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Inorganic–Organic Modified Bentonite as a Functional Sorbent for Cd2+ and Phenol

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ABSTRACT

Functional sorbent Al-DTPA-CTMAB-bentonite (hydroxyl aluminum-diethylene triamine pentaacetic acid-hexadecyl trimethyl ammonium bromide-bentonite) was synthesized by placing hydroxyl-aluminum pillared agent, alkylammonium cation and organic chelating agents onto bentonite. The simultaneous adsorption of organic pollutant (phenol) and heavy metals (Cd^{2+}) mixed contaminant on Al-DTPA-CTMAB-bentonite was investigated. The Al-DTPA-CTMAB-bentonite showed significant adsorption for the mixed contaminant from aqueouss solution. The Langmuir and Freundlich isotherm equations were applied to the data and values of parameters of these isotherm equations were evaluated.

Keyword: modified bentonite; simultaneous adsorption; adsorption isotherm

INTRODUCTION

The heavy metals and organic pollutants account for a large proportion of the whole pollutants in polluted water. In order to minimize the possible damage to people and the environment arising from the production and applications, several studies have been conducted around the world. A number of researchers have used various organoclays for the removal of inorganic or organic pollutants from aqueous solutions [1-3]. Bentonite clays are easily modified by exchanging their inorganic cations with quaternary ammonium cations. This may result in an increase in the inter-lamellar spacing and exposure of new sorption sites of the clays. More importantly, the substituted organic cations are weakly hydrated. As the inorganic cations are progressively replaced by the organic cations, the surface properties of clay may change considerably from highly hydrophilic to increasingly organophilic (hydrophobic).

The mechanisms controlling the sorption of compounds on organoclays are dependent on the type of organic cations forming organoclays. Herein, a new bentonite-based multifunctional adsorbent material was synthesized by modifying bentonite with hydroxyl-aluminum pillared agent, organic chelating agents (diethylene triamine pentaacetic acid, DTPA) and a long-chain cationic surfactant (hexadecyl trimethyl ammonium bromide, CTMAB). The simultaneous sorption of the organic pollutant (phenol) and heavy metal (Cd^{2+}) onto the modified bentonites from the mixed solutions was investigated. Because of its hybrid properties, the modified bentonite has potential application in treating wastewater containing both heaving metals and toxic organic compounds.

MATERIAL AND METHODS

Materials. Bentonite used was primarily Na-montmorillonite from Henan. Its cation-exchange capacity (CEC) is 102.66 mmol /100 g. DTPA, CTMAB and other reagents used were of analytical grade.

Analytical Methods. Phenol concentration of solutions before and after adsorption was analyzed by ultraviolet spectrophotometry. The Cd^{2+} concentration were measured by using a flame atomic absorption spectrometer.

Preparation of Al-DTPA-CTMAB-bentonite. A pillaring solution of hydroxy-aluminum oligomeric cations was prepared by slowly adding NaOH solution (0.48 mol/L) to $AlCl_3$ solution (0.2 mol/L) under vigorous stirring at 60 °C until the OH^-/Al^{3+} molar ratio reached 2.4. The solution was stored at 60 °C for 24 h. The resulting pillaring solutions were mixed with 200 mL of CTMAB (1.126 g) and DTPA (1.215 g) mixed solutions. This mixed solutions (100 mL) added dropwise to 6% (100ml) by weight Na-Bent and were subjected to mechanical stirring for 2 h in a 60 °C water bath. The treated bentonites were separated from water by vacuum filtration and washed twice by distilled water. The modified bentonites were dried at 70 °C, activated for 2 h at 70 °C, ground in an agate mortar to pass through a 200 mesh sieve and kept in a sealed bottle. The inorganic–organic modified bentonite arre designated Al-DTPA-CTMAB-bentonite.

Procedures for Water Treatment. A combination of 0.600 g of Al-DTPA-CTMAB-bentonite and 40 mL of solution with an appropriate concentration of the heavy metals and organic contaminant was combined in 125 mL erlenmeyer flasks with glass caps. The flasks were shaken for 2 h at 25 °C on a gyratory shaker at 120 rpm. After being centrifuged, the

organic compound in the aqueous phase was determined by ultraviolet spectrophotometry and the heavy metals were determined by flame atomic absorption spectrophotometry. The removal percentages for Al-DTPA-CTMAB-bentonite to treat the mixed contaminant in water were calculated. The losses of the compounds by both photochemical degradation and sorption to the Eerlenmeyer flask in water treatment were found to be negligible. The volatilization losses of organic compounds were analyzed by contrasting to the blank with no shaking and centrifugation. The results showed insignificant losses of heavy metals and phenol by shaking and centrifuging. The experiments were duplicated.

RESULTS AND DISCUSSION

Powder XRD analysis. The XRD patterns of the Na-bentonite and Al-DTPA-CTMAB-bentonite counterparts are shown in Fig. 1. The interlayer spacings (d_{001}) obtained using Bragg's equations. The basal spacing (d_{001}) of Na-bentonite is 1.52 nm which indicates a typical XRD pattern of Na-bentonite with the d_{001} plane at about 7.1º. After the treatment of Na-bentonite with mixed modifier, the interlayer galleries of Al-DTPA-CTMAB-bentonite are expanded 2.65 nm indicating a successful intercalation of the mixed modifier.
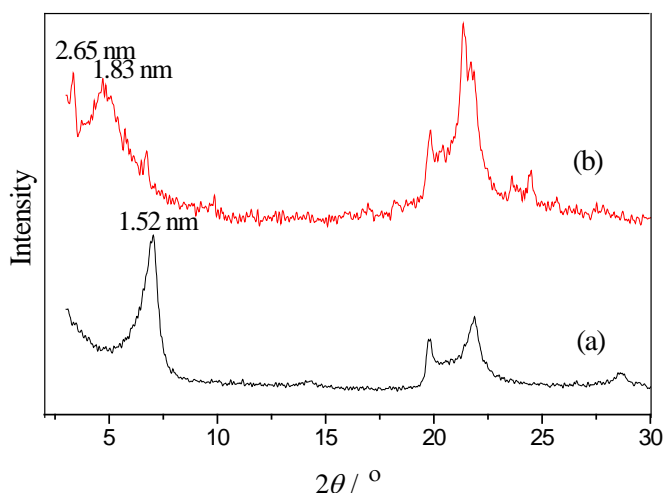

Fig.1. X-ray diffractometer patterns of (a) Na-bentonite and (b) Al-DTPA-CTMAB-bentonite

To observe the simultaneous uptake of the Cd^{2+} and phenol mixed contaminant, the clays were placed in aqueous solutions of the mixed contaminant. Na-bentonites carry a permanent negative charge in their structural framework. The hydration of Na^+ ions in bentonites and the nature of Si-O groups impart a hydrophilic nature to the mineral surfaces. Because of this property, water is preferentially adsorbed by these surfaces, and large organic compounds cannot compete with strongly held water for adsorption sites on the clay surfaces. Thus, Na-clays are ineffective sorbents for small organic molecules. However, it is possible to modify the surface properties of bentonites greatly by neutralizing the anionic framework of layer silicates by using positively charged organic species such as alkylammonim ions. In the modified form (Al-DTPA-CTMAB-bentonite), the bentonites surface may become organophilic and interact strongly with organic

compounds. The mixed contaminants represent a relatively large group of organic chemicals. In a Al-DTPA-CTMAB-bentonite-contaminant system it is possible that adsorption may be enhanced by the hydrophobic interaction between the adsorbed mixed contaminant molecule and Al-DTPA-CTMAB-bentonite. The interlamellar spacing of the Al-DTPA-CTMAB-bentonite was obtained by substracting the thickness of the clay layer from the experimentally determined basal spacing ($d001$). The intercalation of the hydroxyl-aluminum pillared agent, CTMAB and DTPA increased the interlamellar distances. The larger basal spacing ($d001$) of Al-DTPA-CTMAB-bentonite corresponds to the formation of bilayers in which the long-chained surfactant cations are in direct contact with each other, leading to the formation of organic phases consisting mostly of the C16 hydrocarbon groups into which solutes are partitioned. Thus, the degree of sorption of mixed contaminant depends on the amount of the surfactant ions and the organic chelating agents in the bentonite interlayer sites.

The amount of Cd^{2+} and phenol mixed contaminant adsorbed per unit weight of an adsorbent, Q_e, was calculated using the following formula:

$$Q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

Where, Co is the initial concentration of mixed contaminant (mg/L), Ce is the equilibrium concentration of mixed contaminant in solution (mg/L), m is the mass of the bentonite (mg) and V is the volume of solution (L).

The results concerning $Cd2+$ and phenol mixed contaminant adsorption for Al-DTPA-CTMAB-bentonite are presented in Fig. 1. Together with experimental data, the corresponding theoretical adjustment of experimental determinations by the Langmuir equation was also plotted.
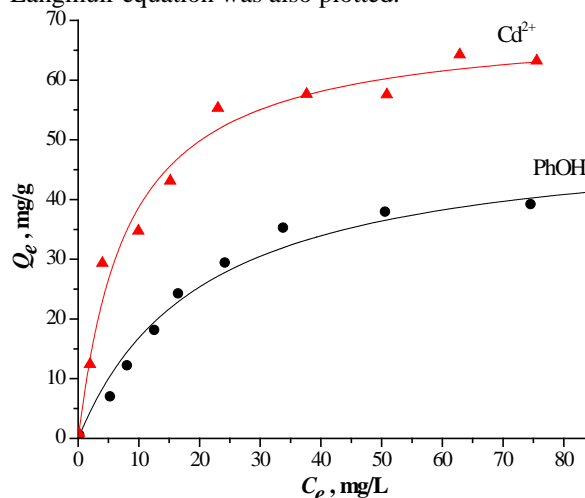

Fig. 2. Adsorption isotherm of Cd^{2+} and phenol mixed contaminant on Al-DTPA-CTMAB-bentonite. ▲(Cd^{2+}), ●(Phenol): Experimental; line: Langmuir isotherm.

It is obvious from Fig. 2 that the adsorption isotherms of Cd^{2+} and phenol mixed contaminant on Al-DTPA-CTMAB-bentonite are all L-type according to the Giles classification [4]. In this type of isotherm, the initial

portion provides information about the availability of the active sites to the adsorbate and the plateau signifies the monolayer formation. The initial curvature indicates that a large amount of mixed contaminant is adsorbed at a lower concentration as more active sites of Al-DTPA-CTMAB-bentonite are available. As the concentration increases, it becomes difficult for a contaminant molecule to find vacant sites, and so monolayer formation occurs. The types of system which give this curve do in fact fulfil these conditions. Thus they have one of the following characteristics: (i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end-on, they suffer little solvent competition.

Solid-liquid equilibrium can be easily described by adsorption isotherms. The Langmuir equation is the mathematical function most commonly used to describe this process.

The Langmuir isotherm can be expressed as

$$Q_e = \frac{Q_{max}\, K C_e}{1 + K C_e} \qquad (2)$$

where Q_e = amount of Cd^{2+} and phenol mixed contaminant adsorbed per unit weight of adsorbent (mg/g), C_e = concentration of Cd^{2+} and phenol mixed contaminant remaining in solution at equilibrium (mg/L), Q_{max} = amount of Cd^{2+} and phenol mixed contaminant adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface (mg/g) and K = a constant related to the energy or net enthalpy. By plotting Q_e versus C_e, a curve is obtained which is linear at low equilibrium concentrations, followed by a curvature (concave to the x-axis), and with an asymptotic tendency to saturation corresponding to a monolayer covering.

The linear form of the Langmuir isotherm equation is represented in equation (3).

$$\frac{C_e}{Q_e} = \frac{1}{K Q_{max}} + \frac{C_e}{Q_{max}} \qquad (3)$$

The values of Q_{max} and K calculated from the slopes and intercepts of the Langmuir plots and correlation coefficients R^2, are reported in Table 1. As it can be seen most of the adsorption isotherms fitted the Langmuir equation with correlation coefficients $R^2 > 0.98$. Many experimental isotherms conforming to a Langmuir isotherm involve monolayer coverage.

Unlike the Langmuir model, Freundlich model can account for the differences in sorption enthalpy between different types of sites [5]. Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with exponential distribution of active centre, and characteristic of heterogeneous surfaces. The amount of adsorbed solute (Q_e) is related to the concentration of solute in the solution (C_e) as equation (4),

$$Q_e = K_f\, C_e^{\frac{1}{n}} \qquad (4)$$

The constants in the Freundlich isotherm can be determined by plotting $\log Q_e$ vs. $\log C_e$:

$$\log Q_e = \log K_f + \frac{1}{n}\, \log C_e \qquad (5)$$

Both K_f and n are empirical constants, being indicative of the extent of sorption and the degree of nonlinearity between solution and concentration, respectively. Herein, the linear line obtained gives a slope of the value of $1/n$, and the y-intercept is $\log K_f$. The intercept is an indicator of sorption capacity and the slope of sorption intensity. A relatively slight slope (hence a high value of n) indicates that sorption is good over the entire range of concentrations studied, while a steep slope (hence small n) means that sorption is good at high concentrations but much less at lower concentrations. A greater value of the intercept K_f indicates a higher capacity for sorption compared with a smaller value of that.

The results concerning Cd^{2+} and phenol mixed contaminant adsorption for Al-DTPA-CTMAB-bentonite are presented in Fig. 3. Together with experimental data, the corresponding theoretical adjustment of experimental determinations by the Freundlich equation was also plotted.
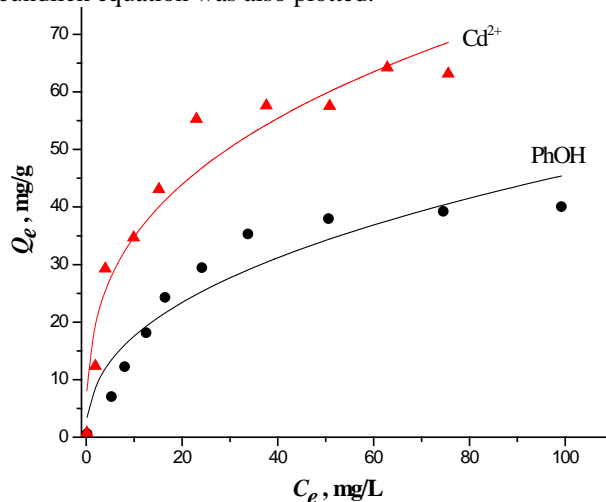

Fig.3. Adsorption isotherm of Cu2+, Cd2+ and phenol mixed contaminant on Al-DTPA-CTMAB-bentonite. ▲ (Cd2+), ● (Phenol): Experimental; line: Freundlich isotherm.

Table 1 Parameters for the calculation using Langmnir and Freundlich models

	Langmuir			Freundlich		
	Q_{max} (mg/g)	K (L/mg)	R^2	$1/n$	K_f (mg^{1-n}L/g)	R^2
Cd^{2+}	63.04	0.010	0.995	0.335	13.407	0.947
phenol	42.71	0.049	0.976	0.414	5.653	0.907

The relative values calculated from the two models are listed in Table 1. For the Langmuir model, the sorption capacity of Al-DTPA-CTMAB-bentonite for Cd^{2+} and phenol is calculated to be 63.04 and 42.71 mg/g under the experimental conditions, respectively. The large value of K_f (Freundlich model) indicates that Al-DTPA-CTMAB-bentonite has a high sorption affinity towards Cd^{2+} and phenol. The deviation of n from unity indicates that a nonlinear sorption takes place on the

heterogeneous surfaces. The nonlinear behavior implies that the sorption energy barrier increases exponentially as the fraction of filled sites on the sorbent increases [6]. The Langmuir isotherm model provides better description of the experimental data than the Freundlich model.

CONCLUSION

We investigated the simultaneous sorption of Cd^{2+} and phenol mixed contaminant on Al-DTPA-CTMAB-bentonite. The bentonite was modified with hydroxyl aluminum, CTMAB and DTPA, rendering it organophilic and heavy metals. The mixed contaminants were strongly simultaneously sorbed on modified bentonite. This could be explained by adsorption interaction between the adsorbed contaminants molecules and hydrophobic alkyl group and organic chelating agents on Al-DTPA-CTMAB-bentonite, which should enhance the adsorptive capacity of the bentonite. There was a good fit between the experimental data for Al-DTPA-CTMAB-bentonite the Langmuir and Freundlich models. At the end of the adsorption studies, it can be said that Al-DTPA-CTMAB-bentonite may be used as an adsorbent for simultaneous adsorption of some heaving metals and toxic organic compounds from waste water solutions. The usability of Al-DTPA-CTMAB-bentonite in industrial waste water requires further investigations.

Acknowledgements

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