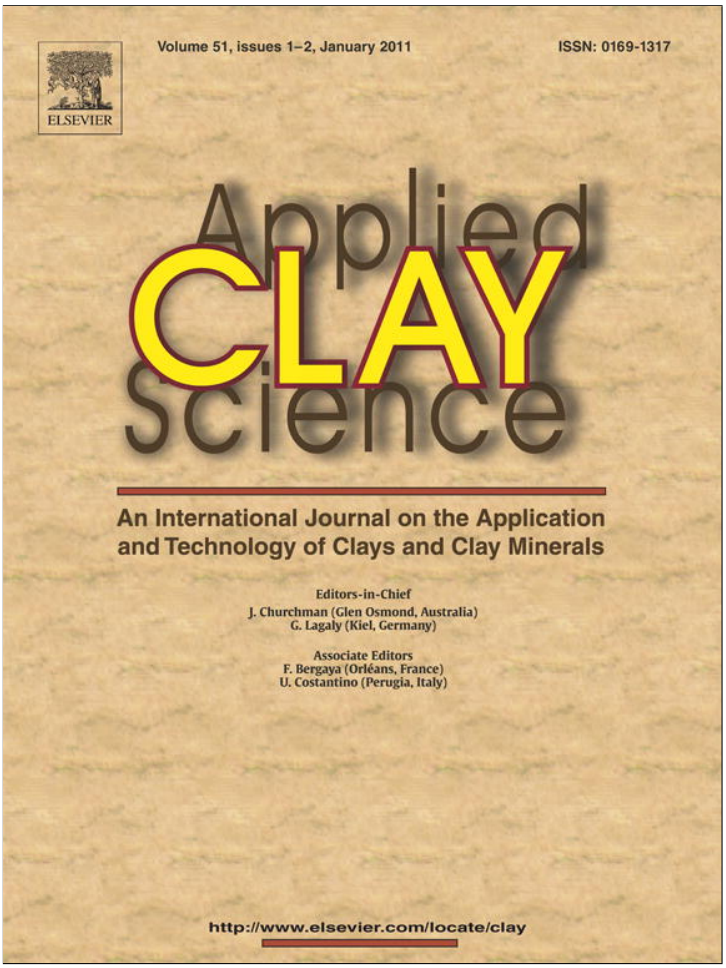

Applied Clay Science 51 (2011) 170–173

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Note

Adsorption of Zn^{2+} and Cu^{2+} onto sulphate and phosphate-modified bentonite

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ARTICLE INFO

Article history:
Received 19 February 2010
Received in revised form 19 October 2010
Accepted 23 October 2010
Available online 5 November 2010

Keywords:
Bentonite
Phosphate
Adsorption
Sulphate
Inner-sphere complex
Outer-sphere complex

ABSTRACT

The modification of bentonite with sulphate and phosphate increased the cation exchange capacity (CEC) and adsorption of Cu^{2+} and Zn^{2+} but decreased the specific surface area (SSA). Phosphate modified bentonite had the highest adsorption capacity for both metal ions. The Fourier transformed infrared spectra indicated the bonding of sulphate and phosphate bentonite with sulphate and phosphate by the hypochromic and hyperchromic shifts are typical of physisorption and chemisorption mechanisms. Phosphate and sulphate were adsorbed through inner-sphere and outer-sphere complex formation. The isotherms were better fitted by the Langmuir model than the Freundlich model.

1. Introduction

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 (Davis et al., 2000). The nitrate forms of both copper and zinc ions are used as mordants in textile industries and in addition copper nitrate is used in electroplating. Provision of clean/safe drinking water is one of the millennium development goals (MDGs) set out by the United Nations for 2025. It is believed that safe water is the key to global health (Schuster-Wallace et al., 2008).

In our previous studies, we have demonstrated how phosphate modified-kaolin can be used to remove Pb^{2+} and Cd^{2+} from aqueous solution (Adebowale et al., 2005; Adebowale et al., 2006; Unuabonah et al., 2007). The use of bentonite and modified bentonite was reported by Arfaouia et al., 2008, Hefne, et al., 2008, Tahir and Rauf, 2004. There are also reports on the amendment of soils and clay minerals with humic acid, sulphate and phosphate (Leung and Kimaro, 1997; Olu-Owolabi et al., 2010). However, there are no reports on the adsorption capacity and the mechanism of phosphate and sulphate modified bentonite in the removal of Zn^{2+} and Cu^{2+} from aqueous solution.

This study reports the mechanisms of the adsorption of sulphate and phosphate onto bentonite and the adsorption of Zn^{2+} and Cu^{2+} onto the modified adsorbents using the Fourier Transformed Infrared (FTIR) technique. The effect of the modifying agent on the adsorption capacity of bentonite was also investigated.

2. Materials and methods

The bentonite used in this study was obtained from the Federal Institute of Industrial Research (FIRO), Lagos, Nigeria. It was used as received. Some physicochemical properties of the bentonite are shown in Table 1. Modification of the samples was carried by the methods described by Adebowale et al. (2005).

2.1. Characterization of the adsorbents

The cation exchange capacity (CEC) of the samples was determined by a modified ammonium acetate method (Chapman, 1965). The oxide content of bentonite was determined by acid digestion using methods described by Vogel (1996). The Fourier Transformed Infrared (FTIR) spectra of the bentonites were obtained using KBr wafers and SHIMADZU 8400S FTIR. The Specific Surface Area (SSA) of the adsorbents was determined via the Sear's method as described in Olu-Owolabi et al., 2010. The moisture content (MC) was determined by removing the water by oven-drying. Samples were weighed to a constant mass at 105 °C.

2.2. Adsorption studies

Twenty milligram each of the samples were dispersed in 20 ml solutions (i.e. Zn $(NO_3)_2.6H_2O$ and Cu $(NO_3)_2$. $3H_2O$). The concentration was varied from 200 to 700 mg/L. The dispersions were agitated

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doi:10.1016/j.clay.2010.10.022

Table 1
Some physicochemical properties of bentonite and modified bentonite.

	Bentonite	S-mod bentonite	P-mod bentonite
%Si	58.4	–	–
%Al	20.3	–	–
%MgO	2.17	–	–
%Na_2O	5.3	–	–
%K_2O	1.15	–	–
%CaO	1.40	–	–
% Fe_2O_3	0.09	–	–
Moisture (%)	11.19	–	–
pH	8.32	8.70	7.91
ECEC (meq/100g)	95 ± 0.2	109 ± 0.2	118 ± 0.3
Specific surface area (m^2/g)	80 ± 0.1	73 ± 0.3	79 ± 0.2

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

Table 2
Langmuir parameters for the adsorption of Zn^{2+} and Cu^{2+} onto bentonite and modified bentonite.

	Bentonite	S-mod bentonite	P-mod bentonite
Zinc			
Q^o (mgg^{-1})	98.04	104.17	111.11
b (Lg^{-1})	6.59×10^{-3}	7.50×10^{-3}	8.07×10^{-3}
r^2	0.8519	0.9568	0.9531
E_L	0.29	0.21	0.48
E_F	0.34	0.22	0.40
Copper			
Q^o (mgg^{-1})	149.25	158.73	166.67
b (Lg^{-1})	4.10×10^{-3}	4.61×10^{-3}	6.18×10^{-3}
R^2	0.9728	0.9034	0.9668
E_L	0.70	0.75	0.89
E_F	0.56	0.50	0.53

Note S = Sulphate; P = phosphate; mod = modified; E_L = model efficiency for Langmuir data; E_F = model efficiency for Freundlich data.

at room temperature for 240 min. The supernatants obtained after centrifugation were analyzed by flame atomic absorption spectrophotometry. The amount adsorbed was calculated from the difference between the initial metal ion concentration and equilibrium concentration. Experiments were carried out in duplicate.

2.3. Model efficiency

The model efficiency was considered to be the best overall indicator of model fitting for its good measure of resistance to errors due to extreme experimental values (Bolster and Hornberger, 2006; Kvalseth, 1985). The model efficiency, E, is calculated as:

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

where S_{wavg} is the mean of the measured values, S_i are the experimental data, $\hat{S}_i$the model data and $w_i$is the number of data points. A model efficiency of 1 indicates a perfect fit to experimental data whereas a value of <0 indicates that taking the average of all the measured values would give a better prediction than the model (Bolster and Hornberger, 2006).

3. Results and discussions

3.1. Adsorbents

The cation exchange capacity (CEC) of the modified bentonite was higher than for raw bentonite because both anions introduced additional adsorption sites when adsorbed onto the bentonite surface (Table 1). Modification of bentonite with phosphate and sulphate anions reduced the specific surface area (Table 1) due to aggregation of the clay mineral particles in the presence of sulphate and phosphate

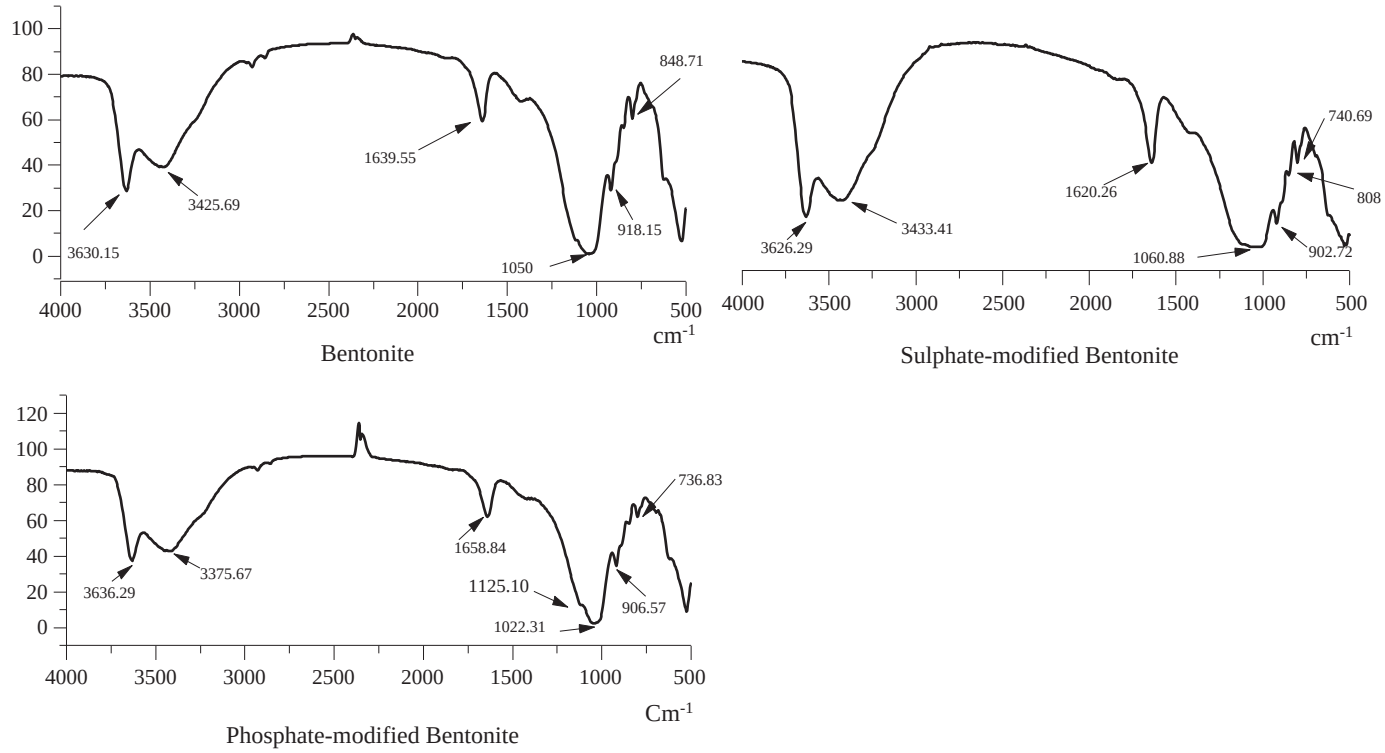


Fig. 1. Fourier transformed infrared spectra of bentonite and modified bentonite.

anions (Liu and González, 1999). Modification of mineral surfaces with ligands tends to block some pore spaces (Li et al., 2007). This may reduce the specific surface area of the bentonite. However, the adsorption capacity of the bentonite was enhanced by the presence of more binding sites (Table 2).

3.2. Data analysis

Adsorption of phosphate and sulphate increased the negative charge of the bentonite and hence the adsorption capacity for Zn^{2+} and Cu^{2+} (Table 2) (Adebowale et al., 2005). Although both Cu^{2+} and Zn^{2+} have similar ionic radius (0.73 Å and 0.75 Å), the amount of Cu^{2+} adsorbed was larger thatof Zn^{2+}. The higher first hydrolysis constant of Cu^{2+} lowers the degree of hydration so that the Cu^{2+} ions can better approach the silicate surface than Zn^{2+} (Cabrera et al., 2005; Seco et al., 1999). The Langmuir model described the adsorption isotherms better than the Freundlich model even though both models well described the experimental data. The model efficiency *E*, was used to compare both equilibrium isotherm models because the Root Mean Square Error (RMSE) analysis showed weak resistance to errors from extreme values (outliers).

3.3. Infrared spectroscopy

The structural –OH vibrations and the OH bending modes were seen in the regions 3700–3200 and 1300–440 cm^{-1} of the FTIR spectrum of bentonite (Fig. 1) (Xu et al., 2000). Characteristic AlAlOH and AlFeOH bending vibrations were observed at 913 and 848 cm^{-1} respectively in their finger print regions at 524 and 462 cm^{-1} (Patel et al., 2007).

There were shifts in the structural –OH vibration and absorbed water from 3636 and 3425 (bentonite) to 3626 and 3433 cm^{-1} (hypochromic shift) for sulphate-modified bentonite and to 3645 and 3376 cm^{-1} (hyperchromic shift) for phosphate modified bentonite. The –OH bending frequency of water at 1640 cm^{-1} of bentonite was shifted to 1620 and 1659 cm^{-1} when it was modified with sulphate and phosphate. Stretching and bending vibrations of structural –OH groups of bentonite shifted from 1050 and 918 cm^{-1} to 1061 and 903 cm^{-1} for sulphate modified bentonite and to 1022 and 906 cm^{-1} for phosphate modified bentonite. Strong S–O^- and P–O^- stretching bands were seen at 1061 and 1022 cm^{-1}. Typical P=O (1340–1235 cm^{-1}), S=O (1383 cm^{-1}) and partial double bond of S = O (1330 cm^{-1}) vibrations were not seen in the FTIR spectra. Mixing the modified bentonite samples with KBr led to a high concentration of Br^- displacing most SO_4^{2-} and PO_4^{3-} ions (Hug, 1997).

3.4. Mechanism of phosphate and sulphate adsorption

Small shifts (13–18 cm^{-1}) associated with the adsorption of sulphate anion onto bentonite may suggests physisorption mechanism (Curtin & Syers, 1990; Uehara & Gillman, 1981). However, the spectra of phosphate modified bentonite showed basically hyperchromic shifts suggesting the chemisorption of phosphate anion onto bentonite (Hinedi et al., 1993, Olu-Owolabi et al., 2010). As pH increased from 5.8 to 6.4 when bentonite was modified with potassium dihydrogen phosphate and from 7.8 to 8.9 when it was modified with sodium sulphate, it is likely that surface –OH groups were exchanged by phosphate and sulphate anions (Uehara and Gillman, 1981; Leung and Kimaro, 1997).

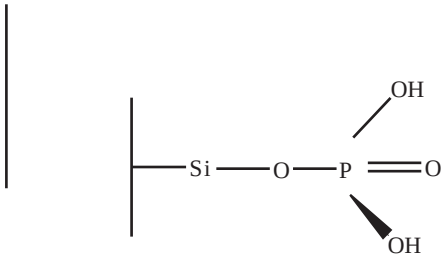
The proposed mechanisms for phosphate anion adsorption onto Al–OH functional groups include ion exchange mechanism involving surface –OH groups, and a precipitation mechanism that arises from dissolution of the adsorbent which produces Al^{3+} (He et al., 1997; Kasama et al., 2004). Thus, phosphate ions may be strongly adsorbed via an inner-sphere complex formation and also by formation of Al–O–P–OH surface precipitates (Fig. 2). The presence of three ν_3 bands (1125.10, 1022.31 and 906.57 cm^{-1}) observed in Fig. 1 is typical of diprotonated phosphate (i.e. $H_2PO_4^-$) and was confirmed by Arai and Sparks (2001) when they studied the mechanisms of the adsorption of phosphate on ferrihydrite by ATR-FTIR spectroscopy. This is consistent with C_{2v} or lower symmetry. Several molecular symmetries are possible for this Si–O–P (P = phosphate anion) monodentate mononuclear (aq) complex with C_{2v} or lower symmetry. However, the increase in CEC observed for phosphate modified bentonite favors the formation of the diprotonated monodentate mononuclear (C_1) (Fig. 2). Perhaps the diprotonated monodentate mononuclear complex forms hydrogen bonds with edge silanol groups (Fig. 2).

Turner and Kramer (1991) and Sparks (1999) demonstrated that sulphate may be adsorbed on variable charge minerals, forming both inner-sphere and outer-sphere complexes. The former becomes more dominant with decreasing pH and increasing sulphate concentration, considering the fact that sulphate were adsorbed at pH as high as 7.8. We conclude that the sulphate ions were adsorbed by outer-sphere complex formation.

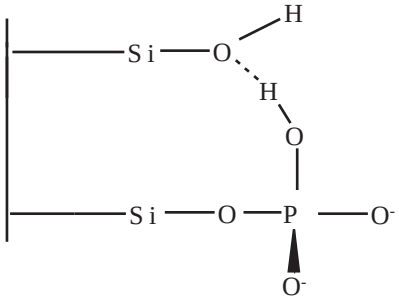
3.5. Mechanism of Cu^{2+} and Zn^{2+} adsorption

The ion exchange mechanism associated with the phosphate modified bentonite can be illustrated as:

$$S - P - OH + M^{2+} + NO_3^- \rightarrow S - P - O^-Me^{2+}NO_3^- + H^+ \quad (2)$$



(a)



(b)

Fig. 2. Possible molecular configurations (C_{2v} or lower) of protonated P inner-sphere complexes at the Si–OH–water interface. (a) diprotonated monodentate mononuclear (C_1), (b) nonprotonated monodentate mononuclear complex with hydrogen bond with a neighboring silanol group (C_1).

and for sulphate

$$S-H_2O-S_1-ONa + Me^{2+} + NO_3^- \rightarrow S-H_2O-S_1-O^-Me^{2+}NO_3^- + Na^+ \quad (3)$$

The Me^{2+} are bound on bentonite by equimolar exchange (see Handbook of Clay Science, chapter 12.10)

$$2(S-OH) + Me^{2+} \leftrightarrow 2S-O^-Me^{2+} + 2H^+ \quad (4)$$

or by equimolar exchange

$$S-OH + Me^{2+} \leftrightarrow S-O^-Me^{2+} + H^+ \quad (5)$$

4. Conclusion

Modification of bentonite with phosphate and sulphate increased its cation exchange capacity (CEC) and the adsorption of Zn^{2+} and Cu^{2+} from aqueous solution but decreased the specific surface area. The adsorption of both metal ions was more effective on the phosphate modified bentonite, and larger amounts of Cu^{2+} were adsorbed than of Zn^{2+}.The modification of bentonite with phosphate and sulphate was confirmed by the hypochromic and the hyperchromic shifts in FTIR spectra.

Acknowledgements

The authors appreciate the Department of Agronomy, University of Ibadan, Nigeria and the Department of Chemical Sciences, Redeemer's University, Nigeria, for the use of FAAS and FTIR respectively, for this research.

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