



# Kinetic and thermodynamics of the removal of $Zn^{2+}$ and $Cu^{2+}$ from aqueous solution by sulphate and phosphate-modified Bentonite clay

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## ABSTRACT

The modification of pristine Bentonite clay with sulphate and phosphate anions was found to increase its cation-exchange capacity (CEC), adsorption capacity and overall pseudo-second order kinetic rate constant for the adsorption of  $Cu^{2+}$  and  $Zn^{2+}$ . Modification with sulphate and phosphate anion decreased the specific surface area of pristine Bentonite clay. Phosphate-modified Bentonite clay was found to give the highest adsorption capacity for both metal ions. The adsorption process was observed to be endothermic and spontaneous in nature for both metal ions with  $Zn^{2+}$  being more adsorbed. Modification with phosphate anion increased the spontaneity of the adsorption process. The effective modification of pristine Bentonite clay with sulphate anion was confirmed from hypochromic shifts in the range of  $13\text{--}18\text{ cm}^{-1}$  which is typical of physisorption while modification with phosphate anion was confirmed by its hyperchromic shifts typical of chemisorption in the infrared red region using Fourier transformed infrared spectroscopy (FTIR). Using the model efficiency indicator, kinetic data were found to show very strong fit to the pseudo-second order kinetic model implying that the adsorption of  $Cu^{2+}$  and  $Zn^{2+}$  were basically by chemisorption.

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## 1. Introduction

One of the main causes of industrial pollution is the discharge of effluents containing heavy metal ions into water bodies. This can have serious health implications on man ranging from cancer, hormonal imbalance to brain impairment. Copper which is one of the most important heavy metal used in electroplating industries causes serious toxicological effects at high doses; after uptake it is known to deposit in brain, skin, liver, pancreas and myocardium [1]. Zinc is an essential element as enzyme activators in humans, but it is equally toxic at levels of 100–500 mg/day and it is a known carcinogen [2]. The nitrate forms of both metal ions are used as a mordant in dyeing in textile industries and in addition copper nitrate is used in electroplating.

Increasing industrialization in Africa is generating large volumes of wastes containing toxic metals. These metals, when discharged into the environment, may get into the food chain causing deleterious effects on humans as well as animals. This has resulted in many waterborne diseases that are currently affecting the health of the workforce of these third world nations with the ultimate negative impact on the socio-economic development of these nations.

Provision of clean/safe drinking water is one of the Millennium Development Goals (MDGs) set out by the United Nations for the year 2025. It is believed that safe water is the key to global health [3].

Several methods have been employed in the recent past to remove high amounts of metal ions from aqueous solutions. These include ion-exchange [4], coagulation, flotation [5], chemical precipitation [6], and membrane processes [7]. The above methods are cost intensive and their application on large-scale treatment of wastewater is largely limited to developed nations.

Adsorption via ion-exchange mode is one of the most popular and efficient methods for the removal of heavy metal ions from industrial wastewater. Since the volume of water to be purified is generally large, the adsorbent required in the process should possess high selectivity with respect to the heavy metal ion(s), non-toxic, regenerable, easily recoverable from filters, relatively cheap and readily available [8]. The use of adsorbents has also been found to circumvent the production of large amounts of sludge, usually generated using alternative wastewater treatment techniques [9]. More so, adsorption processes rarely introduces any secondary pollutant into the water that is treated.

In our previous studies, we have demonstrated how phosphate-modified indigenous kaolinite clay can be used to remove  $Pb^{2+}$  and  $Cd^{2+}$  from aqueous solution [10–13]. Preadsorbed phosphates and sulphate anions onto soils and several other surfaces have been

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**Table 1**  
Some physicochemical properties of pristine and modified Bentonite Clay adsorbents.

	Pristine Bentonite	S-mod Bentonite	P-mod Bentonite
%Si	58.4	–	–
%Al	20.3	–	–
%MgO	2.17	–	–
%Na <sub>2</sub> O	5.3	–	–
%K <sub>2</sub> O	1.15	–	–
%CaO	1.40	–	–
%Fe <sub>2</sub> O <sub>3</sub>	0.09	–	–
Moisture (%)	11.19		
Exchange acidity (meq/100 g)	0.4	0.2	0.4
pH	8.3	8.7	7.9
ECEC (meq/100 g)	95 ± 0.2	109 ± 0.2	118 ± 0.3
Specific surface area (m <sup>2</sup> /g)	80 ± 0.1	73 ± 0.3	79 ± 0.2

Note: S: Sulphate; P: phosphate; mod: modified.

studied before now [14–19]. However, there are no reports on the adsorption dynamics of phosphate and sulphate-modified Bentonite clay in the removal of Zn<sup>2+</sup> and Cu<sup>2+</sup> from aqueous solution.

This paper therefore reports the kinetic and thermodynamic studies of the adsorption of Zn<sup>2+</sup> and Cu<sup>2+</sup> onto pristine, sulphate and phosphate-modified Bentonite clay.

## 2. Materials and method

Bentonite clay used in this study was obtained from the Federal Institute of Industrial Research (FIRO), Lagos, Nigeria. It was used as received without further purification. Some physicochemical properties of the Bentonite clay are shown in Table 1.

### 2.1. Modification of sample

Fifty gram of the pristine Bentonite clay was added to 500 mL of 200 mg/L of Potassium dihydrogen phosphate and sodium tetraoxosulphate (VI) salts in 1 L beaker. The clay suspensions were stirred on a magnetic stirrer for 6 hrs after which they were centrifuged. The supernatant were discarded and the modified samples were washed with distilled-deionized water until test for phosphate or sulphate was negative. They were all dried in an oven at 343 K. The dried samples were gently crushed and packed into plastic containers for further use.

### 2.2. Physicochemical characterization of adsorbents

The effective cation-exchange capacity (ECEC) of the pristine Bentonite clay was determined by the method employed by Juo et al. [20]. It involved the summation of the exchangeable acidity and the cation-exchange capacity of the adsorbent. The cation-exchange capacity (CEC) of both pristine and modified Bentonite clay samples were determined by modified Ammonium acetate method [21]. In this method, 50 mL of 1 M sodium acetate (CH<sub>3</sub>COONa) was added to 2 g of the adsorbents. The suspension was then agitated for 1 hr at 200 rpm. This was then filtered and the residue washed with distilled-deionized water several times to remove excess sodium acetate from the adsorbents. They were filtered and air-dried. The samples were then added to 50 mL of 1 M Ammonium acetate (pH 7.0) and agitated. This step was repeated three times and each time the supernatant were collected and kept for Na<sup>+</sup> analysis using Flame Photometry.

The Fourier transformed infrared (FTIR) spectra of pristine Bentonite, sulphate-modified, and phosphate-modified Bentonite were obtained using KBr wafer in conjunction with SHIMADZU 8400S FTIR instrument. Specific surface area of the adsorbents was determined via the Sears method [22]. In this method, 0.5 g of the sample was acidified with 0.1 M HCl to a pH 3–3.5. The volume was made up to 50 mL with distilled water after addition of 10.0 g of

NaCl. The titration was carried out with standard 0.1 M NaOH in a thermostatic bath at 25 °C to pH 4.0, and then to pH 9.0. The volume, *V*, required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed from the following equation [22]:

$$S \left( \frac{\text{m}^2}{\text{g}} \right) = 32V - 25 \quad (1)$$

where *S* is surface area, *V* is the volume of NaOH used for titration.

### 2.3. Adsorption studies

0.2 g each of pristine and modified Bentonite clay samples were weighed into 60 mL plastic bottles. Twenty millilitres of 200 mg/L of metal ion solutions (i.e. Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) were prepared from their stock solutions. A range of concentration from 200 to 700 mg/L at pH 5.5 ± 0.2 for Cu<sup>2+</sup> and Zn<sup>2+</sup> was used. The solutions were then agitated at room temperature (28 ± 2 °C) for 240 min. Thereafter, they were filtered using Whatman filter paper and the filtrates were analyzed using flame atomic absorption spectrophotometer (FAAS). This procedure was repeated at 40 and 50 °C for thermodynamic studies.

For kinetic studies, 0.2 g of the adsorbents were added to 20 mL of the various known concentrations of Cu<sup>2+</sup> and Zn<sup>2+</sup> (200 and 300 mg/L) and agitated in a reciprocal shaker. Samples were withdrawn at specific intervals, filtered and filtrates analyzed for the metal ions using flame atomic absorption spectrophotometer (FAAS).

All experiments were carried out in duplicate and the amount adsorbed by adsorbent after FAAS reading of equilibrium solution was calculated by difference. The averages of both values were used for data analysis. Different lamps for each metal ion were used during the analysis at their respective wavelengths (Copper 324.8 nm and Zinc 213.9 nm).

### 2.4. Theory of models

#### 2.4.1. Pseudo-second order kinetic model

The pseudo-second order kinetic model (PSOM) derived by Ho and McKay [9] is obtained as follows:

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

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 metal ion adsorbed at equilibrium (mg/g),  $q_t$  is the amount of metal ion adsorbed at time  $t$  (min) in mg/g and  $k$  is the rate constant of the PSOM for adsorption of the metal ion.

The non-linear form of Eq. (2) is:

$$qt = \frac{kq_e^2 t}{(1 + kq_e t)} \quad (5)$$

The approaching equilibrium factor ( $R_w$ ), which represents the characteristics of kinetic curve of an adsorption system is defined as [23]:

$$R_w = \frac{1}{(1 + kq_e t_{ref})} \quad (6)$$

$$kq_e t_{ref} = R_w - \frac{1}{R_w}$$

where  $t_{ref}$  is the longest operation time (based on kinetic experiments) in an adsorption system,  $q_e$  is the amount of metal ion adsorbed at equilibrium (mg/g) and  $k$  is the pseudo-second order kinetic rate constant ( $\text{gm g}^{-1} \text{min}$ ).

The pseudo-second order kinetic model can also be written as:

$$\frac{d(q_t/q_t)}{dt} = kq_e \left[ 1 - \frac{q_t}{q_e} \right]^2 \quad (7)$$

However, it can be written as

$$t = \frac{[q_t/(q_e - q_t)]}{kq_e} \quad (8)$$

At the half-life of the adsorption process i.e. ( $t = t_{0.5}$ ), we have  $q_t = 0.5q_e$  and

$$t_{0.5} = \frac{1}{kq_e} \quad (9)$$

#### 2.4.2. Thermodynamics

The thermodynamic parameters,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ , for the adsorption process are calculated using the relation

$$\ln \left( \frac{q_e}{C_e} \right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where  $C_e$  and  $q_e$  are the equilibrium concentration of metal in solutions (mg/L) and amount of metal ion adsorbed at equilibrium (mg/g), respectively. The plot of  $\ln(C_e/q_e)$  versus  $1/T$  yields straight lines with the slope and the intercept giving values of  $\Delta H^\circ$  and  $\Delta S^\circ$ . These values could be used to compute  $\Delta G^\circ$  from the Gibbs relation,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  at constant temperature. In deriving the values of the thermodynamic parameters, it is assumed that the enthalpy does not change with temperature.

#### 2.4.3. Model efficiency

Numerous methods exist for determining goodness of fit; however, only one measure is used in this study—the model efficiency—because this statistical measure is considered by many to be the best overall indicator of model fit because it shows a good measure of resistance to errors due to extreme experimental values [24]. The model efficiency,  $E$  is calculated as:

$$E = 1 - \frac{\sum_{i=1}^N w_i (S_i - \hat{S}_i)^2}{\sum_{i=1}^N (S_i - \hat{S}_{wavg})^2} \quad (11)$$

where  $S_{wavg}$  is the weighted mean of the measured values and all other variables are as defined above. A model efficiency of 1 indicates a perfect fit to the data, whereas model efficiency value of <0 indicates that taking the average of all the measured values would give a better prediction than the model. Some statistical packages such as SAS refer to the value calculated in Eq. (11) as  $r^2$ ; however, this is a misnomer because Eq. (11) can result in a negative number and the square of the real numbers in Eq. (11) cannot be negative.

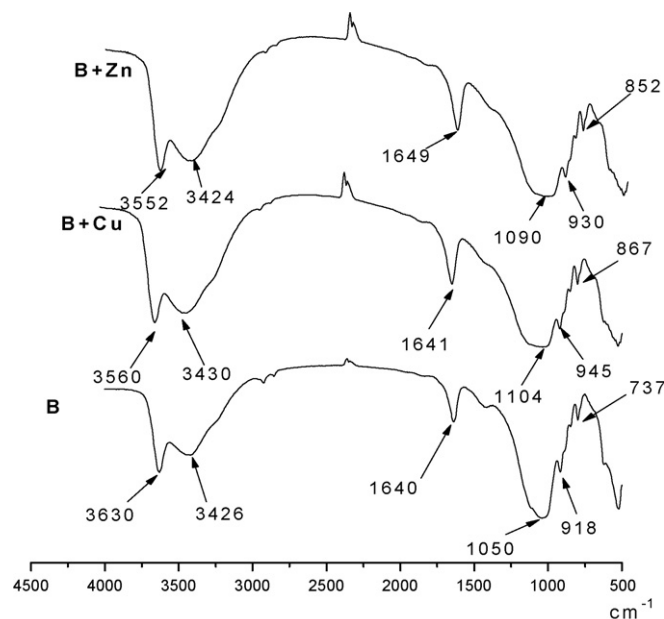


Fig. 1. Fourier transformed infrared spectra of metal ions adsorbed onto Bentonite clay adsorbent where B = Bentonite.

### 3. Results and discussions

#### 3.1. Physicochemical analysis of adsorbents

Some data for the physicochemical analysis of the pristine and modified Bentonite clay adsorbents are presented in Table 1. From Table 1, the cation-exchange capacities (CEC) for the modified Bentonite clay adsorbents were higher than that for the pristine Bentonite with phosphate-modified Bentonite clay given the highest CEC (Table 1). However, modification with phosphate and sulphate anions decreased the specific surface area of pristine Bentonite clay. This has also been observed by Kim and Woo [18], Unuabonah [25], and Li et al. [14]. It is possible the aggregation of clay particles in the presence of sulphate and phosphate (as observed from the better flocculation of the clay mineral in solution) could have decreased the specific surface area of the adsorbents as suggested by Liu and González [26]. Again the modification with these anions could have block some of the pores of bentonite which ultimately led to the decrease in surface area. However, this did not affect their adsorption capacity as the CEC of the modified adsorbents were enhanced by the presence of more binding sites introduced by the modifying reagents.

The infrared spectra of both modified and unmodified Bentonite adsorbents are shown in Figs. 1–3. The structural –OH vibrations and OH bending modes exist in the regions 3700–3200 and 1300–440  $\text{cm}^{-1}$  (a peak and a shoulder), respectively, in the FTIR spectrum of raw Bentonite (Fig. 1) [27,28]. The characteristic –OH stretching vibration observed at 3630  $\text{cm}^{-1}$  is the AlAlOH stretch from the Al-rich octahedral centres of Bentonite. The band at 3426  $\text{cm}^{-1}$  belongs to the –OH stretching of H-bonded water indicating the higher amount of octahedral replacement of Mg atoms than that of Fe atoms [29,30]. The characteristic AlAlOH and AlFeOH bending vibrations were found at 913, 848  $\text{cm}^{-1}$ , respectively with their finger print regions at 524 and 462  $\text{cm}^{-1}$  [31].

Modification of Bentonite clay resulted in a shift in the structural –OH vibrational band and adsorbed water from 3636 and 3425 to 3626 and 3433  $\text{cm}^{-1}$ , respectively (hypochromic shift) for sulphate-modified Bentonite clay and to 3645 and 3376  $\text{cm}^{-1}$ , respectively (hyperchromic shift) for phosphate-modified Bentonite clay, respectively (Figs. 2 and 3). This is a strong indication

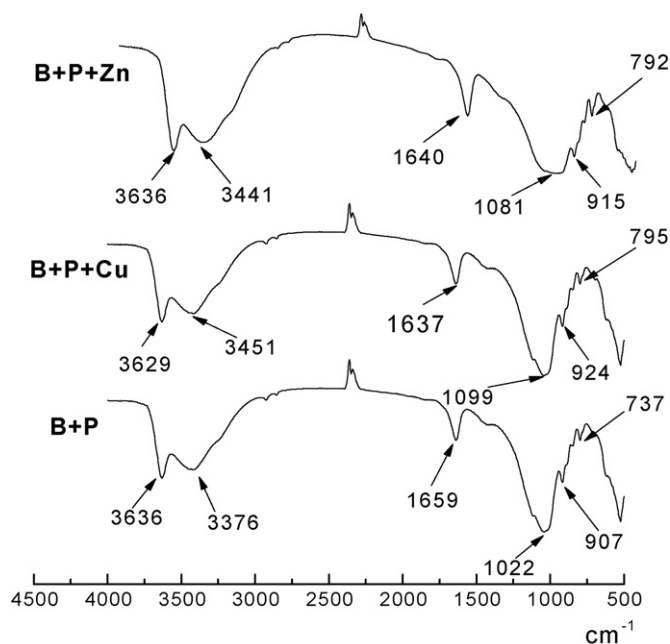


Fig. 2. Fourier transformed infrared spectra of metal ions adsorbed onto phosphate-modified Bentonite clay adsorbent where B = Bentonite, P = phosphate.

that modification was effective on the surface of the Bentonite clay. The  $-OH$  bending frequency of water at  $1640\text{ cm}^{-1}$  in the pristine Bentonite clay was shifted to  $1620$  and  $1659\text{ cm}^{-1}$  when it was modified with sulphate and phosphate anions, respectively indicating the displacement of water molecules during modification. The stretching and bending vibrations of structural  $-OH$  in pristine Bentonite clay shifted from  $1050$  and  $918\text{ cm}^{-1}$  to  $1061$  and  $903\text{ cm}^{-1}$ , respectively for sulphate-modified Bentonite clay and  $1022$  and  $906\text{ cm}^{-1}$  for phosphate-modified Bentonite clay. The  $1061$  and  $1022\text{ cm}^{-1}$  are the  $S-O^-$  and  $P-O^-$  stretching peaks. Usually this stretching vibration of  $P-O^-$  group occurs between  $1120$  and  $1000\text{ cm}^{-1}$  [32] while  $S-O^-$  principally occurs in the ranges of

observed frequencies of  $1180$ – $1030\text{ cm}^{-1}$  [33]. Both peaks usually appear as strong bands as seen in Figs. 2 and 3.

Typical  $P=O$  ( $1340$ – $1235\text{ cm}^{-1}$ ),  $S=O$  ( $1383\text{ cm}^{-1}$ ) and partial double bond of  $S=O$  ( $1330\text{ cm}^{-1}$ ) were not seen in our FTIR spectra. One possible reason for this is because mixing dry Bentonite modified samples with KBr leads to conditions resembling a saturated KBr solution in the layer of water that remains on the surface after drying. A high concentration of  $Br^-$  might have displaced most  $SO_4^{2-}$  and  $PO_4^{3-}$  from the surface, such that surface coordinated sulphate and phosphate anions can no longer be observed. The fact that FTIR measurements with different methods and sample preparations lead to quite different results and interpretations emphasizes the need of *in situ* measurements of complexation on aqueous surfaces [19].

From the foregoing FTIR spectra analysis, it is therefore possible to conclude that the modification of Bentonite clay with phosphate and sulphate reagents was effective on the silica and alumina portions of the clay mineral.

### 3.2. Kinetic analysis

Table 2 shows the pseudo-second order kinetic parameters obtained from kinetic data. From Table 2 it is seen that modification increased the adsorption capacity of pristine Bentonite clay with phosphate-modified Bentonite clay adsorbent giving the highest adsorption capacity. Modification of bentonite clay also increased the overall pseudo-second order kinetic rate of adsorption of both metal ions at initial metal ion concentrations ( $200$  and  $300\text{ mg/L}$ ). This is probably due to the blockage of the pores of the adsorbent by phosphate or sulphate anions. Since the pores are possibly clogged, diffusion process will be shortened and thus equilibrium time reduced. With modification, it is possible that the fast adsorption step was shortened and the slow adsorption step extended.

Table 2

Pseudo-second order kinetic data for the adsorption of  $Zn^{2+}$  and  $Cu^{2+}$  onto pristine and modified Bentonite clay adsorbents.

	Pristine Bentonite	S-mod Bentonite	P-mod Bentonite
200 mg/L			
Zinc			
$q_e$ ( $\text{mg g}^{-1}$ )	16.18 (16.36)	17.21 (17.17)	17.76 (17.50)
$k$ ( $\text{g mg}^{-1} \text{min}$ )	$2.56 \times 10^{-2}$	$2.65 \times 10^{-2}$	$2.60 \times 10^{-2}$
$h$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	6.70	7.86	8.20
$r^2$	0.9996	0.9997	0.9996
$E$	0.9999	0.9999	0.9999
Copper			
$q_e$ ( $\text{mg g}^{-1}$ )	17.54 (16.80)	18.12 (17.06)	18.21 (17.97)
$k$ ( $\text{g mg}^{-1} \text{min}$ )	$2.89 \times 10^{-2}$	$2.92 \times 10^{-2}$	$2.91 \times 10^{-2}$
$h$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	8.90	9.62	9.66
$r^2$	0.9997	0.9997	0.9998
$E$	0.9998	0.9999	0.9999
300 mg/L			
Zinc			
$q_e$ ( $\text{mg g}^{-1}$ )	26.11 (24.48)	26.95 (26.19)	28.01 (26.63)
$k$ ( $\text{g mg}^{-1} \text{min}$ )	$5.47 \times 10^{-3}$	$5.93 \times 10^{-3}$	$5.56 \times 10^{-3}$
$h$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	3.73	4.31	4.36
$r^2$	0.9941	0.9948	0.9953
$E$	0.9982	0.9982	0.9983
Copper			
$q_e$ ( $\text{mg g}^{-1}$ )	26.74 (25.93)	27.78 (26.41)	27.62 (27.00)
$k$ ( $\text{g mg}^{-1} \text{min}$ )	$6.18 \times 10^{-3}$	$6.16 \times 10^{-3}$	$6.04 \times 10^{-3}$
$h$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	4.42	4.61	4.76
$r^2$	0.9962	0.9965	0.9968
$E$	0.9883	0.9903	0.9896

Note: Values in bracket are equilibrium data from equilibrium studies. S: Sulphate; P: phosphate; mod: modified; E: model efficiency.

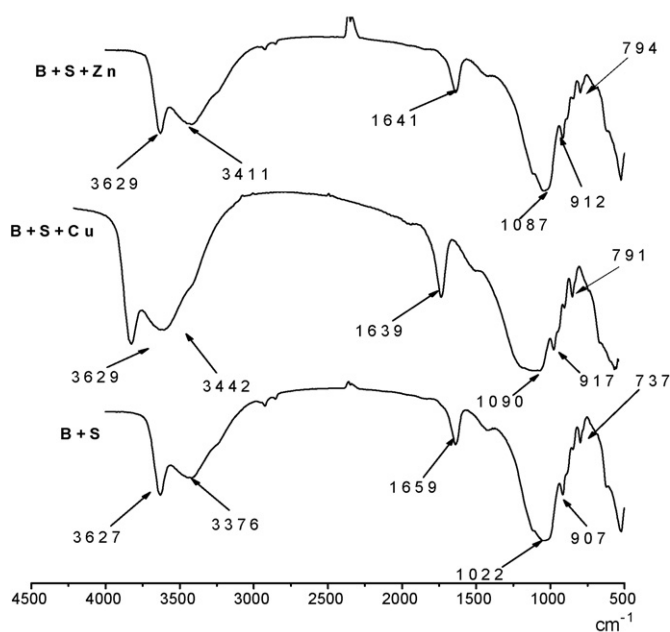


Fig. 3. Fourier transformed infrared spectra of metal ions adsorbed onto sulphate-modified Bentonite clay adsorbent where B = Bentonite, S = Sulphate.

**Table 3**

Approaching equilibrium factor and adsorption kinetic behavior in the pseudo-second order kinetic model.

$R_w$ value	Type of kinetic curve	Approaching equilibrium level	Zone
$R_w = 1$	Linear	Not approaching equilibrium	0
$1 > R_w > 0.1$	Slightly curved	Approaching equilibrium	I
$0.1 > R_w > 0.001$	Largely curved	Well approaching equilibrium	II
$R_w < 0.01$	Pseudo-rectangular	Drastically approaching equilibrium	III

Recently, Wu et al. [23] proposed a second order kinetic rate index ( $k_2q_e$ ) which they suggest really reflect the kinetic performance of an adsorbent and an approaching equilibrium factor which represents the characteristics of the kinetic curve of an adsorption system using a pseudo-second order kinetic model. The various implications of the various  $R_w$  values are shown in Table 3. Applying this to our kinetic data, various data were obtained (Table 4). The second order rate index was increased and the approaching equilibrium factor was decreased by modification of pristine Bentonite clay for the adsorption of both  $Zn^{2+}$  and  $Cu^{2+}$  and at both initial metal ion concentrations applied (Table 4). Data obtained for the second order rate index,  $k_2q_e$ , is supported by the pseudo-second order kinetic rate constants obtained earlier (Table 2). The half-life data ( $t_{0.5}$ , time required for half the amount of adsorbate to be adsorbed from aqueous solution) in Table 4 suggests that modification of pristine Bentonite clay with phosphate or sulphate anions reduces the time for the adsorption of a known concentration of  $Zn^{2+}$  and  $Cu^{2+}$  onto pristine Bentonite. This invariably implies that modification of pristine Bentonite clay with phosphate or sulphate anion improves the rate of  $Zn^{2+}$  and  $Cu^{2+}$  adsorption and thus decrease the time it takes for the adsorption reaction to approach equilibrium.

The adsorption capacities for the modified adsorbents were higher than for pristine Bentonite clay with the phosphate-modified Bentonite showing the highest adsorption capacities for the various metal ions (Table 2). However, the initial adsorption rates for the metal ions were higher at lower initial metal ion concentrations; modified Bentonite clay samples gave higher initial sorption rates for both metal ions (Table 5). Figs. 4–7 show plots for experimental kinetic data fit to the non-linear pseudo-second order kinetic model data. It is observed that for both metal

**Table 4**

Rate index, half-life and approaching equilibrium factor data for the adsorption of  $Zn^{2+}$  and  $Cu^{2+}$  onto pristine and modified Bentonite clay adsorbents.

	Pristine Bentonite	S-mod Bentonite	P-mod Bentonite
200 mg/L			
Zinc			
$kq_e$ ( $\text{min}^{-1}$ )	0.414	0.457	0.461
$t_{0.5}$	2.416	2.189	2.165
$R_w$	0.024	0.019	0.019
Copper			
$kq_e$ ( $\text{min}^{-1}$ )	0.507	0.531	0.530
$t_{0.5}$	1.972	1.884	1.885
$R_w$	0.016	0.015	0.014
300 mg/L			
Zinc			
$kq_e$ ( $\text{min}^{-1}$ )	0.143	0.160	0.156
$t_{0.5}$	7.000	6.253	6.420
$R_w$	0.170	0.140	0.147
Copper			
$kq_e$ ( $\text{min}^{-1}$ )	0.165	0.167	0.171
$t_{0.5}$	6.051	5.989	5.841
$R_w$	0.132	0.130	0.124

Note: S: Sulphate; P: phosphate; mod: modified.

$kq_e$ : rate index.

$t_{0.5}$ : half-life of adsorption process.

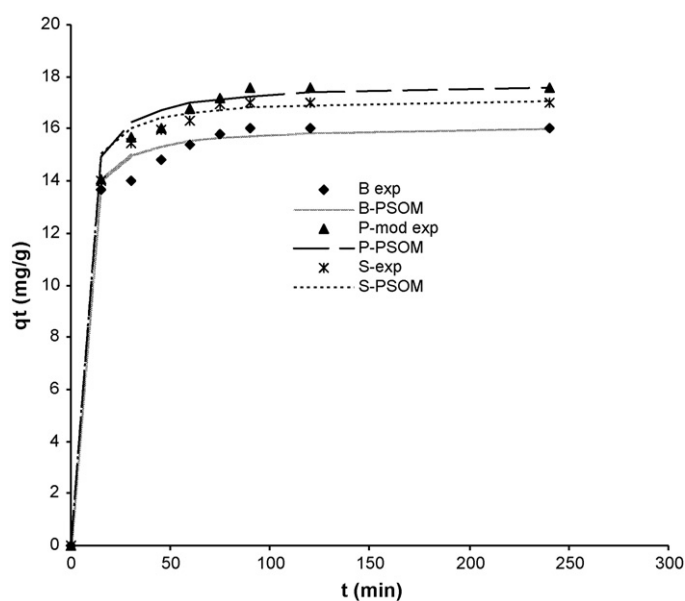
$R_w$ : approaching equilibrium factor.

**Table 5**

Thermodynamic parameters for the adsorption of  $Zn^{2+}$  and  $Cu^{2+}$  onto pristine and modified Bentonite clay adsorbents.

	P-mod Bentonite	S-mod Bentonite	Pristine Bentonite
Zinc			
$+\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )	10.21	9.64	9.69
$+\Delta S^\circ$ ( $\text{J mol}^{-1}$ )	54.97	48.34	45.03
$-\Delta G^\circ$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )	298 K 16.37 313 K 17.20 323 K 17.75	14.40 15.12 15.61	13.41 14.08 14.53
$R^2$	0.9230	0.9944	0.9988
Copper			
$+\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )	5.22	11.57	7.50
$+\Delta S^\circ$ ( $\text{J mol}^{-1}$ )	36.78	55.02	39.13
$-\Delta G^\circ$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )	298 K 10.96 313 K 11.51 323 K 11.87	16.38 17.21 17.76	11.65 12.24 12.63
$R^2$	0.9400	0.9472	0.9401
Zinc			
$+\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )	6.58	4.50	4.13
$+\Delta S^\circ$ ( $\text{J mol}^{-1}$ )	39.86	25.32	29.46
$-\Delta G^\circ$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )	298 K 11.87 313 K 12.47 323 K 12.87	0.76 0.80 0.82	8.77 9.22 9.51
$R^2$	0.9950	0.9998	0.7194
Copper			
$+\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )	6.24	4.89	6.72
$+\Delta S^\circ$ ( $\text{J mol}^{-1}$ )	38.21	33.01	37.86
$-\Delta G^\circ$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )	298 K 11.38 313 K 11.95 323 K 12.33	9.83 10.33 10.66	11.27 11.84 12.22
$R^2$	0.9481	0.9997	0.8014

Note: S: Sulphate; P: phosphate; mod: modified.



**Fig. 4.** Pseudo-second order kinetic model plot for the adsorption of 200 mg/L  $Zn^{2+}$  onto pristine and modified Bentonite clay adsorbents.

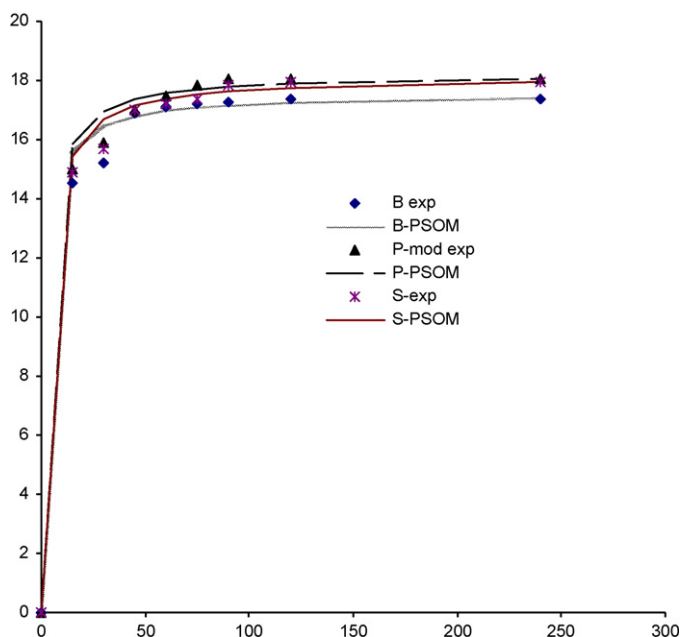


Fig. 5. Pseudo-second order kinetic model plot for the adsorption of 200 mg/L  $\text{Cu}^{2+}$  onto pristine and modified Bentonite clay adsorbents.

ions and at both initial metal ion concentrations, equilibrium was reached within 60 min of the adsorption process. Model efficiency ( $E$ ) data suggests a near perfect fit of kinetic data with the pseudo-second order kinetic model data for all the adsorbents (Table 2). This further suggests that the adsorption of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  onto both pristine and modified Bentonite adsorbents was by chemisorption involving valent forces through sharing or the exchange of electrons as initial concentration of metal ion increases in solution. This result strongly supports the fact that chemical reaction is significant in the rate-controlling step of the adsorption of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  onto pristine and modified Bentonite clay adsorbents.

Modification of Bentonite with sulphate or phosphate anion increased its adsorption capacity with  $\text{Cu}^{2+}$  being slightly more adsorbed than  $\text{Zn}^{2+}$  (Table 5). The adsorption of phosphate and

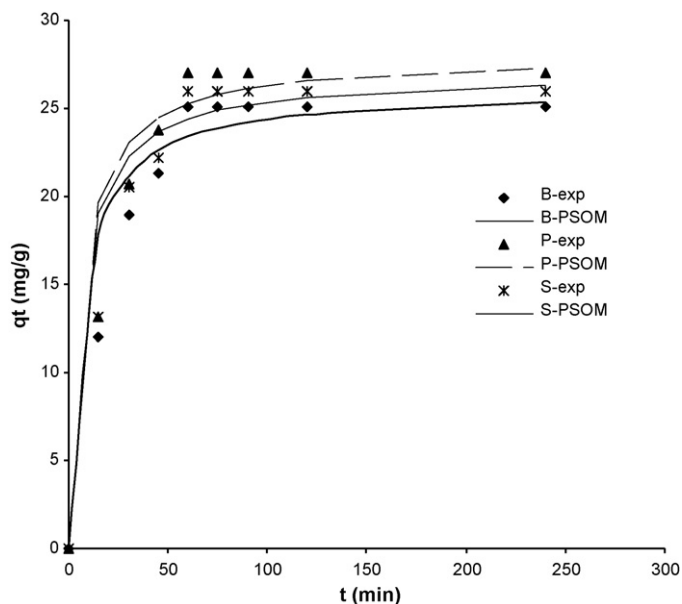


Fig. 6. Pseudo-second order kinetic model plot for the adsorption of 300 mg/L  $\text{Zn}^{2+}$  onto pristine and modified Bentonite clay adsorbents.

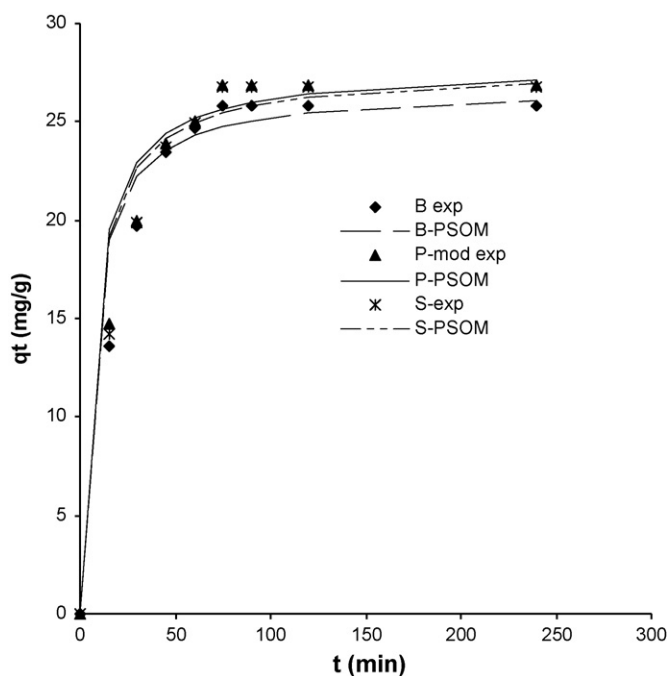


Fig. 7. Pseudo-second order kinetic model plot for the adsorption of 300 mg/L  $\text{Cu}^{2+}$  onto pristine and modified Bentonite clay adsorbents.

sulphate anions increased the negative charge on Bentonite clay surface and hence its adsorption capacity for  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  [10,14,15,17,25,34].

### 3.3. Thermodynamics of adsorption

Table 5 shows thermodynamic parameters obtained for the adsorption of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  onto pristine Bentonite and modified Bentonite clay adsorbents. Change in heat of enthalpy for both metal ions ( $\Delta H^\circ$ ) was endothermic in nature for all adsorbents although previously, Kubilay et al. [35] in their study of the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  onto pristine Bentonite clay at various pHs observed an exothermic adsorption process from at 5.0. This means the uptake of these metal ions is favored with increasing temperatures, since a higher temperature activates the metal ions for enhancing adsorption at the coordinating sites of the minerals [36]. Also, it is mentioned that cations move faster with increasing temperature. Likely explanation for this is the weaker specific or electrostatic interactions between ions with increasing temperature resulting in smaller ions because solvation is reduced [37]. The standard entropy change of the adsorption system ( $\Delta S^\circ$ ) was also positive for all adsorbent surfaces at both initial metal ion concentration for both metal ions. The standard entropy of the reaction system was generally higher for phosphate-modified adsorbents than for other adsorbents. Positive entropy is an indication that the adsorption of the metal ions onto the adsorbents produced a state less ordered in their molecular arrangement [35,38].

The Gibbs free energies ( $\Delta G^\circ$ ) of the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  onto both modified and pristine Bentonite clay were all small and negative suggesting that the adsorption of both metal ions onto both pristine and modified Bentonite clay adsorbents was spontaneous. The free energies were higher for the modified Bentonite than for pristine Bentonite suggesting that modification of Bentonite clay with phosphate or sulphate anions increases the spontaneity and feasibility of the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  on the clay mineral. The increase in free energy change with the rise in temperature indicates an increase in feasibility of adsorption of both metal ions at increasing temperatures.

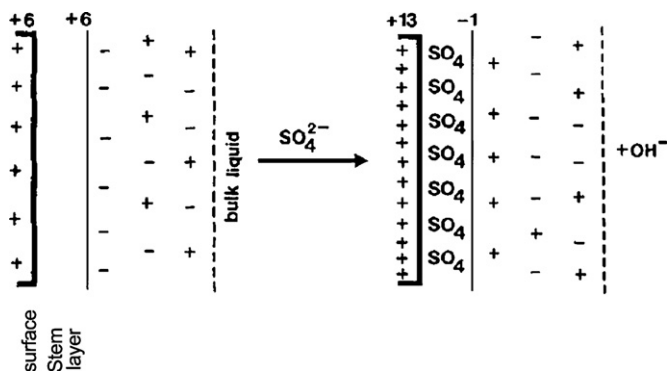


Fig. 8. Adsorption scheme for sulphate onto pristine Bentonite clay surface [39].

### 3.4. Mechanism of adsorption

#### 3.4.1. Phosphate and sulphate

The small shifts associated with the adsorption of sulphate anion onto Bentonite gives some support to the proposed mechanism by Curtin and Syers [17] and Uehara and Gillman [39] that although the adsorption of sulphate anion increased adsorption capacity of soils yet it was not chemisorbed onto the clay mineral surface such that the adsorbed anion becomes part of the surface (Fig. 8). This is collaborated in this study by the small hypochromic shifts in the range of 13–18 cm<sup>-1</sup> which is typical of physisorption. However, for the spectra of phosphate-modified Bentonite we observed basically hyperchromic shifts which might indicate that phosphate anion was chemisorbed onto the Bentonite clay mineral surface to

become part of the surface [40,41]. It is known that aluminum (Al)-containing minerals have high affinity for phosphate anion due to the presence of Al–OH and Al–H<sub>2</sub>O functional groups on the mineral surface.

The proposed mechanisms for phosphate anion sorption on Al–OH functional groups include ion-exchange mechanisms involving surface OH groups [38]. Thus, phosphate anion may be strongly adsorbed onto Bentonite clay via an inner-sphere mechanism (through its less-hindered site) and also by formation of Al–phosphate surface precipitates [15,18,42]. This is supported with a proposed reaction scheme as shown in Fig. 8. Further investigations are being carried out to confirm this mechanism.

#### 3.4.2. Metal ions

From Figs. 2 and 3 it was observed that the adsorption of both Cu<sup>2+</sup> and Zn<sup>2+</sup> broadened the band for structural –OH bending vibrations with the adsorption of Cu<sup>2+</sup> and Zn<sup>2+</sup> shifting this band from 1022 and 907 cm<sup>-1</sup>; 1061 and 903 cm<sup>-1</sup> to 1099 and 924 cm<sup>-1</sup> and 1081 and 915 cm<sup>-1</sup>, respectively for phosphate-modified clay. Similar results were obtained for sulphate-modified bentonite (Fig. 3). This result suggests that –OH from phosphate and sulphate anions were actually involved in the adsorption of both metal ions which supports the proposed mechanisms given in Figs. 2 and 3.

Let us imagine that charged ions present in water, several binding mechanisms is possible at the clay mineral–water interface. For pristine and phosphate-modified Bentonite clay surfaces being negatively charged, a counter layer of positively charged metal cations from the surrounding solution is formed due to electrostatic attraction of opposite charges, i.e., reversible electro-

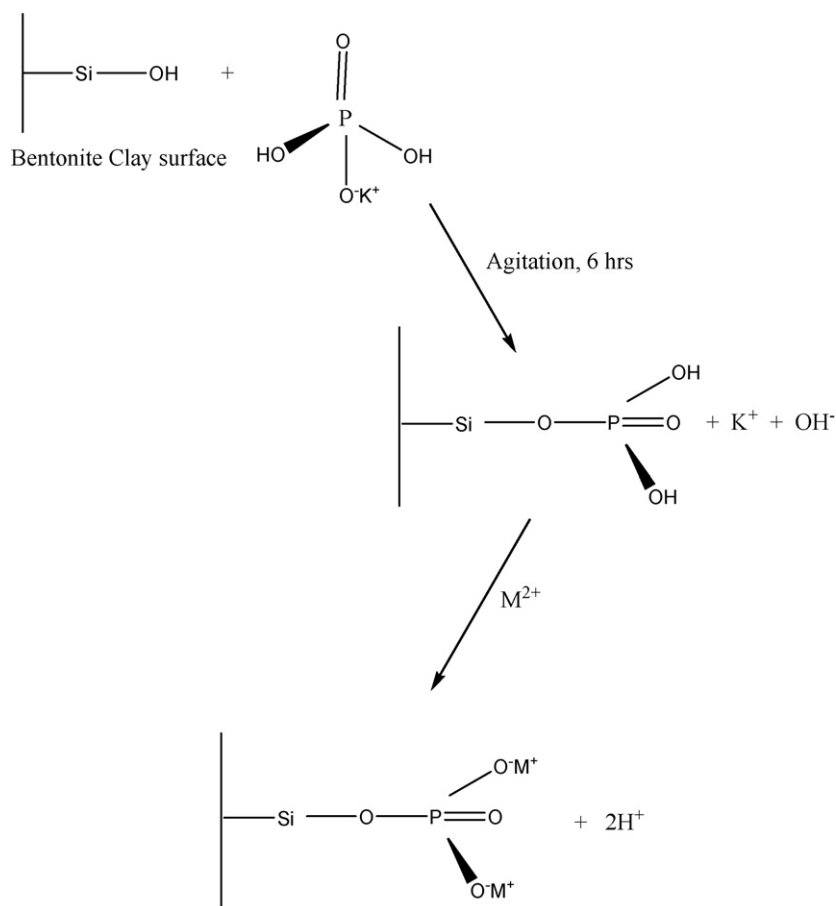


Fig. 9. Adsorption scheme for phosphate onto pristine Bentonite clay surface.

static processes. Thus, a diffuse layer of non-specifically adsorbed cations from the water adjacent to the adsorbent's surface is formed. Some of these counterions may approach the surface more closely to form weak outer-sphere surface complexes (primarily through electrostatic binding or ion pairing) or stronger inner-sphere surface complexes (primarily through chemical bonding), i.e., irreversible chemical adsorption processes (if the chemical adsorption is predominant in equilibrium). Further support for this proposed adsorption reaction mechanism is found in Fig. 9. No mechanism is yet available for the adsorption of metal ions onto sulphate-modified bentonite surfaces.

#### 4. Conclusion

Modification of pristine Bentonite with phosphate and sulphate reagents increased its cation-exchange capacity, adsorption capacity and the overall pseudo-second order kinetic rate constant for the adsorption of  $Zn^{2+}$  and  $Cu^{2+}$  from aqueous solution. Modification decreased slightly the specific surface area of the pristine Bentonite clay. Phosphate-modified Bentonite clay gave higher adsorption capacity for both metal ions.

Adsorption of both  $Zn^{2+}$  and  $Cu^{2+}$  onto both pristine and modified Bentonite was endothermic in nature. The adsorption process for both metal ions onto the adsorbents was spontaneous in nature with modification increasing the spontaneity of the adsorption process. The modification of pristine Bentonite with phosphate and sulphate was effective on the silica and alumina centers of the clay mineral with evident hypochromic and hyperchromic shifts, respectively. It is believed those sulphate and phosphate anions were physisorbed and chemisorbed, respectively onto the surface of the pristine Bentonite clay.

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