , of the polymer–clay composite adsorbent in the adsorption zone decreased with increase in bed height.

With increasing initial metal ion,  $t_x$  was found to decrease as shown in Table 5. It was also observed that  $t_\sigma$  and  $t_f$  also followed a similar pattern. This may be due to decreasing throughput volume at both breakthrough and exhaustion points arising from decreasing number of adsorption sites available for the increasing

concentration of Cd<sup>2+</sup> in solution. The length of the Mass Transfer Zone was found to be constant for the different concentrations perhaps because the same bed height was used for the study at various initial metal ion concentrations. The fractional capacity,  $f$ , of the polymer–clay composite adsorbent was found to increase with increase in the initial metal ion concentration.

The effect of premodification of polymer–clay composite adsorbent bed with electrolytes on the Mass Transfer Zone is given in Table 6. The results showed that  $t_x$  for the PVA-modified adsorbent bed is higher than that for the premodified PVA-adsorbent beds at same initial metal ion concentration. However, the  $t_x$  value for the Na<sup>+</sup> premodified bed was higher than that of the Ca<sup>2+</sup> bed. Similarly,  $t_f$  followed similar trend whereas  $t_\sigma$  values showed a slight variation with this trend (Table 6).

With a regenerated bed,  $t_x$  was found to decrease from 980 min to 772.50 min (Table 6). Similarly,  $t_f$  values decreased from 340 min to 211.67 min and  $t_\sigma$  from 640 min to 560.83 min at the same initial metal ion concentration. The fractional capacity  $f$ , of the bed was found to be higher for the regenerated bed than for premodified or fresh polymer–clay composite adsorbent adsorbent. The depth of the Mass Transfer Zone was found to be same for all the adsorbents perhaps because the bed height is the same.

### 3.3. Breakthrough curve analysis

#### 3.3.1. Polymer–clay composite adsorbent

The breakthrough curves for the adsorption of Cd<sup>2+</sup> onto polymer–clay composite adsorbent at different bed heights are presented in Fig. 1. From the breakthrough curves for the different bed, it was observed that as bed height increased, Cd<sup>2+</sup> had more time to come in contact with the adsorbent, and this resulted in higher removal efficiency of the Cd<sup>2+</sup> in solution as well as decreased solute concentration in the effluent. Table 1 showed that breakthrough time at 10% and 50% concentrations increased with increase in bed heights, at 10.30 cm ( $T_{b10} = 295$  min,  $T_{b50} = 630$  min), 12.88 cm ( $T_{b10} = 422$  min,  $T_{b50} = 850$  min) and at 15.45 cm ( $T_{b10} = 515$  min,  $T_{b50} = 970$  min). Similar observation was made by Malkoc and Nuhoglu [20] in the removal of Ni<sup>2+</sup> using waste of tea factory in a fixed-bed study.

It was also observed that the slopes of the breakthrough curves decreased with increasing bed heights (slope at 10.3 cm = 0.0007, 12.88 cm = 0.0008 and at 15.45 cm = 0.0011) and this resulted in a broadened Mass Transfer Zone, which resulted in an increase in the uptake of Cd<sup>2+</sup> by polymer–clay composite adsorbent. This is, probably, due to an increase in the surface area of the adsorbent, which provides more binding sites for the sorption. A similar trend was reported by Zulfadhly et al. [21] in the adsorption of heavy metals in a fixed-bed column by macro fungus *pycnoporous san-*

**Table 4**

Mass Transfer Zone model characteristics of the polymer–clay composite adsorbent at different bed heights.

Depth (cm)	$t_x$ (min)	$t_\sigma$ (min)	$t_f$ (min)	$\sigma$ (cm)	$f$	$F_m$ (ml/min)
10.3	885	595	290	10.3	0.513	1.2
12.88	1208.7	786.82	412.88	12.88	0.464	1.15
15.45	1530	999.1	530.91	15.45	0.469	1.10

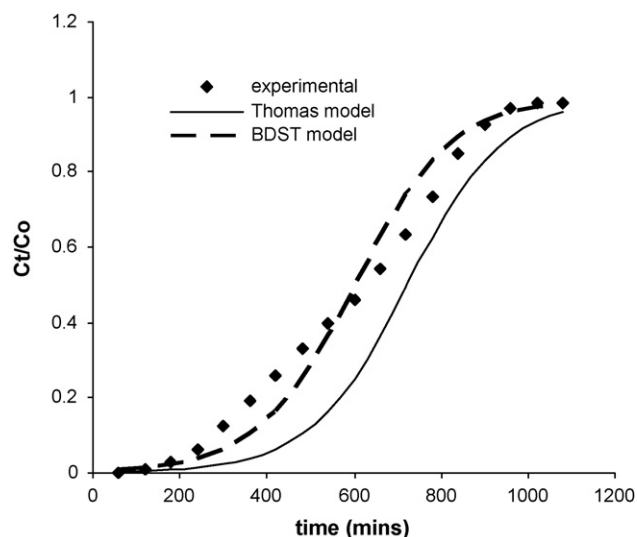
**Table 5**

Mass Transfer Zone model characteristics of the polymer–clay composite adsorbent at different initial metal ion concentrations.

$C_0$ (mg/L)	$t_x$ (min)	$t_\sigma$ (min)	$t_f$ (min)	$\sigma$ (cm)	$f$	$F_m$ (ml/min)
150	1010	665	345	10.3	0.481	1.2
300	980	640	340	10.3	0.469	1.2
500	885	595	290	10.3	0.513	1.2

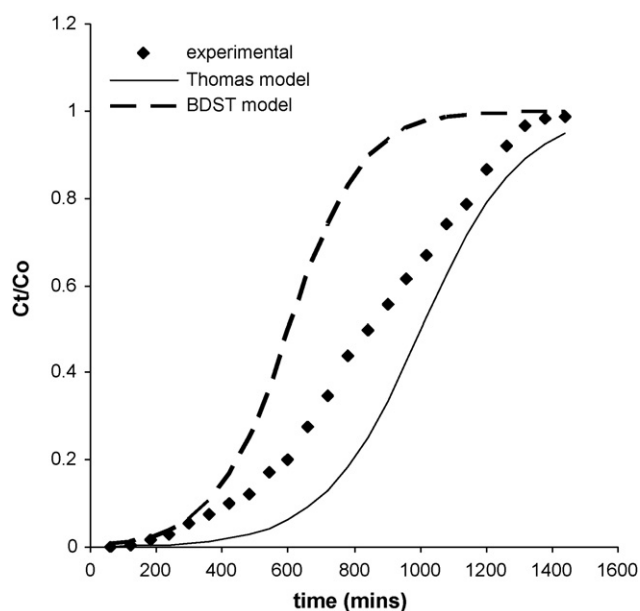
**Table 6**  
Mass Transfer Zone model characteristics of the polymer–clay composite adsorbent premodified with electrolytes.

Adsorbent	$t_x$ (min)	$t_r$ (min)	$t_f$ (min)	$\sigma$ (cm)	$f$	$F_m$ (ml/min)
PVA adsorbent	980	640	340	10.3	0.4688	1.2
Na <sup>+</sup> premodified	907.02	612	295.02	10.3	0.5179	1.183
Ca <sup>2+</sup> premodified	885.88	649.2	236.68	10.3	0.6354	1.183
Re-AD	772.5	560.83	211.67	10.3	0.6226	1.2



**Fig. 1.** Model breakthrough curves for adsorption of 500 mg/L Cd<sup>2+</sup> onto 20 g polymer–clay composite adsorbent.

guineus, Vijaraghavan et al. [22] in the removal of Ni (II) ions from aqueous solution, using crab shell particles in a fixed-bed column and Muhamad et al. [23] in their study of batch and continuous fixed-bed column biosorption of Cd<sup>2+</sup> and Cu<sup>2+</sup>. However, as influent concentration increased, sharper breakthrough curves were obtained. This can be explained by the fact that more adsorption sites were being used up as the concentration of the Cd<sup>2+</sup> increased. Thus, the higher the concentration of the Cd<sup>2+</sup> in aqueous solution,



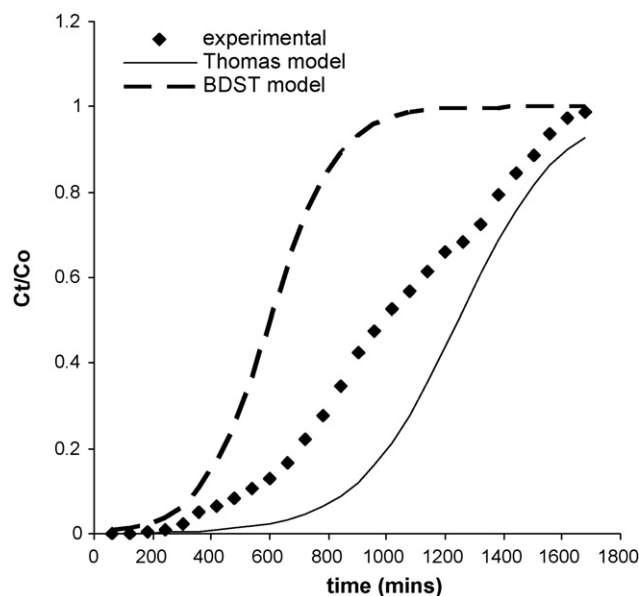
**Fig. 2.** Model breakthrough curves for adsorption of 500 mg/L Cd<sup>2+</sup> onto 25 g of polymer–clay composite adsorbent

the steeper the slope of the breakthrough curve and the smaller the breakthrough time. A similar trend has been reported by Goel et al. [18] for the adsorption of lead (II), using treated granular activated carbon and Singh and Pant [24].

These results suggest that change in concentration gradients affects the saturation rates and the breakthrough time; in other words, the adsorption process is concentration dependent. As the influent concentration increases, Cd<sup>2+</sup> loading rate increases, and so does the driving force increase for mass transfer process, and consequently, a decrease in the adsorption zone.

### 3.3.2. Na- and Ca-impregnated polymer–clay composite adsorbent

The breakthrough curves for the adsorption of Cd<sup>2+</sup> onto polymer–clay composite adsorbent impregnated with 0.1 M NaNO<sub>3</sub> and 0.1 M Ca(NO<sub>3</sub>)<sub>2</sub> are shown in Fig. 3. From Table 3, it was observed that impregnation with Na- or Ca-electrolyte lowered the breakthrough time and thus the service time of the bed,  $t_f$  (Table 6). Similar results were obtained by Lv et al. [25]. The effect of Ca-electrolyte was more pronounced than that of Na-electrolyte at the same electrolyte concentration. The reason could be attributed to competitive effects between the Cd<sup>2+</sup> and the cations of the electrolyte displaced from adsorption sites. This increases the ionic strength within the column and consequently reduces the activity between the Cd<sup>2+</sup> and the adsorption site; and so the adsorption capacity of the adsorbent for Cd<sup>2+</sup> decreases. Since Ca<sup>2+</sup> has more contribution to ionic strength and one more positive charge than sodium, the effect of Ca<sup>2+</sup> was more pronounced than that of Na<sup>+</sup>. However, the electrolyte-impregnated polymer–clay composite adsorbents showed good adsorption capacities for Cd<sup>2+</sup>.



**Fig. 3.** Model breakthrough curves for adsorption of 500 mg/L Cd<sup>2+</sup> onto 30 g of polymer–clay composite adsorbent

**Table 7**

Calculated constants of BDST model for the adsorption of cadmium using linear regression analysis (50% breakthrough).

Adsorbent dose		Initial metal ion concentration				Premodification		
$k_B$ (L/min mg)	$N_0$ (mg/L)	$k_B$ (L/min mg)	$N_0$ (mg/L)	$k_B$ (L/min mg)	$N_0$ (mg/L)	$k_B$ (L/min mg)	$N_0$ (mg/L)	
20 g	$1.20 \times 10^{-4} \pm 0.00001$	19890 $\pm$ 11	150 mg/L	$7.45 \times 10^{-3} \pm 0.0002$	20399.4 $\pm$ 20	PVA-mod	$4.91 \times 10^{-3} \pm 0.0007$	20400.1 $\pm$ 10
25 g	$5.45 \times 10^{-3} \pm 0.00006$	19210 $\pm$ 10	300 mg/L	$4.91 \times 10^{-3} \pm 0.0004$	20400.1 $\pm$ 13	Na-form	$1.63 \times 10^{-3} \pm 0.0006$	18973.4 $\pm$ 09
30 g	$6.00 \times 10^{-3} \pm 0.0004$	19040 $\pm$ 10	500 mg/L	$1.20 \times 10^{-4} \pm 0.00001$	19890 $\pm$ 11	Ca-form	$1.42 \times 10^{-3} \pm 0.0003$	17248.5 $\pm$ 10

### 3.4. Regeneration

The effect of regenerating the polymer–clay composite adsorbent and re-adsorption of  $\text{Cd}^{2+}$  onto polymer–clay composite adsorbent on the breakthrough curve is shown in Fig. 4. The slope of the breakthrough curve increased (from 0.001 to 0.0012) on re-adsorption of  $\text{Cd}^{2+}$  after regeneration of the bed, and this led to a reduction in the Mass Transfer Zone of the bed, and hence, a reduction in the amount of  $\text{Cd}^{2+}$  adsorbed. The breakthrough curve (Fig. 9) and the model breakthrough curves (Fig. 10) showed that re-adsorption of  $\text{Cd}^{2+}$  on the regenerated polymer–clay composite adsorbent bed lowers the breakthrough time [8]. Similar trend was obtained by Sankararamakrishnan et al. [26]. However, the polymer–clay composite adsorbent showed good adsorption capacity for  $\text{Cd}^{2+}$ . This result shows that the polymer–clay composite adsorbent is a good adsorbent that can be regenerated and used over a period of time and its Na-form can still be used for the efficient removal of  $\text{Cd}^{2+}$  from aqueous solutions.

### 3.5. Bed Depth Service Time model parameters

#### 3.5.1. Effect of adsorbent dose

With increasing adsorbent dose, the critical bed depth  $Z_0$  was found to be 0.82 cm, 0.85 cm and 0.87 cm for the three adsorbent doses at  $T_{b50}$ . This suggests that the critical bed depth decreases as  $C_i/C_0$  increases. This also implies that the real bed depth for a fixed-bed adsorption of  $\text{Cd}^{2+}$  by polymer–clay composite adsorbent (in a fixed-bed column with diameter 16 mm) with weight  $\geq 20$  g should be  $\geq 5.54$  cm (Table 7), irrespective of the initial metal ion concentration. However, the adsorption capacity of the adsorbent was found to decrease with increased adsorbent dose (Table 7).

It was also observed that the efficiency of the bed decreased with increasing adsorbent dose (Table 4). This was likely due to the fact that the density of the packed material reduced the contact surface

area of the filter media in the packed column configuration, thereby decreasing the observed adsorption capacities [27]. Further more, increased bed depth (adsorbent dose) increased 50% breakthrough time (Table 1) and exhaustion time (Table 4). Similar observations have been made by Hana et al. [28].

#### 3.5.2. Effect of initial metal ion concentration

With increasing initial metal ion concentrations, critical bed height,  $Z_0$ , was found to be  $T_{b50}$  (0.82 cm) (Table 2). However, adsorption capacity of polymer–clay composite adsorbent,  $N_0$ , was found to increase for up to 300 mg/L and then decreased at 500 mg/L. Rate constants were found to decrease with increasing initial metal ion concentration (Table 7). The adsorption capacity of polymer–clay composite adsorbent in this study (20,400 mg/L  $\approx$  1236 mg/g) was found to be more than that obtained in batch studies (41.67 mg/g [9]). This suggests that the fixed-bed studies provides better adsorption capacity and gives the true efficiency of an adsorbent because of increased mass transfer.

#### 3.5.3. Effect of premodification

The critical bed depth  $Z_0$  decreased as a result of the pre-modification of the polymer–clay composite adsorbent bed with Na- and Ca-electrolyte. At  $T_{b50}$  they were 0.82 cm, 0.78 cm and 0.76 cm respectively. The more pronounced effect of the Ca-electrolyte on the available adsorption sites of the polymer–clay composite adsorbent bed was seen in the value of its critical bed depth which is lower than that of the polymer–clay adsorbent and the Na-impregnated adsorbent. The adsorption capacities  $N_0$  and rate constants were calculated and found to decrease with premodification of polymer–clay composite adsorbent at

**Table 8**

Root Mean Square Error (RMSE) analysis for fitted experimental data against BDST and Thomas models using nonlinear regression analysis (effect of adsorbent dose and initial metal ion concentration).

	BDST	Thomas
20 g	0.06	0.14
25 g	0.23	0.13
30 g	0.32	0.17
150 mg/L	0.11	0.21
300 mg/L	0.04	0.15
500 mg/L	0.05	0.13

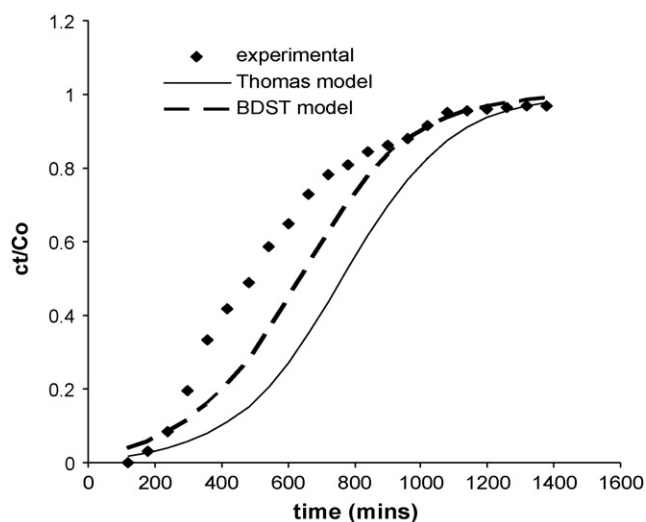
\* $y^{\text{cal}}$  used for the calculation of SS were obtained from non-linear regression analysis and were compared with  $y^{\text{exp}}$  (Eq. (16)).

**Table 9**

Root Mean Square Error (RMSE) analysis data for fitted experimental data against BDST and Thomas models using nonlinear regression analysis (effect of premodification and re-adsorption).

	BDST	Thomas
PVA-mod	0.11	0.15
Na-form	0.07	0.15
Ca-form	0.06	0.14
PVA-Ad	0.11	0.15
PVA-ReAd	0.09	0.15

\* $y^{\text{cal}}$  used for the calculation of SS were obtained from non-linear regression analysis and were compared with  $y^{\text{exp}}$  (Eq. (16)).



**Fig. 4.** Model breakthrough curves for adsorption of 150 mg/L  $\text{Cd}^{2+}$  onto polymer–clay composite adsorbent.

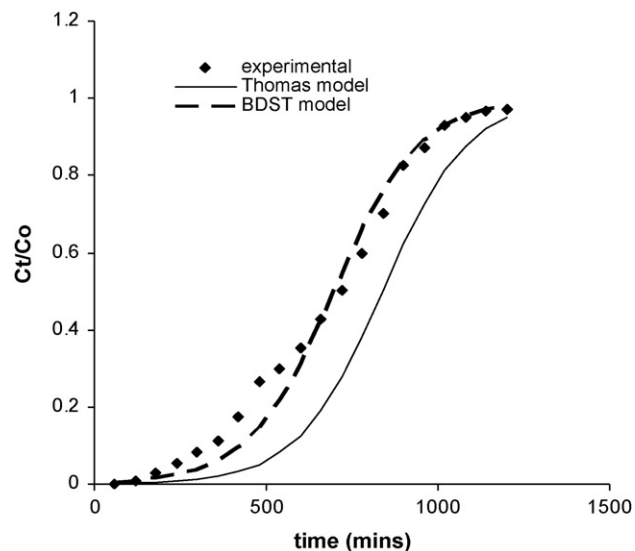


Fig. 5. Model breakthrough curves for adsorption of 300 mg/L  $\text{Cd}^{2+}$  onto polymer-clay composite adsorbent.

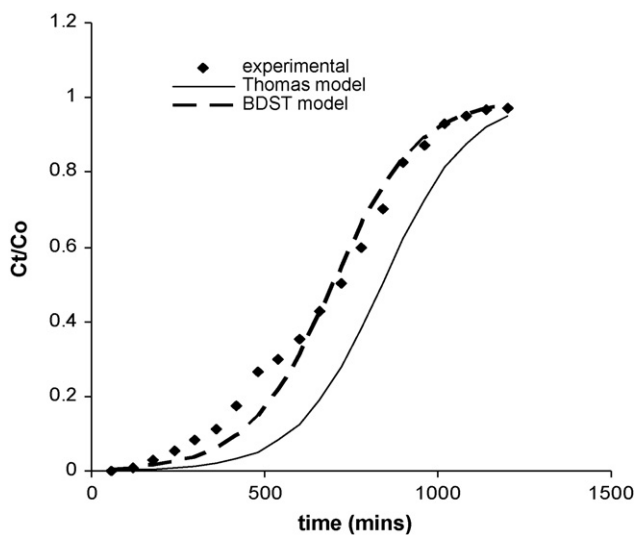


Fig. 6. Model breakthrough curves for adsorption of 500 mg/L  $\text{Cd}^{2+}$  onto polymer-clay composite adsorbent.

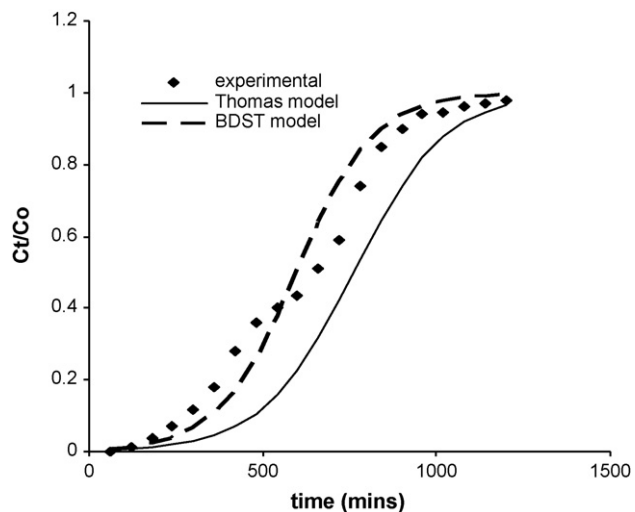


Fig. 7. Model breakthrough curves for the adsorption of 300 mg/L  $\text{Cd}^{2+}$  onto 20 g  $\text{Na}^+$  premodified polymer-clay composite adsorbent.

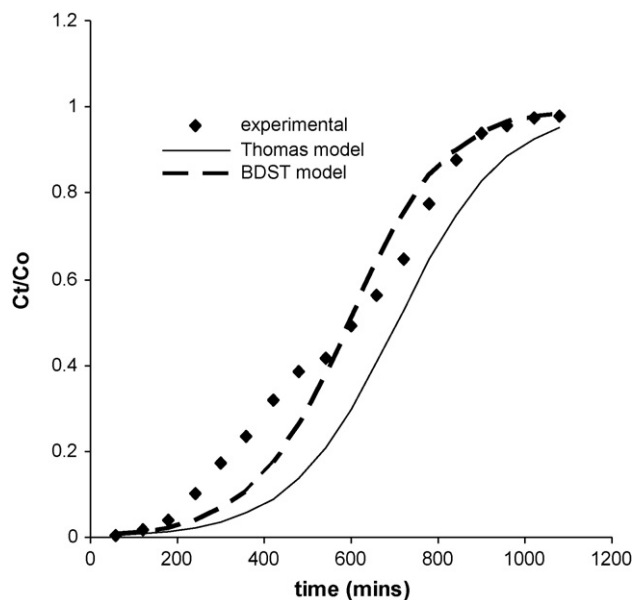


Fig. 8. Model breakthrough curves for the adsorption of 300 mg/L  $\text{Cd}^{2+}$  onto 20 g  $\text{Ca}^{2+}$  premodified polymer-clay composite adsorbent.

50% breakthrough time (Table 7). This suggests that both Na- and Ca-forms of polymer-clay composite adsorbent have reduced adsorption capacities for  $\text{Cd}^{2+}$  and decreased rate of adsorption for the metal ion. This may be because of the divalent nature of  $\text{Ca}^{2+}$  which enhances its competitive ability with  $\text{Cd}^{2+}$  for adsorption sites on the surface of the adsorbent. Thus, some more time will be required for  $\text{Cd}^{2+}$  to dislodge  $\text{Ca}^{2+}$  from the adsorption site than for it to do same to  $\text{Na}^+$  on same adsorption sites.

### 3.6. Data fitting

The Root Mean Square Method of Error analysis was used to fit experimental data to theoretical data obtained from both Thomas and Bed Depth Service Time models. Experimental data obtained were fitted against both BDST and Thomas models. It was observed that experimental data showed stronger fit to BDST model than to Thomas model as shown in Tables 8 and 9, using non linear forms of equations 1 and 4. The plots obtained from these fittings (Figs. 1–8)

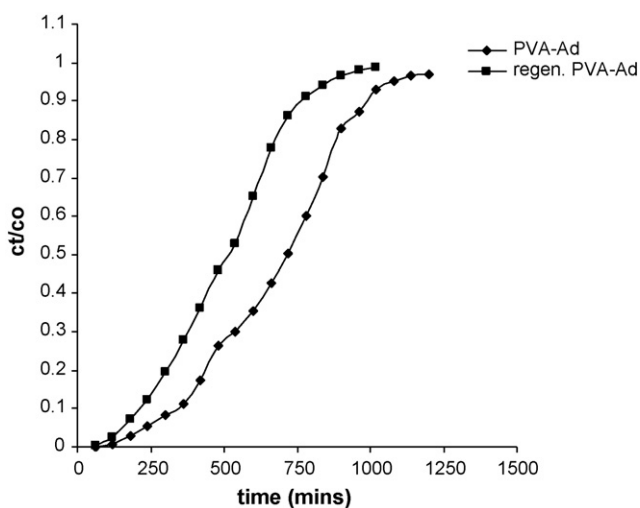


Fig. 9. Breakthrough curves for spent and regenerated polymer-clay composite adsorbent.



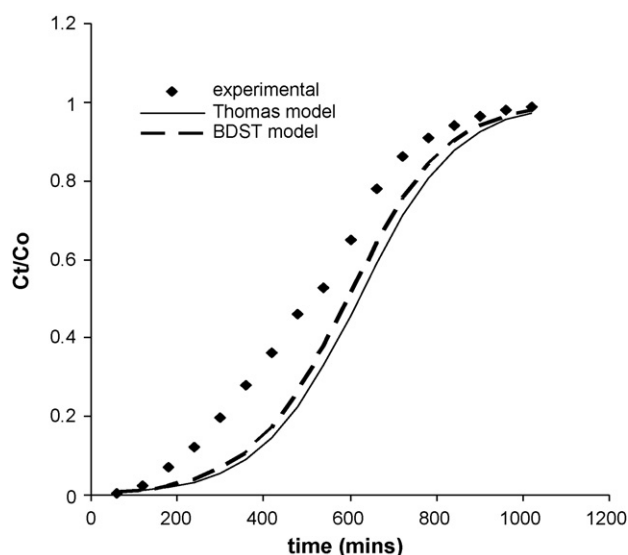


Fig. 10. Model breakthrough curves for the adsorption of 300 mg/L  $\text{Cd}^{2+}$  onto 20 g of regenerated polymer-clay composite adsorbent.

further supports the better fit shown by experimental data to BDST model than to Thomas model.

#### 4. Conclusion

This study showed that variation in bed heights of novel polymer-clay composite adsorbent increased the bed volume at both breakpoint and exhaustion point. The total time taken for the formation of the Mass Transfer Zone to move down the column and out of the column ( $t_x$ ) varied with the bed heights of the polymer-clay composite adsorbent. The adsorption capacity of the polymer-clay composite adsorbent at different bed heights obtained from the BDST model showed a decrease with increasing bed heights at 50% breakthrough time.

Premodification of polymer-clay composite adsorbent with Na- and Ca-electrolytes revealed that the presence of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  reduced the adsorption capacity of the adsorbent and also lowered the breakthrough time of the adsorbent. The bed volumes at both the breakpoint and exhaustion point not only decreased, but were also negatively affected by premodification with  $\text{Na}^+$  and  $\text{Ca}^{2+}$  with the effect being more pronounced with the  $\text{Ca}^{2+}$  premodified bed. However, the premodified adsorbent beds still showed very high adsorption capacities for  $\text{Cd}^{2+}$ .

Regeneration and re-adsorption of  $\text{Cd}^{2+}$  onto the polymer-clay adsorbent revealed that the polymer-clay composite adsorbent is a good adsorbent that can be regenerated and used over a period of time.

Results obtained suggests that the adsorption of  $\text{Cd}^{2+}$  onto novel polymer-clay composite adsorbent showed that the adsorbent has potentials as a low-cost adsorbent for the recovery of heavy metals from wastewater. This adsorbent, because of its good preference for  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , could also be used to desalinate water.

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