Simultaneous Sorption of Cd^{2+} and Phenol to CTMAB-CA Modified Bentonite from Aqueous Solutions

Yin-Xia Sun[*], Xin-Ran Li, Ya-Yuan Zhao, Chun-Yu Li and Zong-Li Ren

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, P. R. China

_____

ABSTRACT

CTMAB-CA-bentonite (hexadecyl trimethyl ammonium bromide-citric acid-bentonite) was synthesized by placing alkylammonium cation and organic chelating agents onto bentonite. The simultaneous adsorption of organic pollutant (phenol) and heavy metals (Cd^{2+}) mixed contaminant on CTMAB-CA-bentonite was investigated. The CTMAB-CA-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.

Key words: modified bentonite, simultaneous adsorption, adsorption isotherm

_____

INTRODUCTION

Bentonite with its unique structural properties, such as high swelling capacity, large specific surface area and high cation exchange capacity, is the most commonly employed adsorbent for water treatment [1]. Bentonite is primarily a Na-montmorillonite, which is a 2:1 layered silicate that swells when contacted by water. The inner layer is composed of an octahedral sheet of the general form $M_{2-3}(OH)_6$ (where M is typically Al^{3+}), which is situated between two SiO_4 tetrahedral sheets. The substitutions of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer result in a net negative surface charge on the clay. The charge imbalance is offset by exchangeable cations such as H^+, Na^+, or Ca^{2+} on layer surfaces. In aqueous systems, water is intercalated into the interlamellar space of the montmorillonite, resulting in expansion of the mineral. Adsorption of nonionic organic solutes from water to bentonite is relatively weak because of the preferential attraction of polar water molecules to the polar mineral surfaces. To enhance the sorption capacity, bentonites are modified in various ways [2].

Herein, a new bentonite-based multifunctional adsorbent material was synthesized by modifying bentonite with organic chelating agents (citric acid, CA) and a long-chain cationic surfactant (hexadecyl trimethyl ammonium bromide, CTMAB). The simultaneous sorption of the organic pollutant (phenol) and heavy metals (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.

MATERIALS AND METHODS

Materials. Bentonite used was primarily Na-montmorillonite from Henan. Its cation-exchange capacity (CEC) is 102.66 mmol /100 g. 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.

155

_____

Preparation of CTMAB-CA-bentonite. A total of 6.0 g of previously dried bentonite was mixed with 200 mL of CTMAB (2.245 g) and CA (1.39 g) mixed solutions. The mixtures were subjected to mechanical stirring for 2 h in a 60-70 °C water bath. The treated bentonites were separated from water by vacuum filtration and washed twice by distilled water. The bentonites were dried at 80-90 °C, activated for 1 h at 105 °C, and mechanically ground to less than 200 mesh. Thus a series of CTMAB-CA-bentonites were made by the exchange of CTMAB and CA for inorganic ions on the bentonite.

Procedures for Water Treatment. A combination of 0.600 g of CTMAB-CA-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 CTMAB-CA-bentonite to treat the mixed contaminant in water were calculated. The losses of the compounds by both photochemical degradation and sorption to the Erlenmeyer 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.

<div align="center">

RESULTS AND DISCUSSION

</div>

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 (CTMAB-CA-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 CTMAB-CA-bentonite-contaminant system it is possible that adsorption may be enhanced by the hydrophobic interaction between the adsorbed mixed contaminant molecule and CTMAB-CA-bentonite. The interlamellar spacing of the CTMAB-CA-bentonite was obtained by substracting the thickness of the clay layer from the experimentally determined basal spacing (d001). The intercalation of the CTMAB and CA increased the interlamellar distances. The larger basal spacing (d001) of CTMAB-CA-bentonite corresponds to the formation of bilayers in which the long-chained surfactant cations are in direct contact with each other [3], 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:

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

Where, C_o is the initial concentration of mixed contaminant (mg/L), C_e 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 Cd^{2+} and phenol mixed contaminant adsorption for CTMAB-CA-bentonite are presented in Fig. 1. Together with experimental data, the corresponding theoretical adjustment of experimental determinations by the Langmuir equation was also plotted.

It is obvious from Fig. 1 that the adsorption isotherms of Cd^{2+} and phenol mixed contaminant on CTMAB-CA-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 CTMAB-CA-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. Examples of (ii) are: (a) systems with highly polar solute and adsorbent, and a nonpolar solvent; and (b) systems with monofunctional ionic substances with very strong intermolecular attraction. It is possible that in the system (b) cases

the adsorbed ions may have become associated into very large clusters and just adsorption takes place. Where the sites are few and widely separated, the surface has large hydrophobic regions [5].
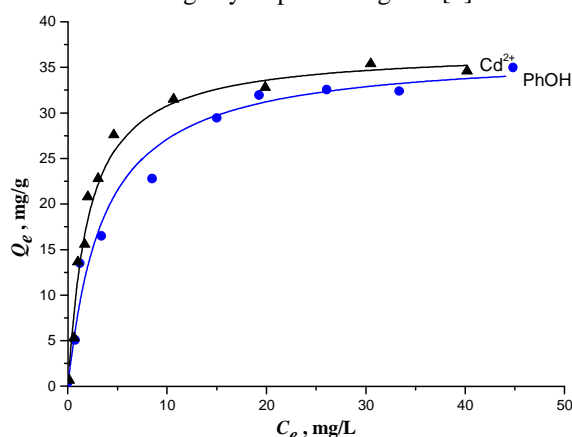

Figure 1. Adsorption isotherm of Cd^{2+} and phenol mixed contaminant on CTMAB-CA-bentonite. ▲(Cd^{2+}), ●(Phenol): Experimental; line: Langmuir isotherm

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

$$Q_e = \frac{Q_{max}KC_e}{1+KC_e} \tag{2}$$

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 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 [6]. 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 (3),

$$Q_e = K_f \, C_e^{\frac{1}{n}} \tag{3}$$

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 logK_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 CTMAB-CA-bentonite are presented in Fig. 2. Together with experimental data, the corresponding theoretical adjustment of experimental determinations by the Freundlich equation was also plotted.
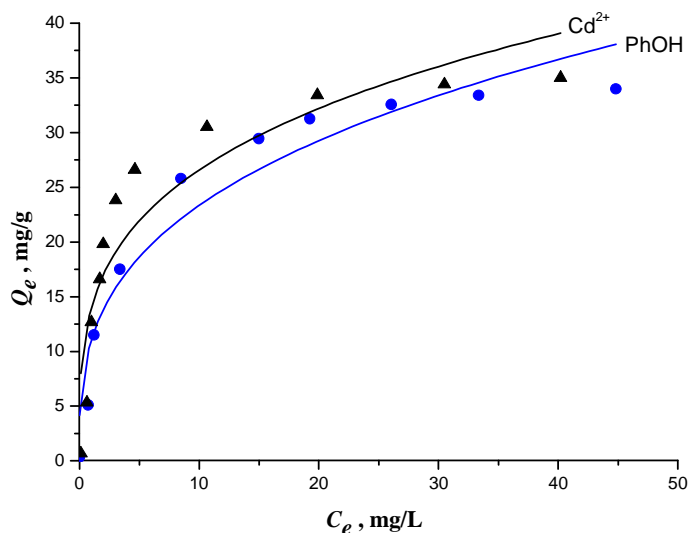
157

_____

Figure 2. Adsorption isotherm of Cd²⁺ and phenol mixed contaminant on CTMAB-CA-bentonite. ▲ (Cd²⁺), ●(phenol): Experimental; line: Freundlich isotherm

The relative values calculated from the two models are listed in Table 1. For the Langmuir model, the sorption capacity of CTMAB-CA-bentonite for Cd^{2+} and phenol is calculated to be 36.96 and 36.77 mg/g under the experimental conditions, respectively. The large value of K_f (Freundlich model) indicates that CTMAB-CA-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 [7]. The Langmuir isotherm model provides better description of the experimental data than the Freundlich model.

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
Cd²⁺	36.96	0.499	0.985	0.277	14.034	0.861
phenol	36.77	0.283	0.996	0.327	10.997	0.940

CONCLUSION

We investigated the simultaneous sorption of Cd^{2+} and phenol mixed contaminant on CTMAB-CA-bentonites. The bentonite was modified with CTMAB and CA, 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 CTMAB-CA-bentonite, which should enhance the adsorptive capacity of the bentonite. There was a good fit between the experimental data for CTMAB-CA-bentonite the Langmuir and Freundlich models. At the end of the adsorption studies, it can be said that CTMAB-CA-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 CTMAB-CA-bentonites in industrial waste water requires further investigations.

REFERENCES

[1] Sharmasarkar S, Jaynes WF, Vance GF, *Water Air and Soil Pollution,* **2000**, 119, 257.
[2] Ding Y, Guo C, Dong JY, Wang Z, *J. Appl. Polym. Sci.,* **2006**, 102, 4314.
[3] Boyd SA, Mortland MM, Chiou CT, *Soil Sci. Soc. Am. J.,* **1988,** 52, 652.
[4] Giles CH, MacEwan TH, Nakhwa SN, Smith D, *J. Chem. Soc.,* **1960**, 3, 3973.
[5] Giles CH, D'Silva AP, Easton IA, *J. Colloid and Interface Soc.,* **1974**, 47, 766.
[6] Atkins PW, *Physical Chemistry*, Oxford: Oxford Univ Press, **1990**, pp 995.
[7] Shahwan T, Erten HN, *J. Radioanal Nucl. Chem.*, **2002**, 253, 115.