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THERMODYNAMIC STUDIES ON THE ADSORPTION OF Cu^{2+}, Ni^{2+} AND Cd^{2+} ON TO AMINE-MODIFIED BENTONITE

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ABSTRACT. Amine-modified bentonite (TEPA-Bn) has been prepared with tetraethylenepentamine (TEPA) as a modifier. The structure of Ca-based bentonite (Ca-Bn), TEPA-Bn and TEPA-Bn after adsorbing Cu^{2+},Ni^{2+},Cd^{2+} had been characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and simultaneous thermal gravimetric/differential thermal gravimetric (TG/DTG) analysis. The TEPA had been intercalated into Ca-Bn interlayer space but had not changed its original crystal structure. The thermal stability of TEPA-Bn was stronger than Ca-Bn while the hydrophilicity of it reduced. The adsorption ability of TEPA-Bn to Cd^{2+}, Ni^{2+}, Cu^{2+} was much better than Ca-Bn, the saturated adsorption capacity to Cd^{2+}, Ni^{2+}, Cu^{2+} were 14.88, 8.88 and 13.05 times as much as Ca-Bn, respectively. The adsorption behavior of Cu^{2+}, Ni^{2+}, Cd^{2+} on to TEPA-Bn were studied by isothermal models, including Freundlich, Langmuir, Dubinin-Radushkevich Florry-Huggins, and Tempkin models. The Freundlich model simulated the experimental data best, the adsorption of Cu^{2+}, Ni^{2+}, Cd^{2+} onto TEPA-Bn was a multilayer, heterogeneous chemical process. The variety of thermodynamic parameters ($\Delta H > 0$, $\Delta S > 0$, $\Delta G < 0$) under different temperature indicated that the adsorption process of Cu^{2+}, Ni^{2+}, Cd^{2+} on TEPA-Bn was endothermic and spontaneous.

KEY WORDS: Amine-modified bentonite, TEPA, Heavy metal ions, Adsorption thermodynamics, Characterization

INTRODUCTION

The pollution problem led by metals is increasingly aggravating, which is a serious threat to human health and ecological environment [1-3]. Unlike other pollutants, heavy metals pollution has non-biodegradable and persistent nature. The treatment methods of heavy metal pollution are divided into physical remediation, chemical remediation and bioremediation [4], the chemical method includes precipitation [5], electrochemical methods [6], adsorption [7], ion exchange [8-9], etc. Adsorption is one of the most effective and low-cost process, therefore, looking for low-cost adsorbent materials has received much attention.

Bentonite is an abundant mineral on earth, it is mainly composed of montmorillonite, consisting of an octahedral sheet sandwiched between two tetrahedral sheets. Bentonite possesses many physical and chemical properties resulting from its structure: pollution-free, and good adsorption capacity for metals [10], but the adsorbability is weak due to its chemical surface structure. Therefore, it becomes necessary to modify nature bentonite to improve its adsorbability.

The organic modification of bentonite is one of the most active fields in the application of mineral materials to environmental management, in particular, amino compounds are used as modifiers. At present, modifiers of bentonite surface include alkyl ammonium salt [11-12], amino silane coupling agent [13-15] and organic amino agent [16-18]. Amino group can form complexation with metal ion, then the amine (amino silane coupling agent and organic amino

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*Corresponding author. E-mail: zhuxiaping@cdut.edu.cn agent) modified bentonite can be a good adsorbent to metals. The tetraethylenepentamine (TEPA) is cheap and it has strong complexing ability to metal ions. In some reports, it was used as material modifier mainly aiming at mesoporous silica [19], activated carbon [20] and magnetic chelating resins [21]. As example, in order to increase the adsorption capacity of CO_2, Ni^{2+} and molybdate anions, Sun[17] synthesized the composite modified bentonite with cetyl trimethyl ammonium bromide and TETA, whose adsorption effect to organic pollutant and heavy metal was better than nature bentonite and single modified bentonite.

In this study, amine-modified bentonite (TEPA-Bn) had been prepared from Ca-based bentonite (Ca-Bn) as raw material. The structure of Ca-Bn, TEPA-Bn and TEPA-Bn after adsorbing Cu^{2+}, Ni^{2+}, Cd^{2+} had been characterized. The adsorption mechanism of TEPA-Bn for Cu^{2+}, Ni^{2+}, Cd^{2+} had been studied. Apart from the low cost of the starting materials, the modification method is simple and environmentally friendly. The modified bentonite has good adsorption capacity to Cu^{2+}, Ni^{2+}, Cd^{2+}. This study provides good remediation materials, and the result of adsorption mechanism concluded from this work gives theoretical guidance for Cu^{2+}, Ni^{2+}, Cd^{2+} and other heavy metal contaminate renovation.

EXPERIMENTAL

Apparatus and reagents

AA7000W atomic absorption spectrometer (Beijing Sanxiong Science and Technology Company, China), Tensor-27 Fourier transform infrared spectrometer (Bruker, Germany), DX-2700 X-ray diffractometer (Dandong Fangyuan Instrument Company, China), and STA409PCLuxx Simultaneous thermal gravimetric analyzer (Netzsch, Germany) were used.

The Ca-Bn used in this work was obtained from Sihui, Guangdong, China (Montmorillonite content is 86.98%). The tetraethylenepentamine (TEPA, $C_8H_{23}N_5$) was provided by Chengdu Kelong Chemical Reagents Co. Ltd. The other reagents including $CdCl_2 \cdot 2.5H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, KNO_3, HCl, and NaOH were of analytical grade. All the glassware was washed with 10% nitric acid and rinsed with distilled water prior to use.

Preparation of TEPA-Bn

TEPA-Bn was prepared with TEPA as modifier. 10.00 g of dry Ca-Bn was dispersed in 400 mL of distilled water, and 0.5 mL of TEPA was added, then the mixed solution was stirred for 5 h at room temperature. The precipitate was filtered, washed with distilled water, dried in vacuum at 313.15 K, then ground into powder.

Adsorption experiment

The solution of metal ions was prepared by dissolving the corresponding amount of metal salt in deionized water. Adsorption experiment was performed at different temperature (298.15, 308.15, 318.15, 328.15 K). The adsorption conditions were chosen according to previous experiment results [22]. The solution containing metal ion and 0.1250 g of TEPA-Bn was shaken on a rotary shaker. The pH of solution was adjusted to 6.0 (Cd^{2+} and Ni^{2+}) and 5.0 (Cu^{2+}) using 0.1 mol/L NaOH and 0.1 mol/L HCl. The adsorption medium is 0.1 mol/L of KNO_3 solution used to simulate the influence of ionic strength on the adsorption. The contact time was 60 min, and then the solution was let sit for 15 h. The suspension was centrifuged at 2500 rpm for 20 min. Finally, the supernatant was kept for Cu^{2+}, Ni^{2+} and Cd^{2+} analysis using an atomic adsorption spectrometer.

Characterization

Fourier transform infrared (FTIR) spectra of Bn, TEPA-Bn, and TEPA-Bn after adsorbing heavy metal ion were measured in the 4000-400 cm^{-1} region using KBr pressed-disk technique. Powder X-ray diffraction (XRD) profile of pressed powder samples was collected with primary beam monochromatized Cu-Kα radiation operated at 40 kV, 30 mA and room temperature, the XRD pattern was recorded from 3 to 70° 2θ with a scanning speed of 0.06° 2θ per second. The thermal analyses of samples was carried out with the help of TG and DTG, the curve was obtained by instrument operating for a temperature range of 303.15-1373.15 K with a heating rate of 10 K/min in nitrogen environment, with a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

Structure characterization

FTIR spectra

The FTIR spectrum of Ca-Bn is shown in Figure 1(A). The characteristic O-H stretching vibration was observed at 3633 to 3453 cm^{-1}, the band at 1642 cm^{-1} belonged to the O–H bending vibration of interlayer water, the characteristic Si-O-Si, Al-Al-OH, Al-Mg-OH, Si-O-Mg and Si-O-Fe bending vibrations were found at 1037, 905, 839, 520, 459 cm^{-1}, respectively.

For the TEPA-Bn, there were some new peaks shown in Figure 1(B). Adsorption peaks around 2922 and 2852 cm^{-1} were asymmetric and symmetric stretching vibration of C–H, respectively. Adsorption peaks around 1475 cm^{-1} was bending vibration of N–H. Adsorption peaks around 2349 cm^{-1} was the peak of CO_2 adsorbed by TEPA. The above four peaks suggested TEPA had successfully inserted into the interlayer of Ca-Bn.

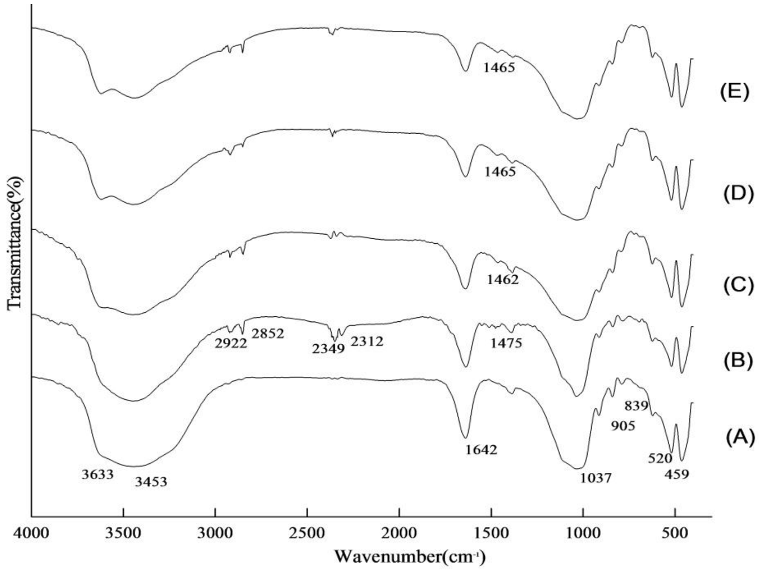

Figure 1. FTIR spectra of Ca-Bn (A), TEPA-Bn (B), TEPA-Bn adsorbing Cu^{2+} (C), TEPA-Bn adsorbing Ni^{2+} (D) andTEPA-Bn adsorbing Cd^{2+} (E).

For the TEPA-Bn after adsorbing Cu^{2+}, Ni^{2+} and Cd^{2+}, there were no new peaks (Figure 1(C), (D) and (E)). However, the adsorption peak intensity of CO_2 decreased, and the bending vibration of N-H moved to the direction of low frequency, it might be that the bond force constant of N-H reduced after chelating Cu^{2+}, Ni^{2+} and Cd^{2+}.

X-Ray diffraction

X-Ray diffraction analysis (XRD) can be used to characterize the interlayer structure of materials. The XRD profile of Ca-Bn, TEPA-Bn, and TEPA-Bn after adsorbing Cu^{2+}, Ni^{2+} and Cd^{2+} is shown in Figure 2. The basal spacing for Ca-based bentonite was observed to be 1.50 nm, equivalent to the aggregate thickness of montmorillonite layer (0.96 nm) and two layers of adsorbed water molecules. The basal spacing of TEPA-Bn decreased to 1.35 nm, owning to the bigger organic molecule (TEPA) replacing the hydrated interlayer Ca^{2+}. In addition, there was no obvious change in the profile, the insertion of TEPA did not change the crystal structure of Ca-Bn.

The type of cation in interlayer space of TEPA-Bn influenced its d_{001} value. The d_{001} values decreased progressively from 1.35 nm to 1.22, 1.25 and 1.28 nm for TEPA-Bn after adsorbing Cu^{2+}, Ni^{2+} and Cd^{2+}, respectively. The intensity of the diffraction peaks decreased, which was associated with the density of holes and the hole wall's structure. The Cu^{2+}, Ni^{2+} and Cd^{2+} might react with $–NH_2$ on the inner surface of TEPA-Bn.

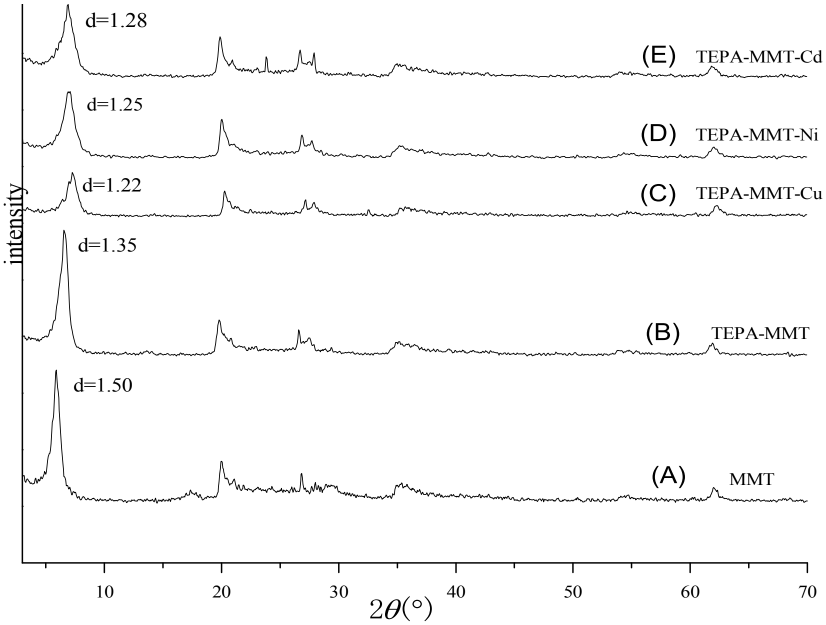

Figure 2. XRD patterns of Ca-Bn (A), TEPA-Bn (B), TEPA-Bn adsorbing Cu^{2+} (C), TEPA-Bn adsorbing Ni^{2+} (D) and TEPA-Bn adsorbing Cd^{2+} (E).

Thermal analysis

The thermal analysis result is reported in Figure 3. The TG and DTG curves of Ca-Bn showed three main steps of weight loss. In the first step (T = 393.75 K), the weight loss (about 8.56 %) corresponds to the surface absorbed water loss. After, the TG and DTG curves showed a slight gradual decrease (about 2.88%) at 440.15 K, which was attributed to the interlayer water loss. The third main loss occurred at 927.35 K, where the TG and DTG curves displayed a step weight loss (about 3.8%) related to the release of structural water.

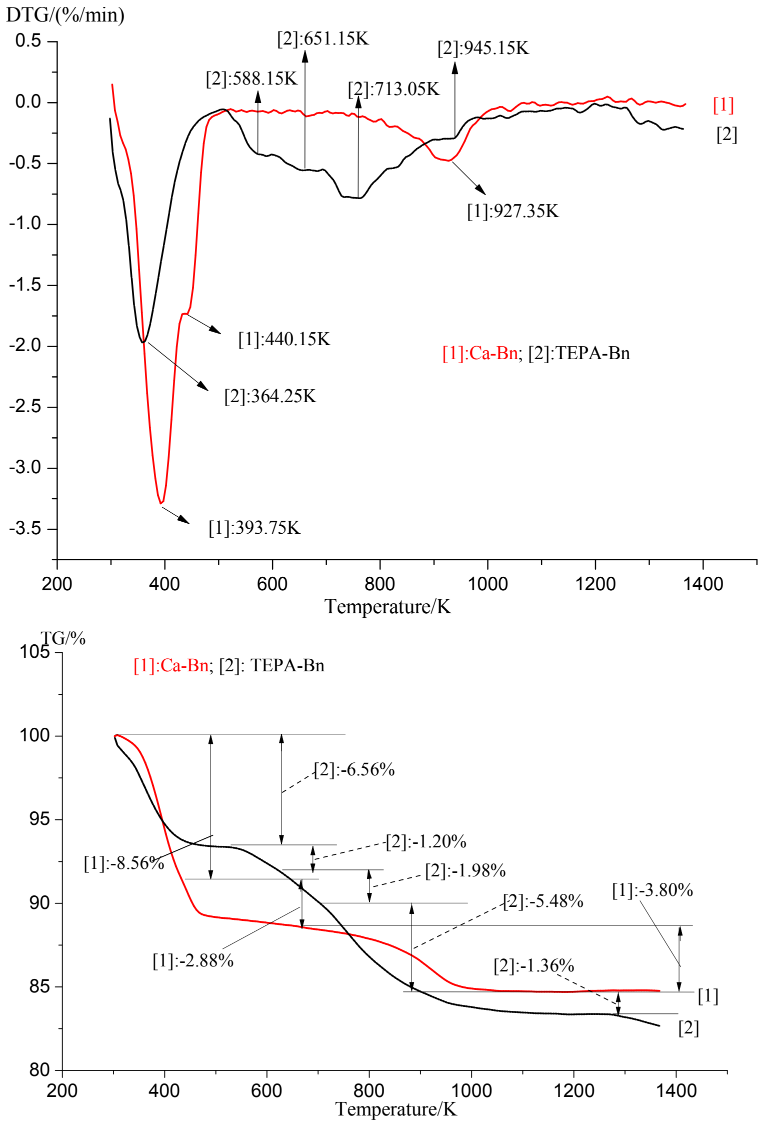

Figure 3. TG-DTG curves of Ca-Bn and TEPA-Bn.

The TG and DTG curves of TEPA-Bn showed five stages of weight loss. The first stage was at 364.25 K related to the weight loss of 6.56%, which was desorption of the adsorbed water on the bentonite surface. The second to the fourth stages were at 588.15 K (1.20% weight loss), 651.15 K (1.98% weight loss) and 713.05 K (5.48% weight loss), respectively, which were corresponded to the decomposition of TEPA molecule. The fifth stage was at 945.15 K (1.36% weight loss) related to the release of structural water of TEPA-Bn.

The desorption temperature of surface absorbed water of TEPA-Bn (364.25 K) was lower than that of the Ca-Bn (393.75 K) because the hydrophilicity of TEPA-Bn is reduced. The step of interlayer water loss of TEPA-Bn disappeared since parts of interlayer water were replaced by modifier.

Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption onto Ca-Bn and TEPA-Bn

The adsorption experiments of Ca-Bn and TEPA-Bn for Cu^{2+}, Ni^{2+} and Cd^{2+} were conducted (Figure 4). The saturated adsorption capacities of Ca-Bn for Cu^{2+}, Ni^{2+} and Cd^{2+} were only 29.9, 34.4 and 19.3 mmol/kg, while the saturated adsorption capacities of TEPA-Bn for Cu^{2+}, Ni^{2+} and Cd^{2+} were found to be 395.7, 352.1 and 272.7 mmol/kg. The adsorption ability of TEPA-Bn was significantly improved, the experiment saturated adsorption capacities to Cd^{2+}, Ni^{2+} and Cu^{2+} were 14.88, 8.88 and 13.05 times as much as Ca-Bn, respectively.

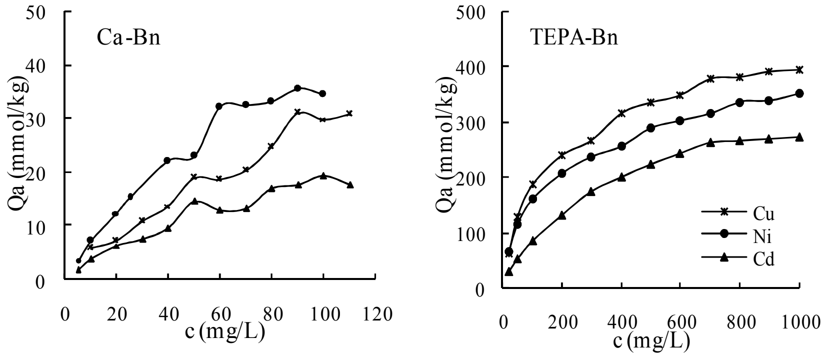

Figure 4. Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption on to Ca-Bn and TEPA-Bn.

The properties of Ca-Bn with good ion exchange capacity, large surface area and electronegativity have generated interest for its use as an adsorbent. Ca-Bn can adsorb heavy metal ions by an ion-exchange mechanism. The bentonite surface is inherently negatively charged due to the isomorphous substitutions within the layers of Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+} for Al^{3+} in the octahedral sheet. The negative charge of bentonite is balanced by the present of exchangeable cations (Ca^{2+}, Na^{+}, etc.) in the lattice structure. The metal ions in the solution can replace the exchangeable cations. In addition, the hydroxyl groups on the bentonite surface can react with the metal ions to form the hydroxyl complexation $[M(OH)_n{}^{n-2}]$. In acidic conditions, the TEPA has positive charge owing to the protonation, then intercalates into the interlayer of Ca-Bn through ion exchange. The amine group of TEPA can complex to metal ions and then, the adsorption capacity of Ca-Bn further increases. The adsorption mechanism of metal ions on TEPA-Bn can be described as follows:

$$\equiv P^- + M^{2+} \xrightarrow{\text{Electrostatic attraction}} \equiv \cdots M$$

$$\equiv P - OH(Ca, Na, K, Mg) + M^{2+} \xrightarrow{\text{Ion exchange}} \equiv \mathrm{P - O}M$$

$$\equiv P - OH + M^{2+} \xrightarrow{\text{Hydroxylcomplexation}} \equiv \mathrm{P - (OH - M)^{+}} + \equiv \mathrm{P - (OH)_2 - M)}$$

$$H_2N\ (CH_2CH_2NH)_3CH_2CH_2NH_2 + H^+ \xrightarrow{\text{Protonation}} R - NH_3^{\ +}$$

$$\equiv P - OH(Ca, Na, K, Mg) + R - NH_3^{\ +} \xrightarrow{\text{Modification}} \equiv P\text{–}O\text{–}R - NH_3^{\ +}$$

$$\equiv P\text{–}O\text{–}R - NH_3^{\ +} + M^{2+} \xrightarrow{\text{Aminocomplexation}} \equiv P\text{–}(O\text{–}R - NH_3^{\ +})_n\text{–}M^{2+}$$

Adsorption thermodynamics of Cu^{2+}, Ni^{2+} and Cd^{2+} on TEPA-Bn

The adsorption isotherms for Cu^{2+}, Ni^{2+} and Cd^{2+} on TEPA-Bn at 298.15, 308.15, 318.15 and 328.15 K are shown in Figures 5-7. The absorption capacity increased with the increase of Cu^{2+}, Ni^{2+} and Cd^{2+} concentration until saturation. The experimental saturated absorption capacities of Cu^{2+}, Ni^{2+} and Cd^{2+} on TEPA-Bn in 298.15, 308.15, 318.15 and 328.15 K were obtained (Cu^{2+}: 395.7, 455.6, 509.5, 583.9 mmol/kg, Ni^{2+}: 352.2, 393.1, 460.2, 504.8 mmol/kg, Cd^{2+}: 272.7, 310.7, 342.0, 369.9 mmol/kg). The saturated absorption capacity increased with the increase of temperature, high temperature was advantageous for Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption on TEPA-Bn.

Freudlich, Langmuir, Dubinin Radushkevich, Florry-Huggins and Temkin models are often used to describe adsorption isotherm [23-24]. The linear forms for various models are expressed as:

Freundlich model: $\lg q_e = \lg k_F + \frac{1}{n} \lg c_e$

Langmuir model: $\frac{c_e}{q_e} = \frac{1}{k_L Q_m} + \frac{c_e}{Q_m}$

Dubinin–Radushkevich (D–R) model: $Inq_e = Inq_D + \gamma\ \varepsilon^2$

Florry-Huggins model: $\lg\frac{\theta}{C_0} = \lg K_{FH} + \lambda \lg(1-\theta)$

Temkin model: $q_e = B_T InA_T + B_T Inc_e$

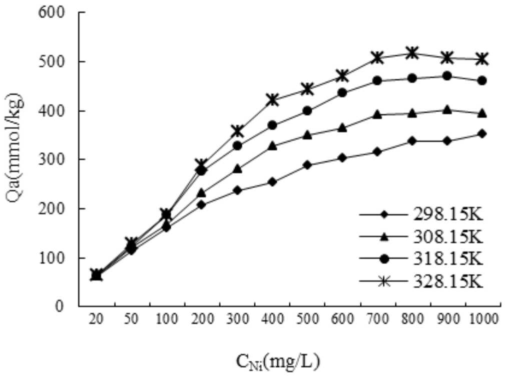

Figure 5. Adsorption isotherm of Cu^{2+} on to TEPA-Bn.

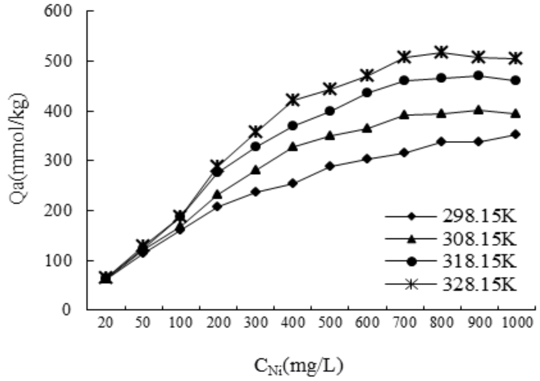

Figure 6. Adsorption isotherm of Ni^{2+} onto TEPA-Bn.

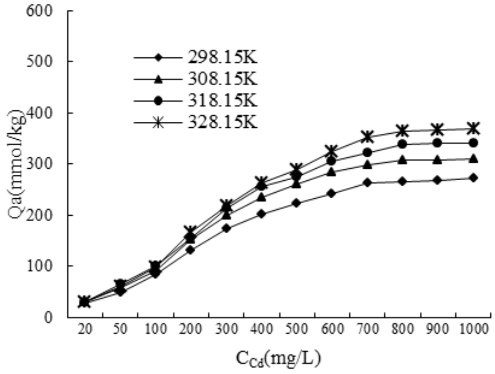

Figure 7. Adsorption isotherm of Cd^{2+} on to TEPA-Bn.

The constant c_0 and c_e are the initial and equilibrium concentration of the heavy metal ions solution (mg/L), q_e is the equilibrium concentration of heavy metal ions on adsorbent (mg/g), Q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant, K_F is Freundlich constant related to adsorption capacity, n is Freundlich constant related to adsorption intensity, γ is the activity coefficient related to mean adsorption energy (mol^2/kJ^2), ε is the Polanyi potential expressed as: $\varepsilon = RT\ln(1+1/c_e)$,the mean adsorption energy, E(kJ/mol) is as follows: $E = (2\gamma)^{-0.5}$, $\theta = 1-c_e/c_0$, is the degree of surface coverage, K_{FH} is equilibrium constant, λ is the amount of adsorbate occupying active sites of the adsorbent, $B_T = RT/b_T$, is Tempkin free energy parameters, A_T is Tempkin adsorption potential (L/mg), b_T is Tempkin adsorption heat (kJ/mol). The adsorption parameters of Cu^{2+}, Ni^{2+} and Cd^{2+} on TEPA-Bn are provided in Table 1. The Freundlich, Langmuir, D-R, Tempkin, and Florry-Huggins models were fitted to the experimental data. It could be concluded from the R^2 value (all >0.99) that Freundlich model simulated in best. The Tempkin equation also well described the experimental data of Ni^{2+} and Cd^{2+}. The Florry-Huggins model was not fit to depict Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption on TEPA-Bn. The K_F value of Freundlich equation indicated that TEPA-Bn had a higher adsorption capacity for Cu^{2+}, Ni^{2+} and Cd^{2+} in higher temperature. All the 1/n values were less than 0.5, which indicated that adsorption reaction was easier to happen.

Table 1. Adsorption model parameters for Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption on TEPA-Bn.

Metals ion	Models	Parameters	298.15 K	308.15 K	318.15 K	328.15 K
Cu^{2+}	Freundlich	K_F	4.351	4.602	4.825	4.963
		1/n	0.2633	0.2836	0.2924	0.3082
		R^2	0.9967	0.9933	0.9923	0.9970
	Langmuir	Qm (mmol/kg)	411.9	485.6	538.9	617.2
		K_L (L/mg)	0.0164	0.0176	0.0169	0.0156
		R^2	0.9876	0.9892	0.9875	0.9838
	Florry-Huggins	Q_{DR} (mmol/g)	0.5153	0.6304	0.7042	0.8103
		E (kJ/mol)	13.39	13.42	13.67	13.78
		R^2	0.9849	0.9813	0.9824	0.9862
	D-R	λ	-1.836	-1.710	-1.647	-1.598
		$K_{HF}*10^4$	2.778	3.023	3.115	3.236
		R^2	0.8091	0.8261	0.8452	0.8579
	Tempkin	A_T	0.5737	0.5095	0.5368	0.4508
		b_T	0.6274	0.5313	0.5023	0.4441
		R^2	0.9585	0.9456	0.9386	0.9484
Ni^{2+}	Freundlich	K_F	3.251	3.274	3.507	3.559
		1/n	0.2705	0.2988	0.3105	0.3287
		R^2	0.9981	0.9936	0.9933	0.9902
	Langmuir	Qm (mmol/kg)	364.8	424.9	499.7	574.4
		K_L (L/mg)	0.0127	0.0145	0.0147	0.0148
		R^2	0.9831	0.9904	0.9902	0.9905
	Florry-Huggins	Q_{DR} (mmol/g)	0.4463	0.5564	0.6662	0.7467
		E (kJ/mol)	12.89	12.70	12.87	13.03
		R^2	0.9723	0.9854	0.9855	0.9679
	D-R	λ	-2.389	-2.296	-2.098	-2.042
		$K_{HF}*10^4$	2.330	2.514	2.764	2.857
		R^2	0.7811	0.7933	0.7981	0.8083
	Tempkin	A_T	0.2836	0.2348	0.2178	0.2061
		b_T	0.6936	0.5760	0.4958	0.4584
		R^2	0.9657	0.9711	0.9795	0.9699
Cd^{2+}	Freundlich	K_F	1.462	1.888	1.982	2.000
		1/n	0.4705	0.4559	0.4633	0.4730
		R^2	0.9906	0.9903	0.9907	0.9936
	Langmuir	Qm (mmol/kg)	313.2	352.9	388.5	427.7
		K_L (L/mg)	0.0077	0.0091	0.0088	0.0080
		R^2	0.9877	0.9777	0.9846	0.9810
	Florry-Huggins	Q_{DR} (mmol/g)	0.6117	0.6843	0.7613	0.8081
		E (kJ/mol)	10.22	10.37	10.62	10.95
		R^2	0.9887	0.9806	0.9841	0.9853
	D-R	λ	-4.515	-3.690	-3.589	-3.266
		$K_{HF}*10^4$	1.304	1.537	1.493	1.727
		R^2	0.9121	0.9221	0.9451	0.9102
	Tempkin	A_T	0.0753	0.0970	0.1076	0.0854
		b_T	0.3301	0.3133	0.3050	0.2742
		R^2	0.9832	0.9754	0.9625	0.9694

Thermodynamics

The variety of thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) can be calculated by saturated adsorption data in different temperature. Generally, the relationship between the distribution coefficient (K_d) and temperature under the assumption that ΔH is constant and can be expressed by:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

The distribution coefficient can be defined as:

$$K_d = \frac{V(c_0 - c_e)}{mc_e}$$

Other thermodynamic parameters such as ΔG and ΔS can be obtained from the calculated ΔH using the following equations: $\Delta G = -RT \ln K_d$

$$\Delta G = \Delta H - T\Delta S$$

Figure 8 shows the relationship of $\ln K_d$ against 1/T, and the calculated values are given in Table 2. The ΔG was negative showing that the metal adsorption process on to TEPA-Bn was a spontaneous process, the value of ΔG increased with the increase of temperature indicating that the spontaneity degree of adsorption increased with the increasing temperature. The ΔH was positive indicated the endothermic behavior of adsorption reaction of Cu^{2+}, Ni^{2+} and Cd^{2+}. High temperature is advantageous for metals adsorption on TEPA-Bn, this was consistent with the earlier results. Furthermore, the ΔS were positive indicated increased randomness at the solid–liquid interface during the fixation of heavy metal ions on the active sites of TEPA-Bn.

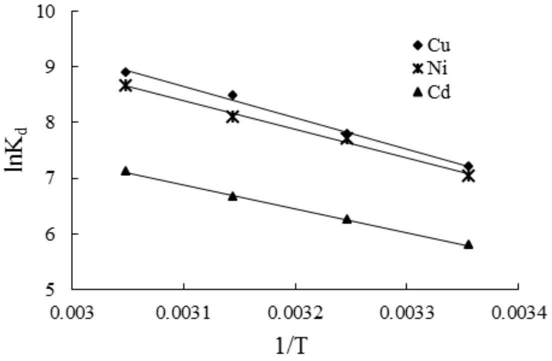

Figure 8. Van't Hoff plot for Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption on TEPA-Bn.

Table 2. Thermodynamics data of Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption on TEPA-Bn.

Ion	T (K)	Vant Hoff equation	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·K)
Cu^{2+}	298.15	y = -5660x +26.204	-17.9	47.1	218
	308.15		-19.9		
	318.15		-22.4		
	328.15		-24.3		
Ni^{2+}	298.15	y = -5132.6x +24.298	-17.5	42.7	202
	308.15		-19.8		
	318.15		-21.4		
	328.15		-23.6		
Cd^{2+}	298.15	y = -4283x + 20.158	-14.3	35.6	168
	308.15		-16.0		
	318.15		-17.6		
	328.15		-19.4		

CONCLUSION

The TEPA had been successfully intercalated into interlayer space of Ca-based bentonite and a TEPA-Bn had been obtained. The stability of the TEPA-Bn was stronger than that of Ca-Bn, and the hydrophilicity of TEPA-Bn reduced. The adsorption ability of TEPA-Bn to Cd^{2+}, Ni^{2+} and Cu^{2+} were much better than Ca-Bn owing the complexation of amine in TEPA. The adsorption experiments data fitted with Freundlich equation in best. The adsorption was spontaneous, endothermic and predominantly chemical reaction.

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