

# Competitive adsorption of metal ions onto goethite–humic acid-modified kaolinite clay

E. I. Unuabonah<sup>1</sup> · B. I. Olu-Owolabi<sup>2</sup> · K. O. Adebowale<sup>2</sup>

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**Abstract** A binary mixture of humic acid and goethite was prepared and used to modify kaolinite to produce goethite–humic acid (GHA)-modified kaolinite adsorbent useful for the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  from Single and Quinary (5) metal ion systems. The cation exchange capacity (CEC) and specific surface area of GHA-modified kaolinite clay adsorbent were found to be 40 meq/100 g and 13 m<sup>2</sup>/g, respectively, with the CEC being five times that of raw kaolinite clay (7.81 meq/100 g). The Langmuir–Freundlich equilibrium isotherm model gave better fit to experimental data as compared with other isotherm models. In Quinary metal ion system, the presence of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  appears to have an antagonistic effect on the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$ , while the presence of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  shows a synergistic effect on the adsorption of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . The GHA-modified kaolinite showed strong preference for the adsorption of  $\text{Pb}^{2+}$  in both metal ion systems. Brouers–Weron–Sotolongo (BWS) kinetic model gave better fit to kinetic data compared with other kinetic models used. Data from BWS kinetic model indicate that adsorption of metal ions onto GHA-modified adsorbent in both metal ion systems followed strictly, diffusion-controlled mechanism

with adsorption reaction proceeding to 50 % equilibrium in <2 min in the Single metal ion system and <1 min in the Quinary metal ion system. Adsorption of metal ions onto GHA-modified kaolinite is fairly spontaneous and endothermic in nature in both metal ion systems although the rate of metal ion uptake and spontaneity of reaction are reduced in the Quinary metal ion system.

**Keywords** Competitive adsorption · Kaolinite · Goethite · Humic acid · Diffusion-controlled transport · Kinetics

## Introduction

In natural systems, the bioavailability of heavy metal ions is largely controlled by adsorption–desorption reactions at the particle interface (Backes et al. 1995). Natural systems are composed of a heterogeneous mixture of mineral and organic solid phases as well as lots of organic and inorganic solutes that compete with heavy metal ions for adsorption sites on solids. The toxicity or bioavailability of these toxic heavy metal ions depends on their activities in solution (Buffle 1985; McBride 1994), and their migration to the biosphere depends on their speciation in the soil and aquatic systems (Choppin 1992; McCarthy et al. 1998).

Humic acid is from humic substances (HSs) found in soil organic matter. The interaction of HS (Saada et al. 2003; Wang and Xing 2005; Alekseeva and Zolotareva 2013) and goethite (Grossi and Sparks 1994; Jung et al. 1998; Lackovic et al. 2003; Gimenez et al. 2007) with clays has been well studied. Wang and Xing (2005) pointed out in their study that the aliphatic fraction of humic acid is preferentially adsorbed by clay minerals, while the aromatic fractions are left in solution. There are also reports on the separate use of humic acid, goethite, humic acid-

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✉ B. I. Olu-Owolabi  
iromidayobamidele@yahoo.co.uk

<sup>1</sup> Environmental and Chemical Processes Research Laboratory, Department of Chemical Sciences, Redeemer's University, Ede PMB 230, Osun State, Nigeria

<sup>2</sup> Department of Chemistry, Faculty of Sciences, University of Ibadan, Ibadan, Nigeria



modified and goethite-modified clay minerals in the immobilization of heavy metal ions (Plavsic et al. 1991; Hiraide 1992; Apak 2002; Tipping et al. 2002; Glover II et al. 2002; Wu et al. 2002; Salman et al. 2007; Olu-Owolabi et al. 2010).

Although we have initially reported the use of a binary mixture of goethite and humic acid for the modification of bentonite (Olu-Owolabi et al. 2010), yet no detailed report exists on the impact of some operational variables on the efficiency of a pre-adsorbed humic acid + goethite-modified clay in immobilizing heavy metal ions from aqueous systems. Furthermore, the influence of this kind of modification on the kinetic parameters of the adsorption process especially in multi-metal ion system is not yet reported even though it has been reported that the reactive edge sites of kaolinite may be coated with adsorbed organic matter (Davies 1982), further enhancing its adsorption capacity for metal ions. Clay particles coated with organics such as humic acid and goethite may find an important application in determining the environmental behavior of various ions (Takahashi et al. 1999) especially in soil systems.

It is in our opinion that a study on the influence of several variables such as pH, adsorbent dose and temperature on the adsorption of a multi-metal ion system will provide better understanding of how clay mineral surfaces pre-modified with a binary mixture of goethite and humic acid will influence the mobility of these toxic heavy metal ions in aqueous media especially when it exists as a sediment in a water body. It is therefore the aim of this study to consider how these variables control the mobility of the simultaneous presence of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in aqueous media through a goethite–humic acid-modified kaolinite.

Kaolinite clay was chosen in this study because it is an abundant clay mineral in Nigeria (Aliyu et al. 1996). Equilibrium data obtained from the multi-metal ion system were fitted to Langmuir, Freundlich, two-site Langmuir and Langmuir–Freundlich equilibrium adsorption models, while kinetic data were fitted to pseudo-first-order (PFOM), pseudo-second-order (PSOM), Elovich, double chemisorption and the Brouers–Weron–Sotolongo (BWS) fractal kinetic models.

## Materials and methods

### Preparation of adsorbate solutions

All chemicals used were analytical grade and were used without further purification. Stock solutions of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions were prepared by dissolving a weighed amount of their nitrate salts in deionized water and made up to mark in appropriate standard 1-L standard

flask. Test solutions of heavy metal ions for the Single system adsorption were prepared using the standard dilution method in a concentration range of 5–100 mg/L. In preparing multi-metal ion stock solution, the amounts of nitrate salts of all the five metal ions required for a particular concentration were weighed into a standard flask (1 L) in equimolar ratio and dissolved with deionized water. The solution was then made up to the mark.

### Preparation of adsorbent

Kaolinite clay obtained from Federal Industrial Research Oshodi (FIRO) with source from Kankari deposit (Maradi, Niger State) was purified according to method described by Adebawale et al. (2005). The humic acid used for modification was extracted from soil using the International Humic Substance Standard (IHSS) method (Swift 1996). Fifty grams of 5 % goethite–humic acid-modified kaolinite clay was prepared by suspending accurately weighed 2.5 g each of goethite and humic acid in 250 mL 0.01 M  $\text{NaNO}_3$  solution in a plastic container. Forty-five grams of kaolinite clay sample was then added to form slurry. This was tightly covered and kept at room temperature (25 °C) for 5 days to age. After aging, the sample was dried at 50 °C, pulverized and sieved through 20- $\mu\text{m}$  sieve. Five percent goethite–humic acid mixture was used for modification based on our previous study (Olu-Owolabi et al. 2010). The modified kaolinite produced is now referred to as GHA-modified kaolinite clay adsorbent.

### Measurement of physicochemical properties of adsorbent

The cation exchange capacity of the adsorbents was determined using the modified ammonium acetate method (Chapman 1965), while specific surface area of samples was estimated using the Sear's method (Sears 1956). The Fourier transform infrared spectroscopy was used to characterize the chemical functionalities on the surface of the adsorbents.

### Contact time studies

One hundred milligrams (0.1 g) of GHA-modified kaolinite clay adsorbent was added to 10 mL of 100 mg/L metal ion solutions of each cation in 50-mL capped polyethylene bottles and agitated on a rotary shaker at constant speed of 150 rpm. Samples were withdrawn at specified time intervals and filtered with the Whatman filter paper, and filtrates were analyzed for various metal ions using a flame atomic absorption spectrometer (FAAS). Results obtained suggested that maximum adsorption was obtained at  $\approx 360$  min (5 h) for Single metal system and  $\approx 120$  min (2 h) for Quinary metal system (Figs. A1 and A2, Appendix 1,

Supplementary document). In further experiments carried out in this study, these equilibrium times were used.

## Adsorption studies

### Effects of solution pH

This was investigated using solutions containing 100 mg/L of metal ions. One hundred milligrams (0.1 g) of GHA-modified kaolinite clay adsorbent was added to 10 mL of 100 mg/L of each metal solution of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in 50-mL capped polyethylene bottles, and pH of solutions was adjusted between 3.0–9.0 (as desired) at room temperature (303 K) using either 0.1 M NaOH or 0.1 M  $\text{HNO}_3$ . Similar preparations were used for Quinary metal ion system with 0.25 g of GHA-modified kaolinite clay in 25 mL solutions containing a 100 mg/L of each metal ion. The suspensions were agitated at 150 rpm for 5 h at 303 K. The solutions were filtered using Whatman filter paper, and the concentration of metal ions in the filtrate measured using flame atomic absorption spectrophotometry (FAAS).

### Effects of adsorbent dose

Batch sorption tests were carried out using various weights of GHA-modified kaolinite clay adsorbent (0.05–1 g) in 10 mL solutions with 100 mg/L of metal ions in 50-mL capped polyethylene bottles. The suspensions were adjusted to pH 5.5 with either 0.1 M NaOH or HCl. Similar preparations were used for Quinary metal ion system with 0.25 g of GHA-modified kaolinite clay in 25 mL solutions containing a 100 mg/L of each metal ion. The suspensions were agitated at 150 rpm for 5 h at 303 K. The suspensions were filtered and the filtrate analyzed for the various metal ions using FAAS.

### Effects of temperature

The effect of temperature was studied using four different temperatures of 303 K, 313 K, 323 K and 333 K. Batch experiment was carried out with 0.1 g of the GHA-modified kaolinite clay adsorbent in 10 mL solutions of 100 mg/L of each metal ion in 50-mL capped polyethylene bottles at these temperatures and at pH 5.5 (for Single metal ion system). Similar preparations were used for Quinary metal ion system with 0.25 g of GHA-modified kaolinite clay in 25 mL solutions containing a 100 mg/L of each metal ion. The suspensions were agitated at 150 rpm for 5 h at various specified temperatures. Samples were agitated at a constant speed of 150 rpm in a thermostated water bath shaker for 5 h. The suspensions were then filtered and the filtrate analyzed for metal ion concentration using FAAS.

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

$$\ln \frac{C_e}{q_e} = \frac{\Delta S_{\text{ad}}}{R} - \frac{\Delta H_{\text{ad}}}{RT} \quad (1)$$

where  $C_e$  and  $q_e$  are the equilibrium concentration (mg/L) and amount adsorbed (mg/L) and  $\Delta G_{\text{ads}}$ ,  $\Delta H_{\text{ads}}$  and  $\Delta S_{\text{ads}}$  are the thermodynamic parameters for change in Gibbs free energy, heat and entropy, respectively. The plot of  $\ln \frac{C_e}{q_e}$  versus  $\frac{1}{T}$  yields straight lines with the slope and the intercept giving values of  $\Delta H_{\text{ads}}$  and  $\Delta S_{\text{ads}}$ . These values could be used to compute  $\Delta G_{\text{ads}}$  from the Gibbs relation, at constant temperature ( $\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}$ ). In deriving the values of the thermodynamic parameters, it is assumed that the enthalpy does not change with temperature.

### Equilibrium studies

Equilibrium experiments were carried out by adding 0.1 g of GHA-modified kaolinite clay adsorbent to 10 mL solutions with different initial metal ion concentrations ranging from 5 to 100 mg/L for each metal ion (Single metal system). Similar preparations were carried out for Quinary metal ion system with 0.25 g of GHA-modified kaolinite clay in 25 mL solutions containing similar metal ion concentration in the range of 5–100 mg/L. The suspensions were agitated at 150 rpm for 5 h, and the temperature maintained at 303 K. Solution (Single or multi-metal ion solutions) pHs were adjusted to pH 5.5 at room temperature (303 K) using either 0.1 M NaOH or 0.1 M  $\text{HNO}_3$ . The suspensions were filtered, and the concentration of metal ions in the solution was determined using flame atomic absorption spectrometry (FAAS).

### Kinetic studies

Hundred milligrams of modified sample was added to 10 mL of 100 mg/L of metal ion in 50-mL capped polyethylene bottles (Single metal system). Similar preparations were used for Quinary metal ion system with 0.25 g of GHA-modified kaolinite clay in 25 mL solutions containing a 100 mg/L of each metal ion. The suspensions were agitated at 150 rpm for 5 h at 303 K. These samples were withdrawn at specified time intervals. The solutions were filtered using Whatman filter paper and the concentration of metal ions in the filtrate measured using flame atomic absorption spectrophotometry (FAAS).

All experiments were carried out in duplicates. The amount of each metal ion adsorbed by the adsorbent was calculated by difference using the equation below:



$$q_e = \frac{C_o - C_e(V)}{w} \quad (2)$$

where  $C_o$  is the initial metal ion concentration in solution (mg/L),  $C_e$  is the equilibrium concentration of the adsorbate (mg/L),  $V$  is the volume of solution (L) and  $w$  is the weight of adsorbent used (g).

The removal percentage ( $E$  %) was calculated according to the equation below:

$$E = \frac{C_o - C_e}{C_o} \times 100 \quad (3)$$

where  $q_e$  (mg/g) is the amount of metal ion adsorbed on the adsorbent,  $C_o$  is the initial metal ion concentration (mg/L),  $C_e$  is the equilibrium concentration of metal ion (mg/L),  $V$  is the volume of metal ion solution used (mL),  $W$  is the weight of adsorbent used (g) and  $E$  is the removal percentage (%). Experiments were carried out in duplicate, and averages of the values were used for further data analysis.

Equilibrium data were fitted to the Langmuir and Freundlich models, while kinetic data were fitted to the pseudo-first-order, pseudo-second-order, Elovich, double exponential, intraparticle diffusion and Brouers–Weron–Sotolongo (BWS) kinetic models. The discussions on the theory of equilibrium and kinetic models used in this study are in the supplementary document (Appendix 2). All model analyses were done using KyPlot version 2.0 software in the quasi-Newton (least square) mode.

## Results and discussion

### Physicochemical properties of adsorbent

Figure 1 shows the Fourier transform infrared spectra of both unmodified and modified kaolinite, respectively. The band assignments of the infrared spectrum of 5 % GHA-modified kaolinite clay adsorbent are shown in Table 1. The adsorption band at 3700, 3619 and 3394  $\text{cm}^{-1}$  for unmodified clay shows the presence of inner surface  $-\text{OH}$  stretching vibrations from the octahedral surface of the clay layers, while those at 1026, 914 and 772  $\text{cm}^{-1}$  represent the  $\text{Si}-\text{O}$ ,  $\text{Al}-\text{OH}$  bending vibrations and  $\text{Si}-\text{O}$  stretching, respectively (Adebawale et al. 2006; Jiang et al. 2009). The adsorption bands at 1615  $\text{cm}^{-1}$  represent  $-\text{OH}$  bending vibration of water molecule (Jiang et al. 2009). On modification with a mixture of goethite and humic acid, the 3619  $\text{cm}^{-1}$  band shifted significantly to 3445  $\text{cm}^{-1}$  assigned to the stretching vibrations of free  $-\text{OH}$  from the mixture suggesting that the mixture would have interacted with the surface of the clay via this site. A new peak at 3125  $\text{cm}^{-1}$  assigned to  $\text{C}-\text{H}$  stretching of alkenes is probably from the humic acid portion of the mixture on the clay surface. It is observed that with the adsorption of metal

ions, the peaks at around 3440 and 1030  $\text{cm}^{-1}$  became broad even though there were no significant shifts in these peaks. This indicates an interaction between the metal ions and the modified material (Olu-Owolabi et al. 2010). With modification of the kaolinite clay with a binary of goethite and humic acid, cation exchange capacity of the clay increase from 7.81 meq/100 g to 40 meq/100 g while the specific surface area (13  $\text{m}^2/\text{g}$ ) was the same as that reported by Adebawale et al. (2006). This increase in CEC might be as result of the humic acid portion of the mixture which have been shown by Saito et al. (2004) to mask the charges of goethite and increase overall negative charges on the surface of a goethite–humic acid mixture.

### Effect of pH

#### Single metal system

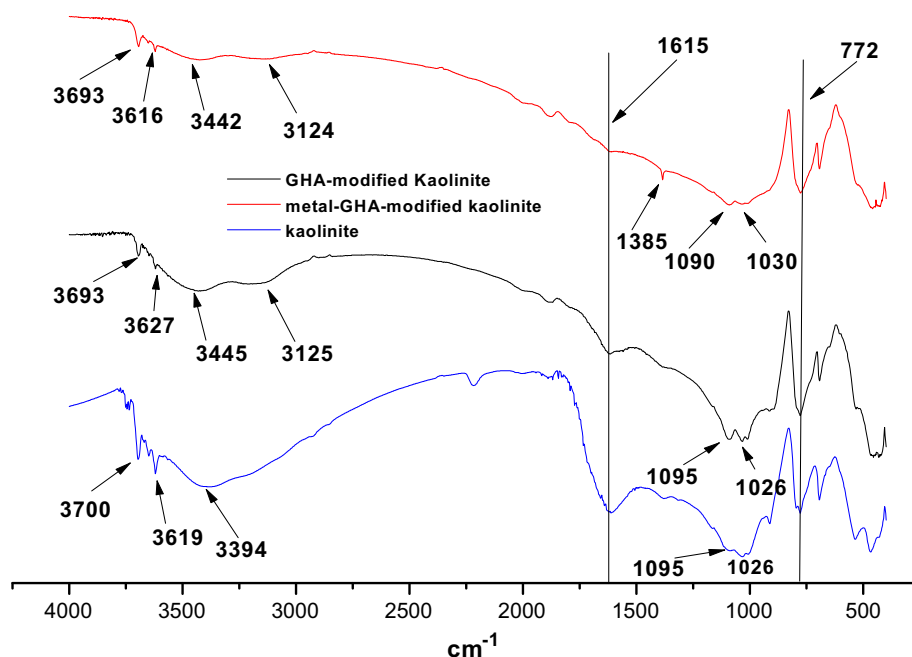
Figure 2 shows the plot for the adsorption of the metal ions onto GHA-modified kaolinite clay adsorbent for a Single metal system at various pHs. In this system, the adsorption of the five metal ions increases gradually with increase in pH. The optimum uptake of metal ions was at pH 6.0 for  $\text{Pb}^{2+}$  (96 %) and  $\text{Cu}^{2+}$  (80 %); pH 5.0 for  $\text{Cd}^{2+}$  (42 %); and pH 7.0 for  $\text{Ni}^{2+}$  (79 %) and  $\text{Zn}^{2+}$  (13 %). The lowest uptake for all the five metals is observed at  $\text{pH} < 4.0$ . At  $\text{pH} > 6.0$ , and there is a decrease in the percentage of  $\text{Pb}^{2+}$  ion adsorbed on the adsorbent from 96 % to 82 %. For the adsorption of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ , a plateau is observed between pH 5.0–6.0, after which there is a rapid increase in the percentage of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  adsorbed. This rapid increase might be an indication of the precipitation of the metal hydroxide. The low adsorption of metal ions at low pH may be attributed to increase in the positive charge (protons, H) density on the surface sites. This results in electrostatic repulsion between the metal ions and the edge groups with positive charges ( $\text{Si}-\text{OH}^{2+}$ ) on the surface of the kaolinite clay as well as other functional groups present on the modified adsorbent. At high pH values ( $\text{pH} > 6.0$ ), the surface of the adsorbent becomes negatively charged and the electrostatic repulsion decreases resulting in an increase in metal ion adsorption (Taty-Costodes et al. 2003) via a mechanism similar to ion exchange interaction (Jiang et al. 2009).

#### Quinary metal system

Figure 3 shows the plot for the adsorption of the various metal ions onto GHA-modified kaolinite adsorbent at various pHs in a Quinary metal ion system. The amount of metal ions adsorbed on GHA-modified kaolinite adsorbent increases slowly up to pH 6.0 for  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions and up to pH 7.0 for  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions after which there



**Fig. 1** Fourier transformed infrared spectra for kaolinite, goethite–humic acid-modified kaolinite and metal–goethite–humic acid-modified kaolinite



**Table 1** Various kinetic data for the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  onto GHA-modified kaolinite clay

PSOM				ELOVICH			DCM			PFOM			BSW	
<i>h</i>		<i>k</i> <sub>2</sub>	<i>r</i> <sup>2</sup>	<i>α</i>	<i>β</i>	<i>r</i> <sup>2</sup>	<i>K</i> <sub>d</sub>	<i>q</i> <sub>e</sub>	<i>r</i> <sup>2</sup>	<i>q</i> <sub>e</sub>	<i>k</i> <sub>1</sub>	<i>r</i> <sup>2</sup>	<i>n</i>	<i>r</i> <sup>2</sup>
<i>Single metal ion system</i>														
Pb	0.46	7.1 × 10 <sup>−3</sup>	0.98	1.33	0.96	0.99	0.45	8.01	0.98	7.20	4.2 × 10 <sup>−2</sup>	0.95	1.14	0.99
Cd	0.31	1.3 × 10 <sup>−2</sup>	0.95	0.77	2.06	0.98	0.30	4.79	0.95	4.28	4.9 × 10 <sup>−2</sup>	0.88	1.03	0.99
Zn	0.31	6.7 × 10 <sup>−2</sup>	0.89	0.26	76.63	0.94	0.31	2.15	0.89	1.96	1.1 × 10 <sup>−1</sup>	0.83	1.07	0.94
Ni	0.23	1.0 × 10 <sup>−2</sup>	0.97	0.81	1.28	0.99	0.24	4.80	0.97	4.30	4.0 × 10 <sup>−2</sup>	0.93	1.02	0.99
Cu	0.68	2.1 × 10 <sup>−2</sup>	0.99	0.69	22.31	0.99	0.68	5.70	0.99	5.29	7.7 × 10 <sup>−2</sup>	0.97	1.09	0.99
<i>Quinary metal ion system</i>														
Pb	0.04	9.5 × 10 <sup>−3</sup>	0.99	0.30	3.07	0.91	0.04	2.09	0.99	1.63	2.1 × 10 <sup>−2</sup>	0.99	1.10	0.99
Cd	0.18	4.7 × 10 <sup>−2</sup>	0.99	0.34	0.41	0.97	0.02	1.98	0.99	1.32	1.3 × 10 <sup>−2</sup>	0.99	1.01	0.99
Zn	0.15	1.4 × 10 <sup>−2</sup>	0.98	0.71	0.65	0.98	0.15	3.30	0.98	2.72	4.0 × 10 <sup>−2</sup>	0.97	1.00	0.99
Ni	0.02	2.7 × 10 <sup>−2</sup>	0.99	0.20	1.16	0.99	0.02	0.88	0.99	0.67	2.6 × 10 <sup>−2</sup>	0.99	1.01	0.99
Cu	0.30	5.4 × 10 <sup>−2</sup>	0.95	0.34	8.58	0.98	0.23	2.06	0.95	1.81	8.3 × 10 <sup>−2</sup>	0.91	1.01	0.99

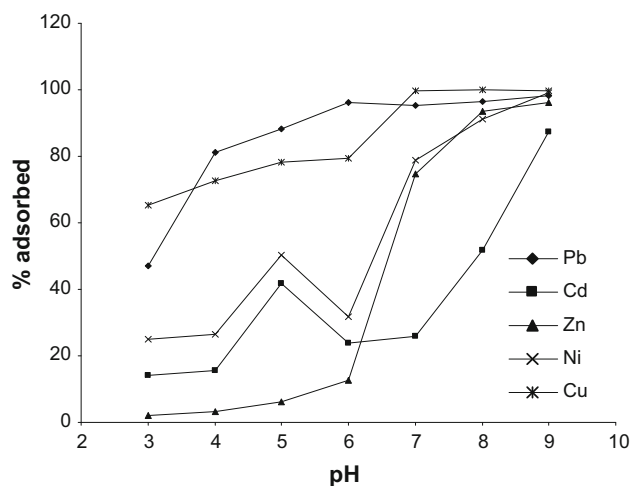
PSOM pseudo-second-order model, DCM diffusion–chemisorption model, PFOM pseudo-first-order model, BSW Brouers, Weron and Sotolongo model,  $h$  ( $\text{mg g}^{-1} \cdot \text{min}^{-1}$ );  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}$ );  $k_1$  ( $\text{min}^{-1}$ );  $K_d$  ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{t}^{0.5}$ );  $q_e$  ( $\text{mg g}^{-1}$ )

was a rapid increase in the amount of metal ion adsorbed indicating precipitation of metal hydroxide (Bayat 2002). When pH is increased from 3.0 to 6.0, the amount of  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions increases from 32 % to 52 %, 6.7 % to 23 % and 26 % to 37 %, respectively, while that of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  increases from 1.5 % to 17.5 % and 30 % to 39 % with pH increase from 3.0 to 7.0.

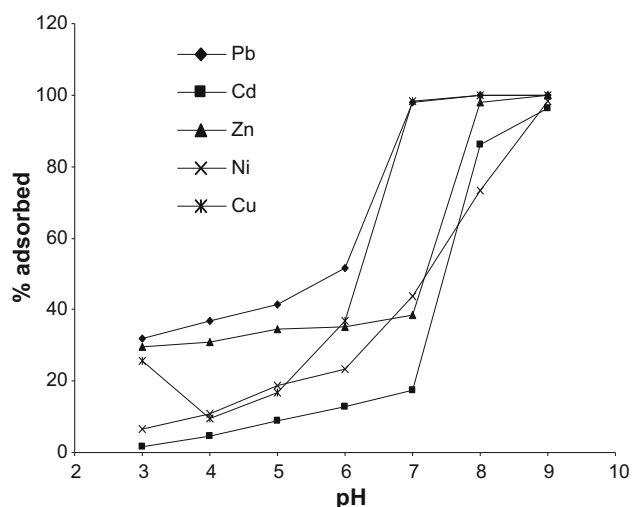
In comparison with the Single metal ion system, the equilibrium capacity of the adsorbent for  $\text{Pb}^{2+}$  in a Quinary metal ion system reduced from 96 to 52 % at pH 6.0, 42 to 13 and 78 to 17 % respectively at pH 5.0 for  $\text{Cd}^{2+}$  and

$\text{Cu}^{2+}$ , and 79 to 44 % at pH 7.0 for  $\text{Ni}^{2+}$ . However, the removal of  $\text{Zn}^{2+}$  ion by GHA-modified adsorbent from aqueous solution increased from 12.79 to 35.18 % at pH 6.0. The decrease in the percentage of adsorbed metal ions may be due to competition between the metal ions for adsorption sites which depends on the affinity of the adsorbent for the metal ions. The presence of co-ions enhanced the uptake of  $\text{Zn}^{2+}$  ions. A plateau was observed for  $\text{Cu}^{2+}$  ions only between pH 3.0–4.0. In order to prevent metal hydroxide precipitation during the adsorption process, pH 5.5 was chosen for further studies.





**Fig. 2** pH plot for the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  onto 5 % GHA-modified kaolinite clay in Single metal system

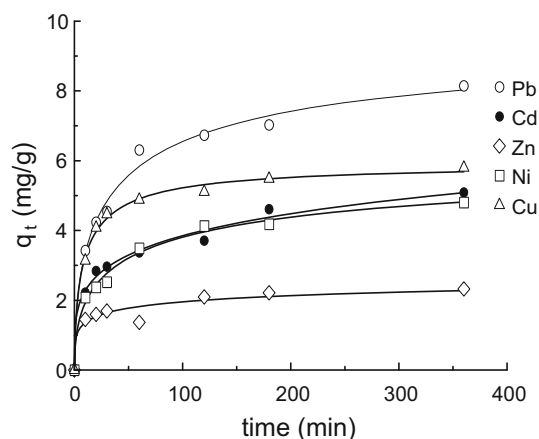


**Fig. 3** pH plot for the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  onto 5 % GHA-modified kaolinite clay in Quinary metal system

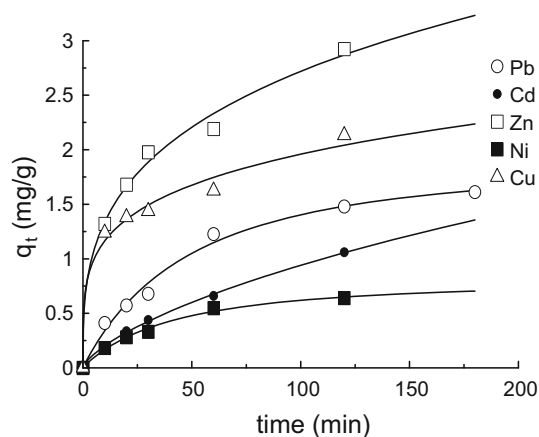
### Effects of adsorbent dosage

From experimental data, increase in adsorbent dose increased the amount of metal ions adsorbed for all five metal ions and in both Single and Quinary metal ion systems. However, above 0.1 g of the adsorbent, the percentage of  $\text{Pb}^{2+}$  removed from aqueous solution remain almost constant irrespective of the increase in adsorbent weight (see Figs. A1 and A2 in Appendix 3 supplementary information for plots).

The increase in the percentage of metal ion adsorbed with increase in the weight of the adsorbent may be attributed to increase in the number of available binding sites (i.e., increase in surface negative charge) and decrease in the electrostatic potential near the solid surface which favors sorbent–solute interaction.



**Fig. 4** BSW( $n,\alpha$ ) kinetic modeling of metal ion adsorption GHA-modified kaolinite (Single metal system)



**Fig. 5** BSW( $n,\alpha$ ) kinetic modeling of metal ion adsorption GHA-modified kaolinite (Quinary metal system)

On the other hand, an increase in the adsorbent weight in aqueous solution produced a remarkable decrease in the adsorption capacity of GHA-modified kaolinite adsorbent (plots not shown). However, the equilibrium adsorption capacity of GHA-modified kaolinite adsorbent for all the metal ions investigated in our study was found to be lower in the Quinary metal ion system than in the Single metal ion system. The reduction in the adsorption capacity of the adsorbent is an evidence of competition between the metal ions for limited number of available binding sites on the GHA-modified kaolinite clay adsorbent.

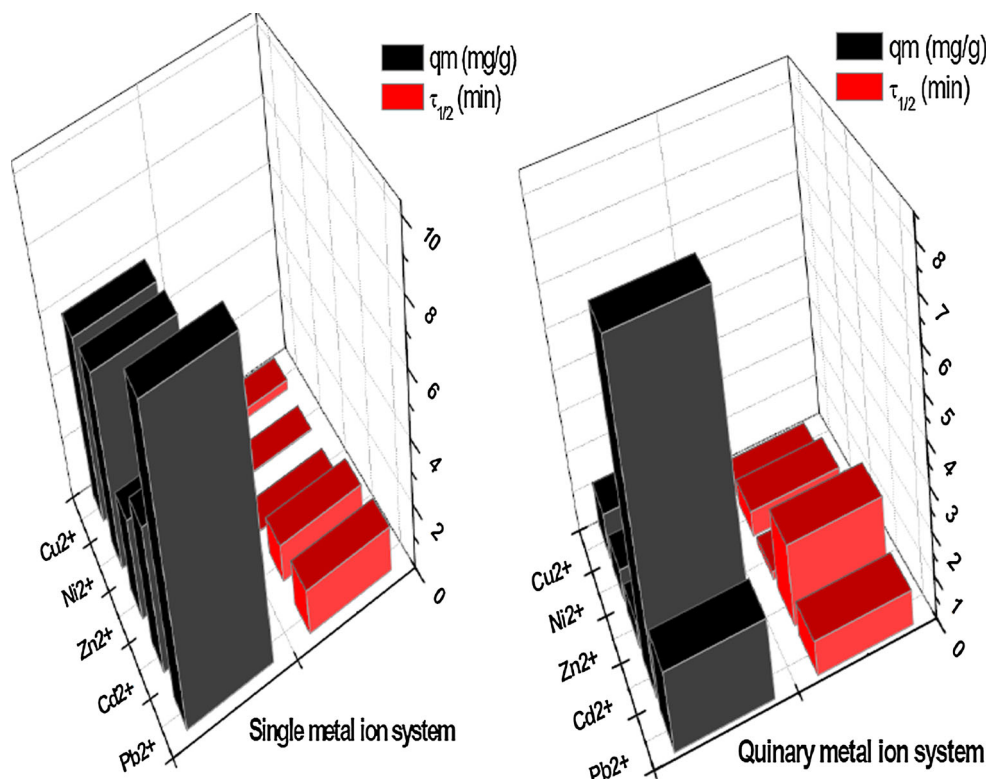
### Kinetic studies

The various parameters in kinetic models used in studying kinetic data obtained are shown in Table 1. The BWS fractal kinetic model (Gaspard et al. 2006) used to describe very complex adsorption systems provides better fit to





**Fig. 6** Three-dimensional plot of BWS fractal kinetic model predicted adsorption capacity ( $q_m$ ) and half-life ( $\tau_{1/2}$ ) of adsorption of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  onto GHA-modified kaolinite clay in both Single and Quinary metal ion systems



experimental data from both Single and Quinary metal ion systems than other kinetic models based on the  $r^2$  values obtained from the nonlinear regression modeling (Figs. 4, 5) of experimental data with the various kinetic models (Table 1). Furthermore, the values of  $n$  in the BSW kinetic model data suggest that the adsorption of the metal ions in both metal ion systems followed the pseudo-first-order reactions mechanism implying that the rate of adsorption of these metal ions by GHA-modified kaolinite is influenced largely by its adsorption capacity and diffusion (Ho 2006). The half-life data (Fig. 6) indicate a kinetically fast adsorption reaction in both metal ion systems that reach half its equilibrium in less than 2 min. With the pseudo-second-order (PSO) kinetic model, experimental data from the Quinary metal ion system suggest that the initial adsorption rate ( $h$ ) for the metal ions onto GHA-modified kaolinite decreased, while the overall kinetic rate for the adsorption process increased when compared with data from the Single metal ion system. This situation is induced by competition for adsorption sites by the metal ions which eventually results in decreased adsorption capacity of the GHA-modified kaolinite. This implies that there are fewer available adsorption sites for each metal ion in solution and thus increased overall adsorption time. Appendices 4 and 5 in the supporting document show the various kinetic model plots (except for BSW Fractal kinetic model) for the adsorption of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  in both metal ion systems.

Conversely, the overall pseudo-first-order kinetic rate constant  $k_1$  for the adsorption of the metal ions decreased in the Quinary systems (Table 1). However, the trend for the initial sorption rate as reflected by the pseudo-second-order kinetic model was also replicated by rate constants  $\alpha$ ,  $K_d$  and  $k_1$  in Elovich, diffusion–chemisorption and pseudo-first-order kinetic models, respectively, suggesting that the adsorption of these metal ions onto GHA-modified kaolinite may also involve other mechanisms of adsorption like chemisorption even though it is predicted to be mainly diffusion controlled. The extent of heavy metal ion coverage of GHA-modified kaolinite clay as depicted by the  $\beta$  constant in the Elovich model portray reduced concentration of the individual metal ions on the modified kaolinite adsorbent in the Quinary metal ion system as compared with the Single metal ion system. This is occasioned by competition among the metal ions for available adsorption sites on the surface of the adsorbent while in the Quinary metal ion system.

From PSO kinetic model, the overall kinetic rate of adsorption of  $Pb^{2+}$  is least in both metal ion systems, while those of  $Zn^{2+}$  and  $Cu^{2+}$  are the highest for Single and Quinary metal ion systems, respectively (Table 1). The initial sorption rate,  $h$ , is highest for  $Cu^{2+}$  and least for  $Ni^{2+}$  in both metal ion systems. The trend for  $h$  in Single metal ion system as seen in Table 1 ( $Cu^{2+} > Pb^{2+} > Cd^{2+} \approx Zn^{2+} > Ni^{2+}$ ) is well described by their diffusion coefficients ( $Cu^{2+} = 1.03$ ,  $Pb^{2+} = 0.9$ ,  $Cd^{2+} = 0.7$ ,  $Zn^{2+} = 0.7$



and  $\text{Ni}^{2+} = 0.7\Delta + 10^5 \text{ cm}^2 \text{ s}^{-1}$ ) (Ricordel et al. 2001; Zhao et al. 2013) except for  $\text{Ni}^{2+}$ . However, in the Quinary metal ion system, the trend is distorted ( $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} \approx \text{Ni}^{2+}$ ) and does not fit any particular trend in relation to ionic radius, ionic mobility, hydration energy or diffusion coefficient of the metal ions.

### Equilibrium studies

Figure 7 shows the nonlinear Langmuir, Freundlich, two-site Langmuir and Langmuir–Freundlich model plots for the adsorption of the various metal ions by GHA-modified kaolinite, and Table 2 shows the equilibrium data obtained from Langmuir–Freundlich model plots for the adsorption. Data from other equilibrium models have been excluded from the table because they clearly showed that these other models were not suitable for describing equilibrium data obtained in this study. Using regression coefficients and error values, it is observed that the Langmuir–Freundlich model, which combines the features of Langmuir and Freundlich, provides a better fit to data in both Single and Quinary metal ion systems (Table 2 and Tables A1–A3 Appendix 6, Supplementary Information). This clearly suggest that the surface of GHA-modified kaolinite adsorbent is likely to be heterogeneous in nature (Akpa and Unuabonah 2011) and a single mechanism will not be appropriate to describe the mechanism of adsorption of these metal ions by the adsorbent. This supports our earlier deductions from kinetic data. Furthermore, the Langmuir–Freundlich model fitting predicts that the GHA-modified kaolinite shows a stronger preference for  $\text{Pb}^{2+}$  than for other metal ions in the Quinary metal ion system and  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  in the Single metal ion system. The trend of metal ion preference shown by GHA-modified kaolinite in the Quinary metal ion system based on its adsorption capacity ( $K_{\text{LF}}$ ) is  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$  (Table 2). The predicted sequence does not exactly follow the order for the ionic radius, ionic mobility, hydration energy or diffusion coefficient values of these metal ions. For example, it is expected that the trend should be  $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$  going by their hydration energies ( $\text{Pb}^{2+} = 362$ ,  $\text{Cu}^{2+} = 507$ ,  $\text{Zn}^{2+} = 497$ ,  $\text{Cd}^{2+} = 539$ ,  $\text{Ni}^{2+} = 511 \text{ kcal/ion g}_{\text{ion}}^{-1}$ ) as provided by Ricordel et al. (2001) and Zhao et al. (2013). The strong preference for  $\text{Pb}^{2+}$  exhibited by GHA-modified kaolinite is possibly due to the ease of this metal ion to loose its hydration shell and be adsorbed as compared with other metal ions with higher hydration shell energies (Unuabonah et al. 2013). The Jahn–Teller effect makes the adsorption capacity of the modified adsorbent for  $\text{Cu}^{2+}$  higher than that for  $\text{Zn}^{2+}$  and thus switches their positions in the traditional trend based on their hydration energies (Zhao et al. 2013). The variable coordination number of

**Fig. 7** Nonlinear equilibrium model plots for the adsorption of metal ions onto GHA-modified kaolinite from Single metal ion system **a** Langmuir, **b** Freundlich, **c** two-site Langmuir and **d** Langmuir–Freundlich model plots; from Quinary metal ion system, **e** Langmuir, **f** Freundlich, **g** two-site Langmuir and **h** Langmuir–Freundlich model plots

$\text{Cd}^{2+}$  ranging from 2 to 8 (Anderson 1981) could possibly have increased its chances of being more preferred for adsorption by GHA-modified kaolinite in a Quinary metal ion system than  $\text{Ni}^{2+}$  which basically has a coordination number of 4 and a tetrahedral geometry (Myers 1981). Similar trend has been reported by Jalali and Moradi (2013).

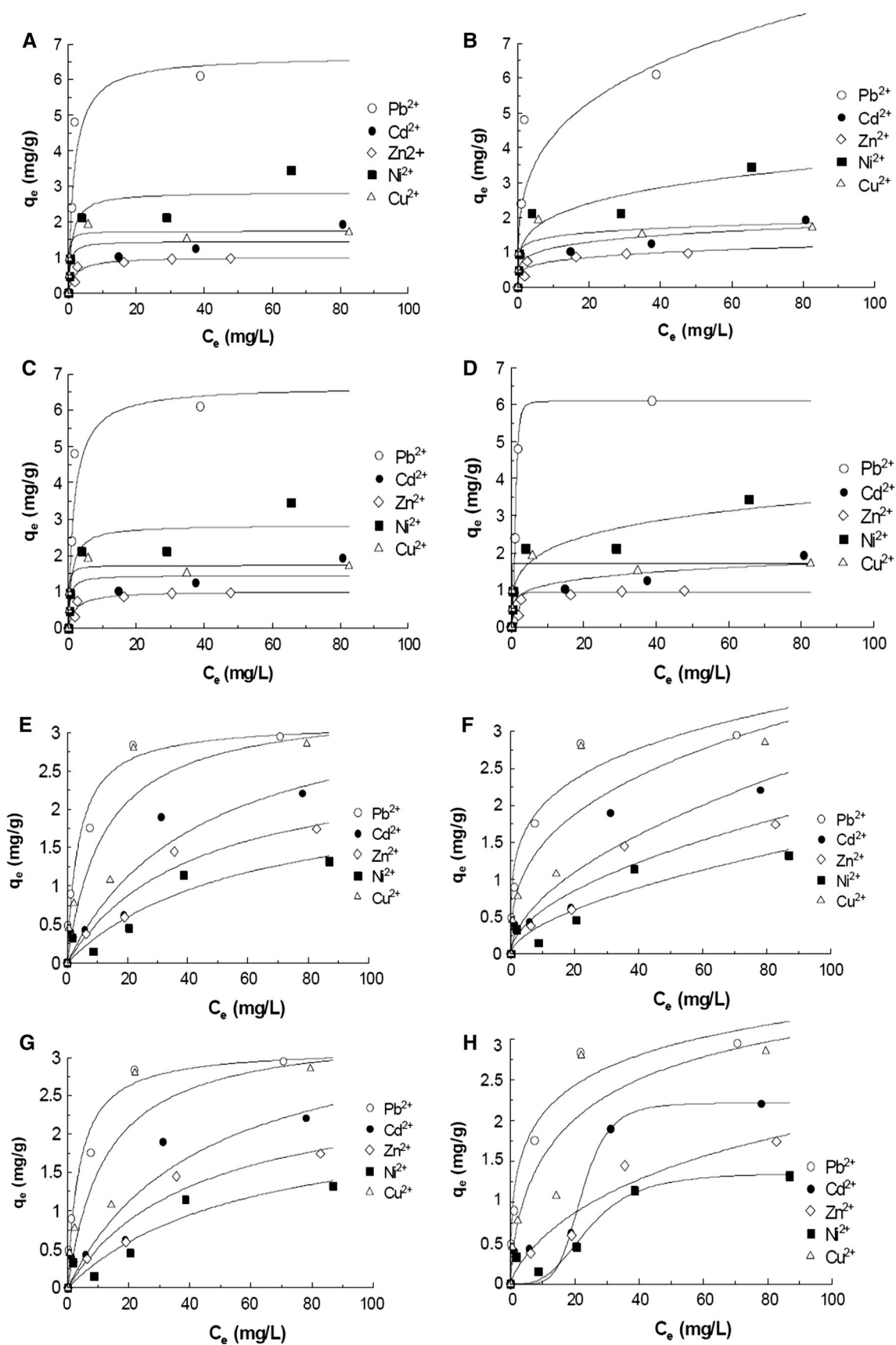
There are three types of interactive adsorption behavior, viz synergism, antagonism or non-interaction. With synergism, the effect of the mixture is greater than the sum of each of the individual effects of the constituents in the mixture. With antagonism, the effect of the mixture is less than that of the sum of the individual effects of the constituents in the mixture. With non-interaction, the effect of the mixture is equivalent to the sum of each of the individual effects of the constituents in mixture (Qi and Aldrich 2008). Since the ratio of  $K_{\text{LF(Q)}}/K_{\text{LF(S)}}$  for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  is lesser than unity as shown in Table 3, it is plausible to suggest that the presence of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  in solution could exert an antagonistic effect on their adsorption by GHA-modified kaolinite. In same vein, the presence of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  in solution could exert a synergistic effect on the adsorption of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions since the ratio of  $K_{\text{LF(Q)}}/K_{\text{LF(S)}}$  for these metal ions is greater than unity (Table 3).

### Effect of temperature

Table 4 shows the thermodynamic parameters obtained from equilibrium data at various temperatures. Results from Table 4 suggest that adsorption of metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ ) in both Single and Quinary metal ion systems by GHA-modified kaolinite was endothermic ( $+\Delta H_{\text{ad}}$ ) and the complex formed between the adsorbate and adsorbent as predicted by  $\Delta S_{\text{ad}}$  was stable with increasing temperature. However, in the Quinary metal ion system, the adsorption process is less endothermic and complex formed between adsorbent and adsorbate is predicted to be less stable (Table 4). This could be inferred from the fact that in a Quinary metal system, since adsorption capacity of the adsorbent decreases for each of the metal ion, the heat of adsorption,  $\Delta H_{\text{ad}}$ , will also decrease.

The magnitude of the adsorption enthalpy,  $\Delta H_{\text{ad}}$ , indicates weak bonding between the metal ions and the clay minerals (Bhattacharyya and Gupta 2011). The sign and magnitude of  $\Delta H_{\text{ad}}$  can be used to provide





**Table 2** Predicted data from Langmuir–Freundlich isotherm model for the adsorption of metal ions onto 5 % GHA-modified kaolinite clay

	$k_{LF}$ ( $\text{mg}^{1-(1/n)}\text{L}^{1/n}/\text{g}$ )	$b_{LF}$ (L/g)	$n$	$r^2$	Error
<i>Single metal ion system</i>					
Pb	6.10	3.04	0.90	0.9845	0.16
Cd	13.85	0.21	$5.9 \times 10^{-7}$	0.8868	0.08
Zn	0.93	6.20	0.47	0.9915	0.002
Ni	13.89	0.28	$2.2 \times 10^{-4}$	0.9097	0.25
Cu	1.71	17.79	6.78	0.9707	0.03
<i>Quinary metal ion system</i>					
Pb	5.58	0.39	0.025	0.9619	0.10
Cd	2.22	5.34	0.045	0.9152	0.12
Zn	3.97	0.76	0.010	0.9340	0.05
Ni	1.37	3.24	0.041	0.9172	0.04
Cu	4.37	0.65	0.039	0.8611	0.34

**Table 3** Ratio of adsorption capacity ( $q_{e(\text{mix})}/q_{e(\text{single})}$ )

Metal ions	$q_{e(\text{single})}$	$q_{e(\text{quinary})}$	$q_{e(\text{quinary})}/q_{e(\text{single})}$
Pb <sup>2+</sup>	6.10	5.58	0.91
Cd <sup>2+</sup>	15.55	2.22	0.14
Zn <sup>2+</sup>	0.93	3.97	4.27
Ni <sup>2+</sup>	13.88	1.37	0.10
Cu <sup>2+</sup>	1.71	4.37	2.56

information about the adsorption reaction and mechanism of possible ligand retention. The small but positive adsorption enthalpy are strong indications that the outer-sphere complexation mechanism may have played a major role in the adsorption of these metal ions GHA-modified kaolinite in both Single and Quinary metal ion systems (Journey et al. 2010). This simply implies that the inner-sphere adsorption sites at the edges of the kaolinite reported by Srivastava et al. (2005) may have been used up for modification or possibly ‘blocked’ by the modifying reagent such that these cations are not able to access them. Outer-sphere complexation occurs via weak electrostatic bonds requiring ions existing in close proximity to one another on the surface (Journey et al. 2010). From  $\Delta S_{ad}$  values in Table 3, it is predicted that Pb<sup>2+</sup> and Ni<sup>2+</sup> form a more stable complex with GHA-modified kaolinite in Single and Quinary metal ion systems, respectively. Adsorption of these metal ions (Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup>) was observed to be fairly spontaneous ( $-\Delta G_{ad}$ ) in both metal ion systems with reduced spontaneity for adsorption in the Quinary metal ion system (Table 4). Increasing temperature, however, did not significantly improve the spontaneity of the adsorption of these metal ions by GHA-modified

**Table 4** Thermodynamic parameters for the adsorption of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> onto GHA-modified kaolinite clay

	$+\Delta H_{ad}$	$+\Delta S_{ad}$	$r^2$	$-\Delta G_{ad}$			
				303 K	313 K	323 K	333 K
<i>Single metal ion system</i>							
Pb <sup>2+</sup>	0.89	32.05	0.92	8.82	9.14	9.46	9.78
Cd <sup>2+</sup>	0.95	18.77	0.92	4.74	4.93	5.11	5.33
Zn <sup>2+</sup>	1.61	19.89	0.87	4.42	4.62	4.81	5.01
Ni <sup>2+</sup>	0.56	13.39	0.99	3.50	3.63	3.76	3.90
Cu <sup>2+</sup>	1.04	22.36	0.98	5.74	5.96	6.18	6.41
<i>Quinary metal ion system</i>							
Pb <sup>2+</sup>	0.27	1.15	0.80	0.078	0.090	0.10	0.11
Cd <sup>2+</sup>	0.36	1.81	0.95	0.19	0.21	0.22	0.24
Zn <sup>2+</sup>	0.66	8.53	0.86	1.92	2.01	2.10	2.18
Ni <sup>2+</sup>	0.86	11.88	0.90	2.74	2.86	2.98	3.10
Cu <sup>2+</sup>	0.44	2.36	0.81	0.28	0.30	0.32	0.35

$\Delta H_{ad}$  = kJ/mol;  $\Delta S_{ad}$  = J/mol;  $\Delta G_{ad}$  = kJ/mol K

kaolinite in both metal ion systems. The  $\Delta G_{ad}$  values obtained in this study suggest that the adsorption of these metal ions by GHA-modified kaolinite in both metal ion systems is mainly diffusion-controlled transport and electrostatic (physical adsorption) since they are below  $-20 \text{ kJ mol}^{-1}$  (Unuabonah et al. 2007).

Entropy change,  $\Delta S_{ad}$ , for the adsorption process in both metal ion systems was positive within the temperature range of 303–333 K with values in the range of 1.15 and  $32.05 \text{ J K}^{-1} \text{ mol}^{-1}$  (Table 4). We can thus predict that adsorption of these metal ions onto GHA-modified kaolinite adsorbent was accompanied with some structural changes in the adsorbate and adsorbents during the adsorption process from aqueous solution onto the adsorbents (Unuabonah et al. 2007; Bhattacharyya and Gupta 2011).

The magnitude of the thermodynamic parameters obtained in this study is quite low compared with those obtained in reports by Yavuz et al. (2003), Echeverria et al. (2003), Gupta and Bhattacharyya (2008) and Bhattacharyya and Gupta (2009) for the adsorption of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup>. Given our earlier discussions on the kinetic data of the adsorption of these metal ions by GHA-modified kaolinite adsorbent, it is possible to suggest that the adsorption process in both metal ion systems is more kinetically driven (by diffusion-controlled transport) than it is thermodynamically.

## Conclusion

The competitive adsorption of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> in Quinary metal system onto a geothite–humic acid (GHA)-modified kaolinite was reported in this study. The

presence of external surface –OH and C–H stretch at 3445 and 3125  $\text{cm}^{-1}$  from Fourier transformed infrared (FTIR) studies suggests that the modification was effective on the surface of the kaolinite clay. The surface properties of kaolinite were improved by modification with a mixture of goethite and humic acid. Adsorption capacity of GHA modified kaolinite was found to increase with increasing adsorbent weight for both single and multi-metal ion solutions with adsorption in multi-ion giving lower adsorption capacities. However, the adsorption of  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  was suppressed by the simultaneous presence of other metal ions. The increase in pH and temperature increased the adsorption capacity of GHA-modified kaolinite for heavy metal ions in both single and multi-metal ion systems, but competition for adsorption sites tends to reduce the heat of adsorption of system. Similarly, increase in adsorbent dosage reduced the adsorption capacity of GHA-modified adsorbent. The presence of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  suppressed that adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  with  $\text{Ni}^{2+}$  being the most suppressed. The Brouers–Weron–Sotolongo (BWS) fractal kinetic model predicted that the adsorption of metal ions onto GHA-modified kaolinite follow the pseudo-first order kinetic model and adsorption of the metal ion is thus predicted to be diffusion controlled in the Single metal ion system, but a combination of BWS and pseudo-second-order kinetic models predicts a combination of adsorption mechanisms with no special preference to any. From thermodynamic point of view, the adsorption of metal ions in both Single and Quinary metal systems was endothermic and spontaneous although the spontaneity of the adsorption process was well reduced in the Quinary metal system. Change in temperature did not improve the spontaneity of the adsorption process in both metal systems significantly.

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