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Removal of Cu^{2+} and Cd^{2+} from Aqueous Solution by Bentonite Clay Modified with Binary Mixture of Goethite and Humic Acid

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Abstract Pre-modification of bentonite clay with goethite, humic acid, and a binary mixture of goethite and humic acid reagents increased its cation exchange capacity from 95 to 105.32, 120.4, and 125.8 meq/100 g of bentonite clay, respectively. The effective pre-modification of bentonite clay with goethite, humic acid, and goethite–humic acid reagents was confirmed from their Fourier transform infrared spectra which suggested that modification was effective on the AlAlOH and Si–O sites for goethite and humic acid modification and AlAlOH for goethite–humic acid modification. The presence of 0.001 M $NaNO_3$ electrolyte increased the adsorption capacity of bentonite clay. Temperature was observed to favor the adsorption of Cu^{2+} and Cd^{2+} onto both the raw and modified bentonite clay samples. The goethite–humic acid-modified bentonite gave the best adsorption capacity of ≈10 and 16 mg/g at 30 and 50°C, respectively, for both metal ions. The inner sphere complexation mechanism was suggested for the adsorption of both metal ions onto the modified adsorbents. Modifying bentonite clay with a binary mixture of goethite and humic acid reduced the selectivity of bentonite clay for either Cu^{2+} or Cd^{2+}. Preadsorbed goethite and humic acid on bentonite clay will further reduce the mobility of heavy metal ions in soils and in aquatic environments.

Keywords Bentonite · Cation exchange capacity · Adsorption · Goethite · Humic acid · Copper · Cadmium

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1 Introduction

Bentonite is considered as a main alternative in the decontamination and treatment of detrimental metal ions (Tsai et al. 2001; Al-Qunaibit et al. 2005; Kaya and Ören 2005; Tahir and Naseem 2004). The adsorption of metal ions on bentonite has been extensively studied in recent years (Caglar et al. 2009; Hefne et al. 2008; Inglezakis et al. 2007; Xu et al. 2006; Sato 1998). The results suggested that the adsorption of metal ions increased with increasing pH values, and the adsorption was dominated by outer sphere complexation or ion exchange at low pH and by inner sphere complexation or precipitation at high pH.

Soil organic matter (SOM) refers to the sum total of all organic carbon containing substances in soils

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(Hayes and Swift 1978). However, SOM consists basically of humic substance. Adsorption of humic substance onto clay is important in relation to speciation and mobility of pollutants in the environment (Chorover et al. 1999; Guzman et al. 2003). Because of its high functionality (carboxyl, hydroxyl, and amino groups), humic substance can strongly complex metal ions and thereby modify the retention, adsorption, migration, and bioavailability of metal ions in the natural environment (Chen and Wang 2006; Wang et al. 2005, 2006; Montavon et al. 2002; Xu et al. 2008; Stevenson 1994). The results indicate that humic substance enhances cation adsorption at low pH values but reduces the adsorption at high pH values. The increase of adsorption is explained by the adsorption of humic substance on mineral surface followed by the interaction of metal ions with surface adsorbed humic substance, whereas the reduction of adsorption at high pH is interpreted by the formation of soluble metal–humic substance complexes in solution, which reduces the metal ion adsorption (Montavon et al. 2002).

Although there have been some reports on the adsorption of metal ions in the presence of humic acid and goethite onto clay mineral phase (Wu et al. 2002; Heidmann et al. 2005; Hizal and Apak 2006; Terdkiatburana et al. 2008) and even on humic acid pre-modified vermiculite (Abate and Masini 2005), there are no reports on the use of binary mixture of goethite–humic acid to pre-modify bentonite clay for the removal of metal ions from aqueous solution.

This research, therefore, reports the use of humic acid, goethite, and geothite–humic acid pre-modified bentonite clays for the adsorption of Cu^{2+} and Cd^{2+} from aqueous solutions with the view to providing insight into the fate and transport of heavy metal ions in soils and aquatic environments. First, there was the optimization of some variables that influence the adsorption of these metal ions on the raw bentonite clay and thereafter the use of data from this process to consider the adsorption capacity of the modified bentonite clays for Cu^{2+} and Cd^{2+}.

2 Materials and Methods

2.1 Physicochemical Analysis of Samples

Analar grade (Aldrich) bentonite and humic acid were purchased while goethite was synthesized in the laboratory. Goethite was prepared following the method described by Hingston et al. (1974). Twenty grams of analytical reagent grade ferric chloride (anhydrous) was dissolved in 200 ml of deionized distilled water. NaOH solution (2 M) was slowly added with constant stirring; this was followed by aging the suspension for 48 h at 333 K in an oven. After aging, the suspension was filtered by suction pump and washed free of chloride with deionized distilled water. The solid was dispersed in 10^{-3}M $NaNO_3$ solution and wet-sieved with a sieve of mesh size 0.74 mm. The point of zero charge of the goethite was determined by the Kinniburgh et al. (1976) method and the value was 8.0.

Analar grade (Aldrich) cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) and copper nitrate ($Cu(NO_3){\cdot}3H_2O$) were used. Analytical grade reagents and chemicals were used throughout the investigation.

The cation exchange capacity (CEC) of the unmodified bentonite was determined by the method employed by Juo et al. (1976). It involved the summation of the exchangeable acidity and the cation exchange capacity of the adsorbent. The CEC of modified bentonite clay samples were determined by modified ammonium acetate method (Chapman 1965). In this method, 50 ml of 1 M sodium acetate (CH_3COONa) was added to 2 g of the adsorbent. The suspension was then agitated for 1 h 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 supernatants were collected and kept for Na^+ analysis using flame photometry.

The Fourier transform infrared (FTIR) spectra of unmodified bentonite, goethite-modified, humic acid-modified, and goethite–humic acid-modified bentonite were obtained using KBr wafer in conjunction with a Shimadzu 8400 S FTIR instrument. Specific surface area of the adsorbents was determined via the Sears method (Sears 1956). In this method, 0.5 g of the sample was acidified with 0.1 M HCl to pH 3–3.5. The volume was made up to 50 ml with distilled-deionized 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:

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

2.2 Effect of Operating Variables on Unmodified Bentonite

2.2.1 pH

One gram each of bentonite was weighed into 60-ml plastic bottles. Two hundred milligrams per liter of metal ion solutions (i.e., Cd $(NO_3)_2$ and Cu $(NO_3)_2$) were prepared from their stock solutions. The pH of 30 ml of 200 mg/l metal ion to be investigated was adjusted to several pH required in the range of 3–10 and were subsequently added to the different bottles containing the bentonite clay. The solutions were the agitated at room temperature (28±2°C) for 16 h. Thereafter, they were filtered using Whatman filter paper and the filtrates analyzed using flame atomic absorption spectrophotometer (FAAS).

2.2.2 Time

One gram each of bentonite was weighed into 60-ml plastic bottles. Two hundred milligrams per liter of metal ion solutions (i.e., Cd $(NO_3)_2$ and Cu $(NO_3)_2$) were prepared from their stock using 0.001 M $NaNO_3$ as electrolyte. Thirty milliliters of 200 mg/l of the metal ion to be investigated was added to the different bottles. Based on results from pH studies and also in consideration of metal ion precipitation, the pH of adsorbate solutions were adjusted to 5.05 for Cu^{2+} and 6.03 for Cd^{2+} using 0.1 M NaOH or 0.1 M HCl solutions. Samples were agitated at room temperature (28±2°C) and were removed from shaker at different time intervals. The solution was filtered and the filtrate was analyzed for the metal ion concentration using FAAS.

2.2.3 Adsorbent Dose

The effect of adsorbent dose, presence of electrolyte, and presence of co-ion were studied using 1 g of the bentonite clay and 30 ml of 200 mg/l of the metal ion to be investigated (Cu^{2+} and Cd^{2+}). A range of 5 mg to 2 g of bentonite clay was used for adsorbent dose studies with pH of adsorbate solution being 5.03 for Cu^{2+} and 6.01 for Cd^{2+}. Concentrations of electrolyte solutions ($NaNO_3$ and KNO_3) were in the range of 0.001 M to 0.1 M. Two hundred milligrams per liter of both Cu^{2+} and Cd^{2+} was used for binary metal ion studies.

2.2.4 Initial Metal Ion Concentration

A range of concentration from 50 to 700 mg/l at pH5.00 and 6.00 for Cu^{2+} and Cd^{2+}, respectively, was used. All Cu^{2+} samples were agitated for 4 h and all Cd^{2+} samples were agitated for 8 h. $NaNO_3$ (0.001 M) was used as electrolyte based on data obtained in the initial experiments on the effect of electrolyte. NaOH (0.01 M) and HCl (0.1 M) were used to adjust the pH of adsorbate solutions. The solution was filtered and the filtrate analyzed using FAAS.

2.2.5 Preparation of Modified Bentonite clay

Several goethite-modified bentonite clay samples were prepared using 1%, 2%, 5%, and 10% of goethite in 99%, 98%, 95%, and 90% of bentonite. For humic acid-modified bentonite, 2%, 4%, 10%, and 20% of humic acid in 98%, 96%, 90%, and 80% of bentonite were used.

Each sample was suspended in 50 ml 0.001 M $NaNO_3$ in different plastic containers and mixed to form slurry. This was tightly covered, agitated at room temperature (28±2°C) for 5 days and later centrifuged at 100 rpm. Thereafter, the samples were dried at 50°C, pulverized, and sieved through a 0.5-mm-mesh-size sieve.

Goethite–humic acid-modified bentonite were prepared by agitating 1%, 2%, 5%, and 10% each of goethite and humic acid and 98%, 96%, 90%, and 80% of bentonite clay. Each sample was suspended in 50 ml 0.01 M $NaNO_3$ in different plastic containers, respectively. This was tightly covered and agitated at room temperature (28±2°C) for 5 days. Thereafter, samples were dried at 50°C, pulverized, and sieved through a 0.5-mm-mesh-size sieve.

The relatively long time needed for modification is due to the difficulty for large-size humic acid molecules to enter between the bentonite layers (Kerndorff and Schnitzer 1980; El-Eswed and Khalili 2006).

2.3 Adsorption of Metal Ions on Modified Bentonite

Results from precipitation of midfied Bentonite clay suggests that 5% of modifying reagent was most

appropriate for modification. In this regard, 0.2 g of 5% modified adsorbent was weighed into four different 60-ml plastic bottles. Initial metal ion concentrations in the range of 50 to 700 mg/l were prepared from their stock solutions using 0.001 M $NaNO_3$ as electrolyte. Twenty milliliters of metal ion solution to be investigated was added to the different sample bottles. The pH was adjusted with either 0.1 M NaOH or 0.1 M HCl to 5.07 for Cu^{2+} and 6.02 for Cd^{2+} and sample solutions were agitated at room temperature (28±2°C) for 4 and 8 h for Cu^{2+} and Cd^{2+}, respectively. The solutions were filtered and the filtrates analyzed using FAAS. The experiment was repeated at 50°C. At the pH of the adsorbate solution in this study, it is known that humic acid adsorbed on the surface of the bentonite will not be desorbed (Salman et al. 2007).

All experiments were carried out in duplicate and amount adsorbed by adsorbent after the 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 cadmium 228.9 nm).

2.4 Theory Equilibrium Models

2.4.1 Langmuir Isotherm

The Langmuir isotherm has been extensively used by many authors for the sorption of heavy metal ions in clay, metal oxides, soils, etc. The Langmuir isotherm is a valid monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. The Langmuir equation may be written as

$$q_e = \frac{Q^o b C_e}{1 + bC_e} \qquad (\text{non} - \text{linear form}) \qquad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \qquad (\text{linear form}) \qquad (3)$$

Where Q^o is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/l), Q^o is the monolayer adsorption capacity (mg/g), and b is the constant related to the energy of adsorption (l/g). It is the value reciprocal of the concentration at which half the saturation of the adsorbent is attained.

2.4.2 Freundlich Isotherm

The Freundlich isotherm theory states that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution is not constant at different concentrations. The Freundlich equation may be written as

$$q_e = K_F C_e^{1/n} \qquad (\text{non} - \text{linear form}) \qquad (4)$$

$$\log q_e = \log K_F + 1/n \ \log C_e \qquad (\text{linear form}) \qquad (5)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/l), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg/g), and $1/n$ is the constant indicative of the intensity of the adsorption.

3 Results and Discussion

3.1 Some Physicochemical Analysis of Unmodified Bentonite and Modified Bentonite

Data for the physicochemical analysis of the unmodified bentonite are presented in Table 1. It was observed that the CEC for the modified bentonite clay was higher than that for the unmodified with goethite–humic acid-modified bentonite given the highest CEC (Table 1). However, for their specific surface areas, the reverse trend was observed. It is possible that the aggregation of clay particles in the presence of humic acids could have decreased the specific surface area of the adsorbents as suggested by Liu and González (1999). It is possible that goethite had similar effect on the Specific surface area of Bentonite clay. 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.

3.1.1 Effect of pH

pH is one of the most important parameters in assessing the adsorption capacity of an adsorbent for

Table 1 Some physicochemical characteristics of unmodified bentonite clay adsorbent

	Bentonite	Bentonite–goethite	Bentonite–humic acid	Bentonite–goethite–humic acid
%Si	61.4	–	–	–
%Al	18.1	–	–	–
%MgO	2.58	–	–	–
$\%Na_2O$	4.3	–	–	–
$\%K_2O$	0.15	–	–	–
%CaO	1.45	–	–	–
$\%\ Fe_2O_3$	1.09	–	–	–
% LOI (at 200°C)	11	10.2	10.4	10.3
Exchange acidity	0.4	0.2	0.4	0.4
pH	8.3	8.1	7.9	7.8
CEC (meq/100 g)	95	105.32	120.4	125.8
Specific surface area (m^2/g)	80	72	77	64

metal ion sequestration from aqueous solution. The pH of the system controls the adsorption capacity due to its influence on the surface properties of the adsorbent and on the ionic forms of the cations in solutions. Figure 1 shows the effect of pH on the adsorption of Cu^{2+} and Cd^{2+} onto bentonite. Increasing pH enhanced the uptake of metal ions with the Cu^{2+} being more adsorbed on the unmodified bentonite sample than Cd^{2+}. Adsorption of Cu^{2+} increased from pH 3.0 up to pH 5.0 and a plateau was observed between pH 5.0 and pH 7.0 after which further adsorption was observed at pH 8–10. However, for

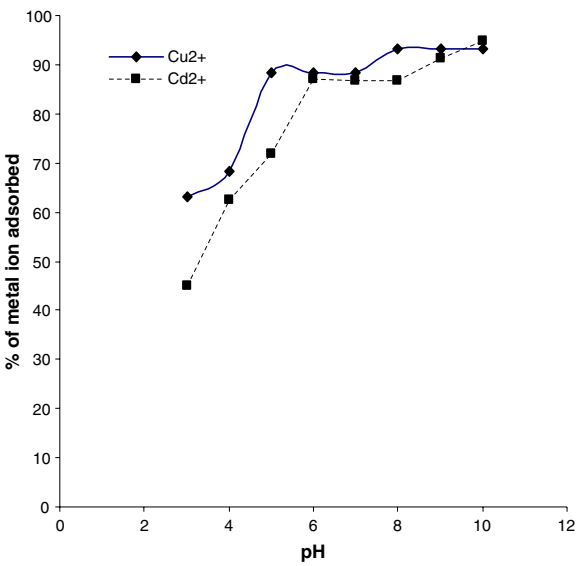

Fig. 1 Effect of pH on the adsorption of Cu^{2+} and Cd^{2+} onto bentonite clay

Cd^{2+}, the pH increased from 3 to 6 and reached a plateau between pH 6 and 8 after which a further increase in pH>8 caused a further increase in adsorption (Fig. 1). This difference may be as a result of increased overall negative charge on the unmodified bentonite especially between pH 4 and 7. In addition, increasing pH decreases the concentration of H^+, thereby reducing the competition between metal ions and protons for adsorption sites on the particle surface. Further increase in adsorption capacity of bentonite clay at pH above 7 for both metal ions may be as a result of the strong contribution from the precipitation of the metal ions which usually occurs at pH above neutral.

On the other hand, decrease in solution pH influences the hydrolysis of the metals. Hydration is followed by hydrolysis, according to the following reversible reaction, giving acidic properties to heavy metal solutions.

$$\left[M(H_2O)_x\right]^{c+} + H_2O \leftrightarrow \left[M(H_2O)^{x-1}(OH)\right]^{(c-1)+} + H_3O^+$$

Consequently, at lower acidity, the above equilibrium is shifted to the left and more highly charged metal complexes are formed, which favors the adsorption reaction (Inglezakis et al. 2007).

3.1.2 Effect of Contact Time

This was carried out to know how long it will take for the adsorbent to adsorb metal ions at optimum pH. As the contact time increased from 10 to 120 min for Cu^{2+},

the amount of metal ion adsorbed increased. However, as contact time reached 240 min, the amount of metal ion adsorbed reached maximum, with percent adsorbed remaining approximately constant. For Cd^{2+}, as contact time increased from 10 to 480 min, there was a corresponding increase in adsorption even at 480 min where the amount of metal ion adsorbed reached maximum after which the amount adsorbed remained approximately constant. From these results, it was observed that the optimum adsorption time for Cd^{2+} was achieved at 480 min while that of Cu^{2+} was achieved at 240 min. Despite the longer duration taken by Cd^{2+}, the amount of Cu^{2+} adsorbed (at 240 min) was higher than that of Cd^{2+} (at 480 min) as shown in Fig. 2.

3.1.3 Effect of Adsorbent Dose

The effect of varying adsorbent dose 0.2–2 g for the removal of metal ion from 200 mg/l solution is shown in Figs. 3 and 4. Equilibrium adsorption capacity of bentonite for Cu^{2+} and Cd^{2+} decreased. However, the percentage adsorption of these metal ions showed a reverse trend (Figs. 3 and 4). The increased percentage adsorption of these metal ions with increasing bentonite adsorbent dose could be as a result of the increase in surface negative charge and decrease in electrostatic potential near the solid surface that favors solid–solute interaction (Adebowale et al. 2006; Unuabonah et al. 2007). However, the decreased

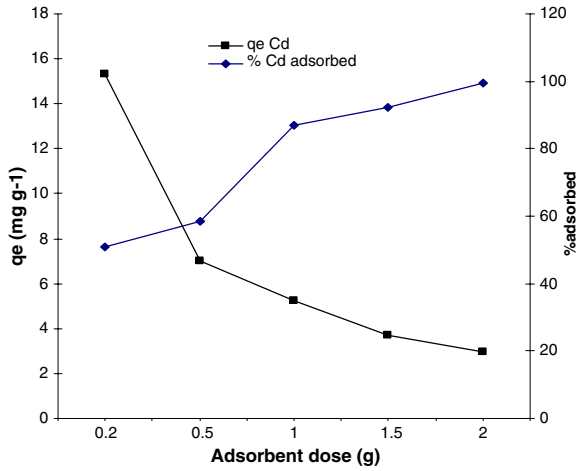

Fig. 3 Effect of adsorbent dose on the adsorption of Cd^{2+} onto bentonite clay

equilibrium adsorption capacity, q_e, of bentonite for the metal ions as its mass was increased can be attributed to decreasing total surface area of the adsorbent, which is the result of aggregation of bentonite clay particles. This aggregation becomes increasingly significant as the mass of the adsorbent is increased (Shukla et al. 2002; Bordas and Bourg 2001). Secondly, at constant volume of adsorbate, there is increase in the solid/liquid ratio which leaves many sites unoccupied during adsorption process and hence a reduction in the adsorption capacity of the

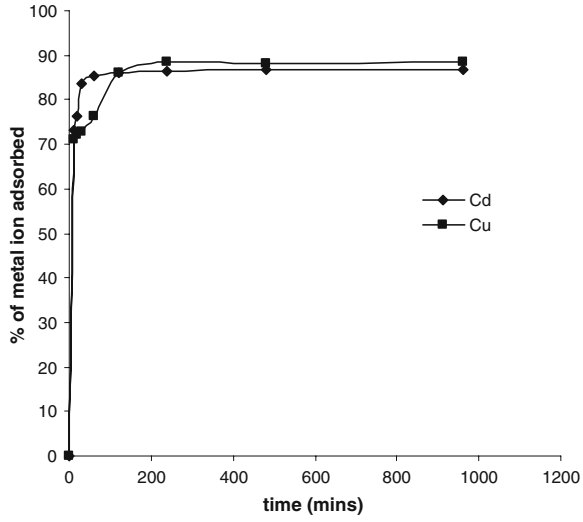

Fig. 2 Effect of time on the adsorption of Cu^{2+} and Cd^{2+} onto bentonite clay

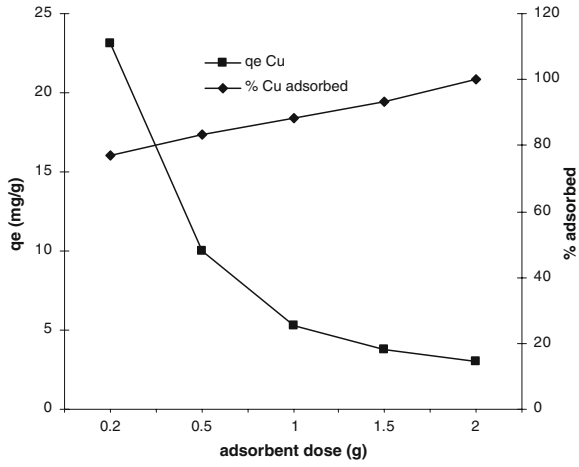

Fig. 4 Effect of adsorbent dose on the adsorption of Cu^{2+} onto bentonite clay

adsorbent. This same trend has been reported in our previous work (Unuabonah et al. 2007) and by Arpa et al. (2000) using modified kaolinite clay and smectite clay minerals, respectively.

3.1.4 Effect of Initial Concentration

The amount of metal ion adsorbed (q_e) increased with the increase in initial metal ion concentration, while the percentage of metal ion adsorbed decreased with the increase in initial metal ion concentration (Fig. 5) with Cu^{2+} being more adsorbed than Cd^{2+}. This occurrence might be due to smaller ionic radius of Cu^{2+} (0.73 Å), which made it possible for it to enter the crystal lattice of bentonite as compared with Cd^{2+} (0.97 Å) with a larger ionic radius, hence cannot occupy all the sites available on the bentonite surface. This result was also obtained by Abollino et al. (2003).

Another reason for this trend is that the selectivity of metal ions by an adsorbent is increased with metal ions that easily form hydroxyl complexes. Thus, the pK (equilibrium constant) values of the reaction determine the adsorption behavior of the different metal ions. Selectivity increases with decreasing pK values. Lower pK will lower the degree of salvation of metal ions, assisting them to easily approach the solid surface and thus increase adsorption. Thus, Cu^{2+} is more adsorbed on bentonite surface because it has a lower pK value of 7.7 compared with 10.1 for Cd^{2+} (Alloway 1990).

The decrease in percentage of metal ion adsorbed is due to the decrease in active sites on the adsorbents as more metal ions are adsorbed, while the increasing adsorption capacity is due to increasing driving force of metal ions towards the active sites. Increasing adsorption capacity with increasing initial metal ion concentration for both metal ions on the adsorbent is due to increasing driving force that leads to increasing surface saturation per gram of adsorbent.

3.1.5 Effect of Temperature

From Table 2, it was observed that the increase in adsorbate temperature resulted in the increase in adsorption for all the adsorbents with the humic acid–goethite-modified bentonite system giving the best adsorption capacity for both metal ions. This, according to Chen and Wang 2006, might be due to the hydrated nature of both metal ions. For ions to be adsorbed on the adsorbents, they have to lose their hydration shell, and this dehydration process needs energy. The removal of water molecules from ions is essentially an endothermic process.

3.1.6 Data Fitting Analysis

An error is required to evaluate the fit of an equation to the experimental data obtained from the optimization process employed. In this research work, linear coefficients of determination and a non-linear chi-square test were used. The linear coefficient of determination, r^2, represents the percentage of variability in the dependent variable that has been explained by the regression line. The values of the coefficient of determination were generally above 0.90 for both models indicating that the experimental data fit into both isotherms. However, the linear method of fitting experimental data is usually associated with errors. To reduce these errors and have better qualitative results, a non-linear method is applied. Therefore, it is necessary to also analyze the dataset using the non-linear chi-square test to confirm the isotherm with the best fit for the sorption system.

The chi-square test statistic is basically the sum of the squares of the differences between the experimen-

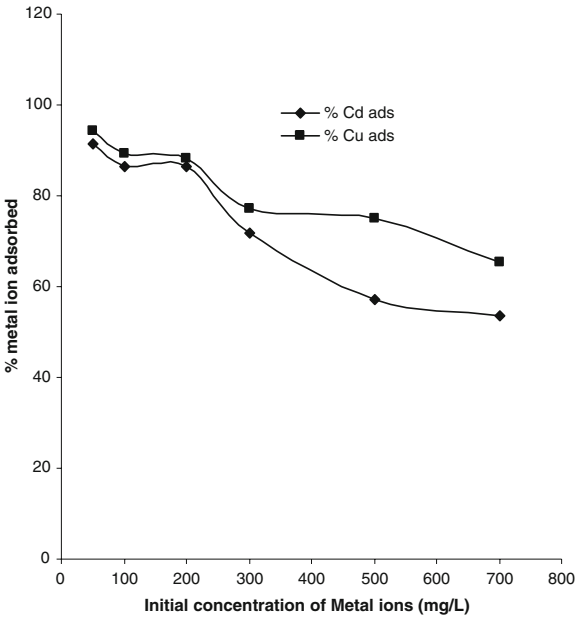

Fig. 5 Effect of initial metal ion on the adsorption Cd^{2+} and Cu^{2+} onto bentonite clay

Table 2 Data for Langmuir and Freundlich parameters for adsorption of Cd^{2+} and Cu^{2+} onto unmodified bentonite adsorbent

	30°C						50°C					
	Langmuir model			Freundlich model			Langmuir model			Freundlich model		
	Q^o	b	r^2	K_F	$1/n$	r^2	Q^o	b	r^2	K_F	$1/n$	r^2
Cadmium												
B	7.73	0.486	0.9426	0.82	0.46	0.9518	11.26	0.031	0.9548	2.40	0.26	0.9400
B+G	9.56	0.070	0.9243	0.70	0.57	0.9846	12.34	0.034	0.9437	1.08	0.43	0.9787
B+H	9.90	1.152	0.9195	1.89	0.41	0.9470	15.92	0.98	0.9003	2.82	0.28	0.9822
B+G+H	10.09	2.155	0.7994	1.61	0.46	0.9200	16.00	0.11	0.9207	2.65	0.30	0.9642
Copper												
B	9.72	1.175	0.9257	0.84	0.52	0.9826	11.29	0.047	0.9347	2.87	0.28	0.9729
B+G	9.90	0.929	0.9309	1.00	0.54	0.9636	13.91	0.047	0.9545	2.76	0.29	0.9728
B+H	10.33	1.310	0.9357	1.92	0.42	0.9514	16.13	0.10	0.9150	3.13	0.28	0.9826
B+G+H	10.03	0.329	0.9165	1.38	0.41	0.9415	16.42	0.11	0.9031	2.11	0.37	0.9883

B+ G bentonite+goethite, *B+ H* bentonite+humic acid, *B+ G+ H* bentonite+ geothite+humic acid

tal data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The equivalent mathematical statement is:

$$X^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from model (mg/g) and q_e is experimental data of the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, X^2 will be a small value, while if they differ, X^2 will be a bigger value. The results from Table 3 show lower X^2 values for Freundlich isotherm for both metals at 30 and 50°C showing that experimental data fit best into Freundlich isotherm. This was confirmed from the data fit plots shown in Fig. 6a–h. This further suggests that the adsorption sites on the adsorbents are heterogeneous in nature in accordance with the principle of Freundlich isotherm.

Table 3 Data Fitting analysis using linear regression coefficient and non-linear chi-square test

	B		B+G		B+H		B+G+H	
	LM	FM	LM	FM	LM	FM	LM	FM
$Cu_{30°C}$	4.85	0.42	13.90	1.01	10.83	0.66	4.82	8.35
$Cd_{30°C}$	1.28	0.75	4.66	0.41	10.19	0.61	12.48	1.37
$Cu_{50°C}$	6.72	0.47	33.22	0.45	19.51	0.19	4.26	0.30
$Cd_{50°C}$	2.24	0.59	0.66	0.41	13.00	0.27	12.96	0.48

LM Langmuir model, *FM* Freundlich model, *B+ G* bentonite+ goethite, *B+H* bentonite+humic acid, *B+ G+H* bentonite+ geothite+humic acid

3.1.7 Effect of Ionic Strength of Electrolyte

Using 0.01 M $NaNO_3$ as electrolyte, 88.39% and 84.41% were adsorbed for Cu^{2+} and Cd^{2+}, respectively, while using 0.01 M KNO_3 as electrolyte 86.78% and 82.80% were adsorbed for Cu^{2+} and Cd^{2+}, respectively, as seen in Fig. 7. This was due to smaller hydrated radius of K^+ (0.53 nm) as compared with Na^+ (0.79 nm) which caused an increased competition between metal ions and K^+ for adsorption sites of bentonite clay.

Effect of ionic strength on adsorption of Cu^{2+} and Cd^{2+} adsorption on bentonite was carried out to study how the ionic potential created by increasing the ionic strength of $NaNO_3$ will affect adsorption. It was observed that decreasing concentration of the electrolyte increased the adsorption capacity of bentonite clay adsorbent for both Cd^{2+} and Cu^{2+} in the range of 21.0–40.3% for Cu^{2+} and 16.2–40.0% for Cd^{2+} with 0.001 M $NaNO_3$ electrolyte concentration giving the highest adsorption capacity (Fig. 7). This observation is due to the fact that the increase in ionic strength makes the surface of the adsorbent less negative, hence the potential in the plane of adsorption is getting increasingly positive and hence decreased

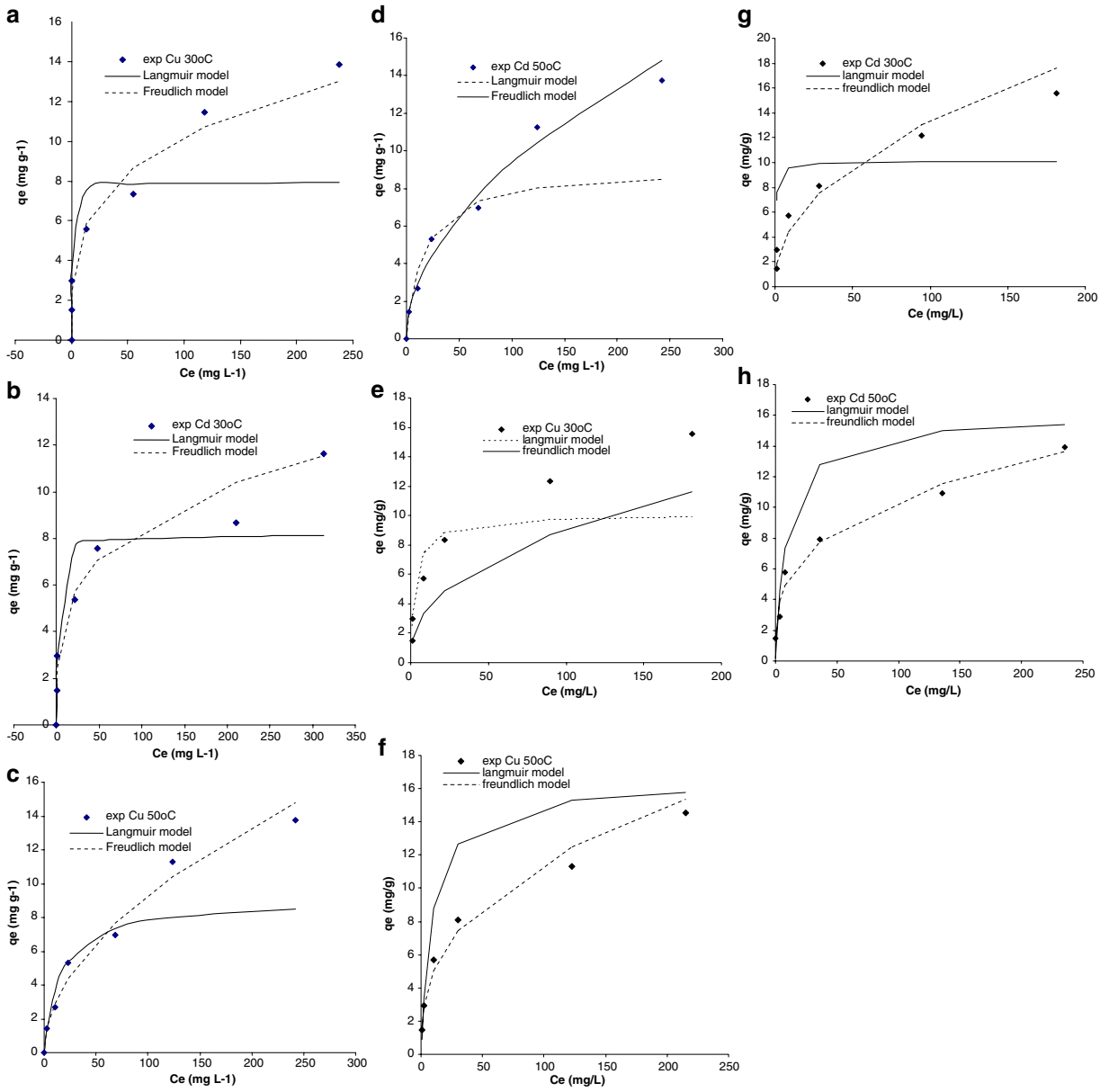

Fig. 6 **a** Model plot for the adsorption of Cu^{2+} onto bentonite clay at 30°C. **b** Model plot for the adsorption of Cd^{2+} onto bentonite clay at 30°C. **c** Model plot for the adsorption of Cu^{2+} onto bentonite clay at 50°C. **d** Model plot for the adsorption of Cd^{2+} onto bentonite clay at 50°C. **e** Model plot for the adsorption of Cu^{2+} onto goethite–humic acid-modified bentonite clay at 30°C. **f** Model plot for the adsorption of Cu^{2+} onto goethite–humic acid-modified bentonite clay at 50°C. **g** Model plot for the adsorption of Cd^{2+} onto goethite–humic acid-modified bentonite clay at 30°C. **h** Model plot for the adsorption of Cd^{2+} onto goethite–humic acid-modified bentonite clay at 50°C

adsorption (Naidu et al. 1994; Undabeytial et al. 2002; Gu and Evans 2007).

This study shows that there is a strong dependence of adsorption of the metal ions on the ionic strength of $NaNO_3$ electrolyte. This same observation was made by Xu et al. 2008 when they adsorbed Ni^{2+} onto montmorillonite clay. They suggested that the strong ionic strength dependence indicates that outer sphere complexes are formed on the surface of the adsorbent, or cation exchange with –Na or –H at the surface of the adsorbent contributes to the binding of the metal ion on solid surface. From the ionic strength

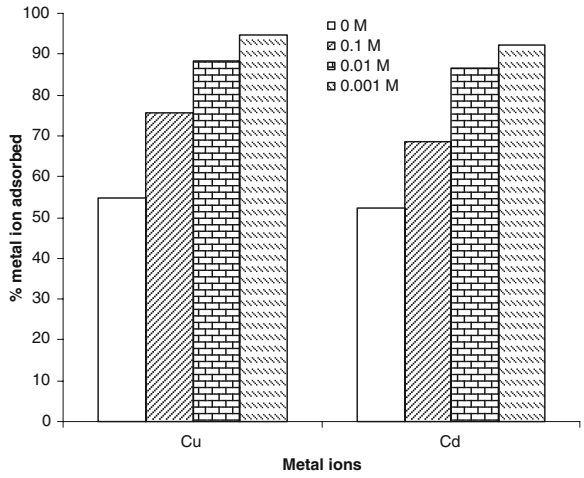

Fig. 7 Effect of electrolyte on the adsorption of Cu^{2+} and Cd^{2+} onto bentonite clay

dependence, one can deduce that cation exchange is the main mechanism for Cu^{2+} and Cd^{2+} adsorption on bentonite clay. This exchange can be expressed in two ways:

1. Exchange with ions on the surface of bentonite clay:

$$2 \equiv S - OH + M^{2+} \leftrightarrow (\equiv S - O)_2M + 2H^+$$

2. Exchange with Na^+ ions on the surface of bentonite clay:

$$2 \equiv S - ONa + M^{2+} \leftrightarrow (\equiv S - O)_2M + 2Na^+$$

3.1.8 Effect of Binary Metal Ion

Figure 8 shows the effect of binary mixture of metal ion on the adsorption of either Cu^{2+} or Cd^{2+} onto bentonite clay. Binary mixture of 200 mg/l Cu^{2+} and 200 mg/l Cd^{2+} led to an observed decrease in the amount of both metal ions adsorbed on bentonite clay with Cu^{2+} having a more significant decrease (q_e= 4.70 mg/g) than Cd^{2+} (q_e=4.96 mg/g) unlike in single metal solution where Cu^{2+} was more adsorbed (q_e= 5.30 mg/g) than Cd^{2+} (q_e=5.22 mg/g). Adsorption of Cu^{2+} from a binary solution of Cu^{2+} and Cd^{2+} was 10.08% lower than in single metal adsorption while Cd^{2+} was 4.20% lower than in single metal adsorption. This could be due to the smaller ionic radius of Cu^{2+} (0.73 Å) to Cd^{2+} (0.97 Å), which allows it to effectively compete for adsorption sites.

The effect of binary mixtures of Cu^{2+} and Cd^{2+} in aqueous solution on the adsorption capacity of unmodified bentonite clay may be represented by the ratio of the adsorption capacity for one metal ion in the presence of the other metal ion, Q^{mix}, to the sorption capacity for the same metal when it is present alone in the solution, Q^o, so that for:

$$\frac{Q^{mix}}{Q^o} > 1 \tag{6}$$

the sorption is enhanced by the presence of other metal ions,

$$\frac{Q^{mix}}{Q^o} = 1 \tag{7}$$

there is no observable net interaction,

$$\frac{Q^{mix}}{Q^o} < 1 \tag{8}$$

Sorption is suppressed by the presence of other metal ions.

Table 4 shows the depression in the ratio of Q^o and Q^{mix} with the ratio of $\frac{Q^{mix}}{Q^o}$ being less than 1 which further supports the observed decrease in the adsorption capacity of the bentonite clay. This same observation was reported by Srivastava et al. (2005) for the adsorption of Pb^{2+} and Cu^{2+} onto raw kaolinite and Unuabonah et al. (2007) for the adsorption of Pb^{2+} and Cd^{2+} onto raw kaolinite and tripolyphosphate-modified kaolinite clay.

3.1.9 Effect of Modifying Reagent

The elemental composition of humic acid used in this study is C 61.44%, H 3.63%, N 4.12%, O 30.31%,

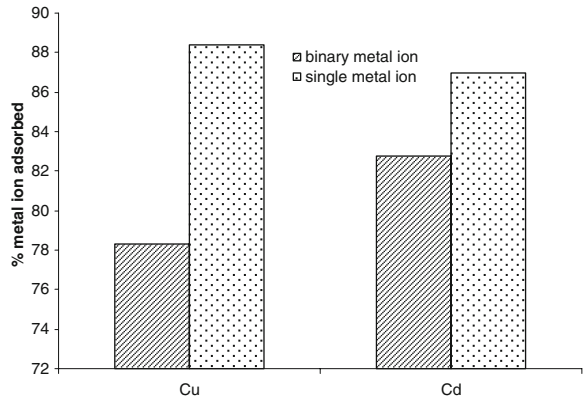

Fig. 8 Effect of binary metal ion on the adsorption of Cu^{2+} and Cd^{2+} onto bentonite clay

Table 4 Ratio of sorption capacity (Q^{mix}/Q^{o}) of Cu^{2+} and Cd^{2+} onto bentonite clay

	Q^{o} (mg/g)	Q^{mix} (mg/g)	Q^{mix}/Q^{o}
Cu^{2+}	5.30	4.70	0.89
Cd^{2+}	5.22	4.96	0.95

and S 0.50%, while goethite had SiO_2 0.34%, Fe_2O_3 89.45%, and H_2O 10.41%. Figure 9 shows the effect of varying percentage modification of bentonite using humic acid and goethite on the adsorption of the metal ions. It was observed that Cu^{2+} was more adsorbed than Cd^{2+} on all adsorbents with geothite–humic acid-modified bentonite adsorbent showing the highest adsorption capacity at all percentage of modifications. The Pearson classification classified metals into three broad categories: those that are polarizable or "soft", those that are non-polarizable or "hard", and those that are borderline (Dean 1985). Copper ions are classified in the borderline category according to this classification, while cadmium ions fall into the "soft" category. "Soft" cations form more stable complexes with "soft" donors such as sulfhydryl and amino groups while "hard" cations prefer "hard" donors such as carbonate, phosphate, sulfate, carboxylate, and hydroxyl (Williams et al. 1998; Buffle 1988; Bell 1977). This perhaps explains while Cd^{2+} was less favored compared with Cu^{2+} because the ligands on the surface of the adsorbents used in this study are hydroxyl and carboxylate.

Furthermore, complexation is more likely with the empty d-orbital of Cu^{2+} ([Ar] $3d^9$) than with the filled d-orbital of Cd^{2+} ([Kr] $4d^{10}$). It is very likely that Cd^{2+} will be adsorbed by these modified surfaces via its 5s orbital which has far less stable energy than the 4d-orbital.

Five percent (5%) modification of bentonite with either goethite or humic acid or a binary mixture of goethite–humic acid gave the highest adsorption capacity after which there was a decrease or no significant increase in adsorption capacity of bentonite clay (Fig. 9). This agrees with findings by Abate and Masini (2005) who, from their studies on the effect of humic acid on the adsorption of Pb^{2+} and Cd^{2+} onto vermiculite, suggested that a high concentration of adsorbed humic acid may decrease the adsorption capacity by physically blocking access to the adsorbing sites. This is probably the case also with goethite. Based on this data, 5% modification with the different modifying reagents was adopted for use in this study.

From Table 2, it was observed that there was an increase in the adsorption capacity of bentonite clay for Cu^{2+} and Cd^{2+} when it was modified with either 5% humic acid or 5% goethite with Cu^{2+} being adsorbed more. The adsorption capacity of bentonite clay was better enhanced by the modification of its surface with a binary mixture of goethite and humic

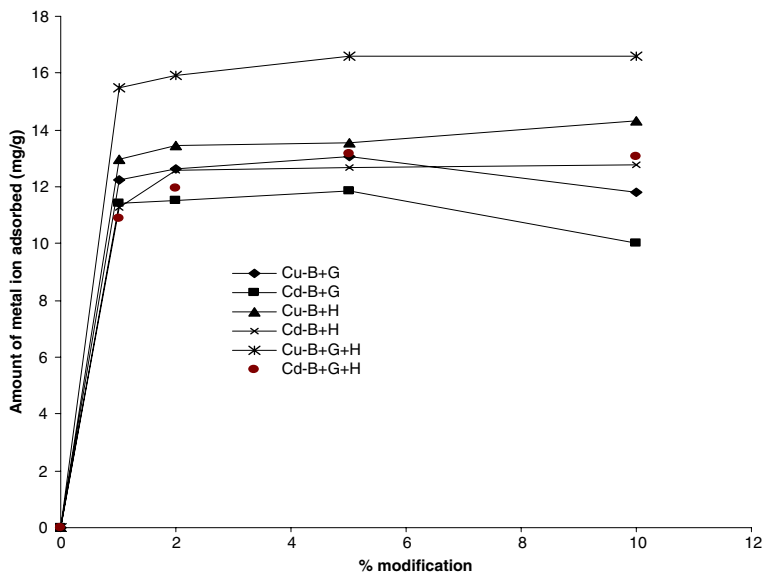

Fig. 9 Effect of modification on the adsorption Cu^{2+} onto unmodified and modified bentonite clay adsorbents (where *B*+*G*, *B*+*H*, and *B*+*G*+*H* are goethite-modified, humic acid-modified, and goethite–humic acid-modified bentonite, respectively)

acid. This increase in adsorption capacity of bentonite clay with modification is possibly so because the adsorption of either goethite or humic acid onto bentonite clay may have introduced some sites (via their functional groups) on the surface of the clay. Furthermore, the presence of $NaNO_3$ electrolyte at pH of 5.0 and 6.0 (used in this experiment) would have reduced the hydrodynamic thickness of the adsorbed humic acid or goethite (Liu and González 1999) compressing the electric double layer on the adsorbents surfaces, thus favoring the inner sphere complexation process involving the binding sites from humic acid or goethite.

Humic acid molecules adsorbed onto the surface of clay minerals can increase the adsorption of metallic cations because humic substances have strong complexing sites. Besides, the complexation capacities of humic acids (in terms of moles per gram) are significantly higher than usually reported for the adsorption capacities of clay minerals (Liu and González 1999; Schmitt et al. 2002).

However, it was observed in Langmuir adsorption capacity, Q^o, (Table 2) that the binary mixture of goethite and humic acid on bentonite clay adsorbent reduced the selectivity of the bentonite for either of the metal ion even with increased temperature. This is possibly because of the presence of at least more than one adsorption site on the modified adsorbent.

Increasing temperature of adsorbate solution from 30 to 50°C increased the adsorption capacity of the adsorbents (Table 2). This may suggest that the adsorption of Cd^{2+} and Cu^{2+} is endothermic in nature (Yong and Mourato 1988; Wu 2000).

The role of goethite and humic on the surface of bentonite is to enhance the complexation of Cu^{2+} and Cd^{2+} from aqueous solution. While it is has been proven that goethite holds divalent metal ions (e.g., Cu^{2+}) by the bidentate and tridendate surface complexation modes (Peacock and Sherman 2004)

$$3(\equiv \mathrm{FeOH}) + 2\mathrm{Cu}^{2+} + 3\mathrm{H_2O} = \left(\equiv \mathrm{Fe_3O(OH)_2}\right)\mathrm{Cu_2(OH)_3^0} + 4\mathrm{H}^+$$

and

$$2(\equiv \mathrm{FeOH}) + \mathrm{Cu}^{2+} + 2\mathrm{H_2O} = (\equiv \mathrm{FeOH})_2\mathrm{Cu(OH)_2^0} + 2\mathrm{H}^+$$

humic acid adsorbed Cd^{2+} by its carboxylic and phenolic groups via inner sphere complexation mechanism at low concentrations of the cadmium ions and by ion exchange at high concentrations of the cadmium ion (Abate and Masini 2005).

3.2 Fourier Transform Infrared Spectra Analysis of Adsorbents

The infrared spectra of both modified and unmodified bentonite adsorbents are shown in Fig. 10. The structural –OH vibrations and the Si–O stretches and the OH bending modes exist in the regions 3,700–3,200 and 1,300–440 cm^{-1} (a peak and a shoulder), respectively, in the FTIR spectrum of raw bentonite (Fig. 10; Olson et al. 2000; Xu et al. 2000). The characteristic –OH stretching vibration observed at 3,630 cm^{-1} which originates from the AlAlOH stretch is due to the Al-rich octahedral centers of bentonite clay. In addition, the peak at 3,426 cm^{-1} which belongs to the –OH stretching of H-bonded water signifies the higher amount of octahedral replacement of Mg atoms than that of Fe atoms (Kloprogge et al. 2002; Madejová 2003). The characteristic AlAlOH and AlFeOH bending vibrations were observed at 913 and 848 cm^{-1}, respectively, with their fingerprint regions at 524 and 462 cm^{-1}, respectively (Patel et al. 2007).

In goethite-modified bentonite, the (cation-OH) H-bonded band shifted by 18 cm^{-1} to give a value of 3,445 cm^{-1}. Caglar et al. 2009 suggested that this shift could occur within 5–20 cm^{-1} depending on the type of exchanging cation involved. However, this band (3,426 cm^{-1}) was observed to be broad in the goethite modified bentonite clay and shifted to 3,445 cm^{-1}, indicating an interaction between –OH and goethite. A further evidence of modification of bentonite clay by goethite was observed from the shift in the AlAlOH and Si–O stretching peaks from 918 and 1,050 cm^{-1} to 914 and 1,045 cm^{-1}, respectively, and the peaks were also broader. The O–H bending frequency band of 1,650 cm^{-1} in the raw bentonite sample shifted to 1,636 cm^{-1} for goethite-modified bentonite clay. There was an observed shift in the AlFeOH peak from 848 to 891 cm^{-1}.

For humic acid-modified bentonite clay, the AlAlOH peak of raw bentonite shifted from 3,426 to 3,448 cm^{-1}. This may have been influenced by the presence of –OH from carboxylic acid and phenol

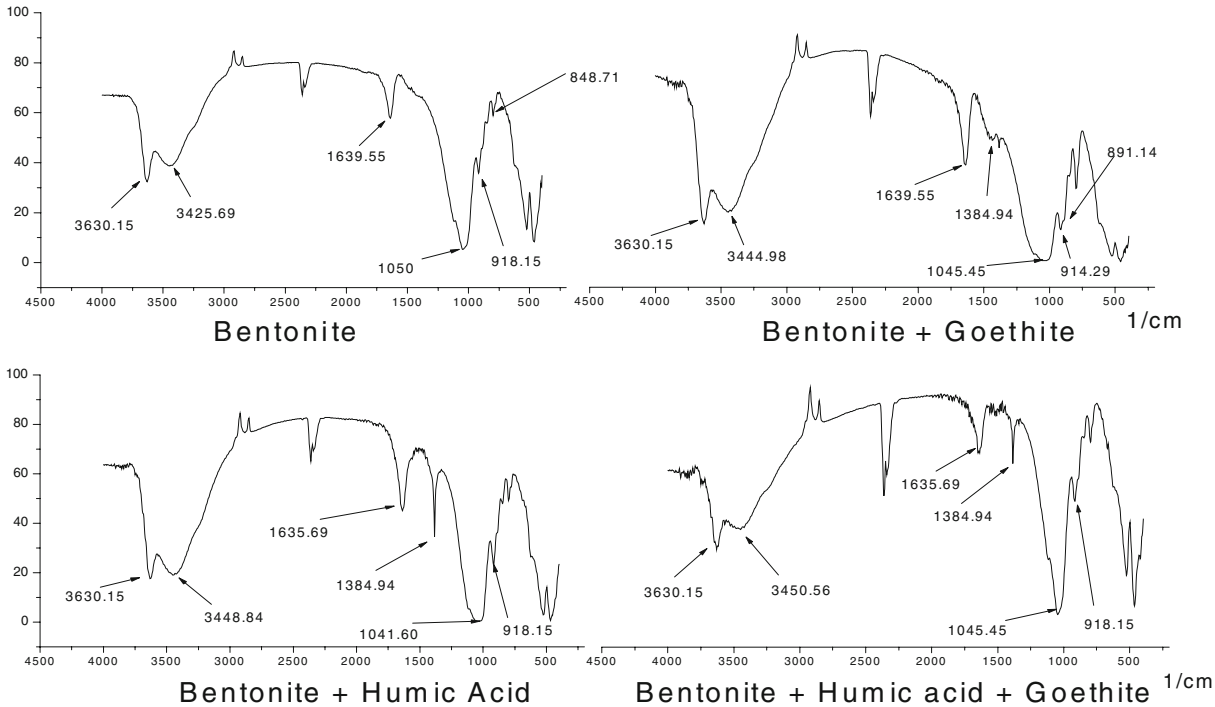

Fig. 10 Fourier infrared spectra of raw and modified bentonite clay

introduced by the humic acid. The Si–O stretching peak in raw bentonite clay shifted from 1,050 to 1,041 cm^{-1} in humic acid-modified bentonite clay. While Si–O bending peak did not show any shift, the AlAlOH bending peak shifted to 1,042 cm^{-1}. However, these peaks were also observed to be broad. The AlFeOH peak was also broad but without any observed shift.

For humic acid–goethite-modified bentonite clay, the AlAlOH stretching band was shifted further to 3,450 cm^{-1} but not as broad as that of the goethite-modified bentonite clay perhaps due to the presence –OH from carboxylic or phenolic groups in humic acid used for modification. The characteristic AlFeOH bending peak shifted to 890 cm^{-1}. It was also noticed that the intensity of 1,385 cm^{-1} peak of the humic acid-modified bentonite decreased when the goethite–humic acid complex system was on the surface of the bentonite. Again, it was observed that the 1,042 and 1,045 cm^{-1} peaks in humic acid and goethite-modified bentonite samples respectively appeared as a sharp 1,045 cm^{-1} peak on the goethite–humic acid-modified bentonite. This might suggest the stronger influence of goethite on the adsorption of humic acid when both are simultaneously adsorbed on another surface as suggested by Orsetti et al. (2006) in their study of the adsorption of Pb^{2+} onto a binary mixture of goethite and humic acid complex. They used the substrate–crystal interaction to explain this phenomenon where it has been observed that goethite is more favorably adsorbed on crystal surfaces than humic acid when they are both adsorbed on a crystal surface. They also observed that some amount of humic acid was adsorbed on the surface of the goethite, which explains the reduced intensity observed at 1,385 cm^{-1} for the goethite–humic acid-modified bentonite adsorbent as compared with humic acid-modified bentonite. Further studies are needed to investigate the mode of interaction of binary mixtures of goethite and humic acid on bentonite clay mineral surface.

The 1,639 cm^{-1} band obtained in all the spectrum of the adsorbents is attributed to the –OH bending of adsorbed water while the sharp peak of 1,384 cm^{-1} observed in all the modified samples was due to incorporated or adsorbed NO_3^- (Rao 1963).

From the above, we can thus say that modification of raw bentonite with either goethite or humic acid reagent was effective on the AlAlOH and on Si–O sites in raw bentonite clay while modification with a binary mixture of both was effective basically on the

AlAlOH site. The primary adsorption site on these modified adsorbents is possibly the –O–H and –COOH adsorption sites. This was verified by following the change in pH of adsorbate solution during adsorption process and it was observed that there was a drop in pH of equilibrium solution in the order of 0.32 to 0.74 with increasing initial metal ion concentration.

4 Conclusion

Adsorption of Cu^{2+} and Cd^{2+} onto bentonite was studied. It was observed that adsorption of Cu^{2+} and Cd^{2+} was maximum at pH 5.0 and 6.0, respectively, for an optimum solid–liquid ratio of 0.2:30 (g:ml). Increasing initial metal ion increased the adsorption capacity of the bentonite clay for the metal ions. Bentonite clay showed greater preference for the adsorption of Cu^{2+} than for Cd^{2+}. The simultaneous presence of both metal ions in aqueous solution decreased the adsorption capacity of the bentonite clay for either of them.

However, modifying the surface of the adsorbent with goethite, humic acid, and a binary mixture of goethite–humic acid reagents increased its adsorption capacity for the adsorption of either metal ion. Goethite–humic acid-modified bentonite clay gave the highest adsorption capacity implying that bentonitic soils with already preadsorbed humic acid and goethite on its surface will further reduce the mobility of Cu^{2+} and Cd^{2+} in the soil systems. In an aquatic environment, soil sediments could serve as better sinks for heavy metal ions especially when they have preadsorbed goethite and humic acid. Furthermore, modifying bentonite clay with a binary mixture of goethite and humic acid reduced the selectivity of bentonite clay for either Cu^{2+} or Cd^{2+}.

The effective pre-modification of bentonite clay with goethite, humic acid, and a binary mixture of goethite–humic acid reagents were confirmed from their FTIR spectra. However, further studies are required to investigate the interaction between a binary mixture of goethite and humic acid on bentonite clay mineral to ascertain how the adsorption of the binary mixture is established on bentonite clay surface.

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