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Special Topic
Deep Sea Processes and Evolution of the South China Sea

Compressible flow past a tabbed cylinder
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Experimental evidence for steady non-Fourier behavior

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COVER   The South China Sea is one of the largest seas in the world, and the most important deep sea basin off the Chinese coast. The major research program "Deep Sea Processes and Evolution of the South China Sea", launched by the National Natural Science Foundation of China in January 2011, is the first large-scale basic research program in oceanography in China. Its overall scientific objectives are to explore the deep sea basin of the South China Sea using several new techniques, to reveal deep sea processes and evolution, and to reconstruct its "life history". Implementation of the program involves three major themes: Deep basin evolution, deep-water sediments, and marine biogeochemistry. The Special Topic in this issue comprises seven papers, all of which review current research status and discuss scientific questions addressed by the research program, from different aspects. Cover is based on an isopach map showing sediment thickness in the South China Sea since the Oligocene (34 Ma). (Source from Figure 4 in HUANG Wei & WANG PinXian's paper published in *Sci China Ser D*: *Earth Sci*, 2006, Vol. 49 (11)).

Volume 57   Number 24
August   2012

CONTENTS

Adsorption of Cd(II) from acidic aqueous solutions by tourmaline as a novel material

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Batch experiments were conducted to investigate the behavior and mechanisms for the adsorption of Cd(II) from aqueous solutions by tourmaline under acidic conditions. The results indicated that the adsorption of Cd(II) significantly depend on the adsorption time, temperature, and the initial concentration of the metal ion. Furthermore, tourmaline had a very good adsorption capacity for Cd(II) in acidic, neutral and alkaline aqueous solutions. This good adsorption capacity is attributed to the observation that tourmaline can automatically adjust the pH values of acidic (except pH 2.0 and 3.0), neutral or alkaline aqueous solutions to 6.4. Specifically, the removal capacity for Cd(II) was higher at strongly acidic pH values (in contrast to industrial wastewater pH values) compared to that obtained for other types of adsorbents. Furthermore, the results obtained in this study showed good fits to the Langmuir and Freundlich adsorption isotherms. However, the Langmuir model fit better than the Freundlich model. The maximum uptake of Cd(II) by tourmaline was 31.77, 33.11 and 40.16 mg/g at pH 4.0 at 15, 25 and 35°C, respectively. Therefore, tourmaline is an effective adsorbent for the removal of Cd(II) from acidic aqueous solutions. In addition, the kinetics for the Cd(II) adsorption by tourmaline closely followed the pseudo-second-order model. The thermodynamic parameters indicated that adsorption was feasible, spontaneous, and endothermic. Furthermore, the pH variation after adsorption, ζ-potential, metal ions desorbed and released, and FT-IR analysis indicated that the physisorption and chemisorption mechanisms of tourmaline for heavy metals. These mechanisms included water that was automatically polarized by tourmaline, the ion exchange process, and electropolar adsorption. Among the mechanisms, the automatic polarization of water caused by tourmaline is a unique adsorption mechanism for tourmaline.

tourmaline, cadmium, acidic aqueous solutions, adsorption, mechanisms

With the increase in industrialization and urbanization, wastewater containing many heavy metals has been produced by electroplating, dyes, and the metallurgical and chemical industries. Furthermore, heavy metal pollution has become increasingly serious. Heavy metals have a negative impact on the environment because they are toxic to humans, animals, and plants, and they are not biodegradable. Therefore, heavy metals are prone to bioaccumulation in food chains, which results in a long-term toxic effect, even at low concentrations. Cadmium is one of the most dangerous heavy metals because of its presence in nature. Most of the cadmium that enters the body accumulates in the liver, kidney, pancreas and bones, which causes diseases such as anemia, hypertension, neuralgia, nephritis and secretion disorder [1]. Developing methods for effectively removing heavy metals from wastewater has become an important issue. Accordingly, a number of methods, including adsorption, chemical precipitation, ion exchange, and membrane technologies have been developed and implemented for removing heavy metal ions from different types of wastewater. However, the costs of removing heavy metal from wastewater using chemical precipitation, ion exchange, and membrane technologies are very high. Adsorption is a very effective and widely used method for removing heavy

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metals from water. In recent years, many natural adsorbents have been investigated for removing heavy metals from water. Different types of minerals, including zeolites [2], quartz [3], apatites [4], goethite [5], calcite [6], and dolomite [7] have been successfully utilized collectively and separately to remove heavy metal ions from aqueous solutions using adsorption techniques. However, when the above sorbents were used to remove heavy metals from acidic solutions, their maximum adsorption capacity was very low. Therefore, the development of a new material for treating acidic wastewater is an area of major concern for environmental science.

Tourmaline is a type of smart, functional ecological material, and it is also a green environmental protection material. Tourmaline is a type of complex borosilicate mineral and has a very complex chemical composition. The general chemical formula of tourmaline is expressed as XY_3Z_6-$(T_6O_{18})(BO_3)_3V_3W$, where $X=Na^+$, K^+, Ca^{2+} or a vacancy; $Y=Li^+$, Fe^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+}, Cr^{3+}, V^{3+}, (Ti^{4+}); $Z=V^{3+}$, Fe^{3+}, Cr^{3+}, Al^{3+}, Mg^{2+}, Fe^{3+}; $T=Si^{4+}$, Al^{3+}, (B^{3+}); $B=B^{3+}$, $V=[O(3)]=OH^-$, O^{2-}; $W=[O(1)]=OH^-$, O^{2-}, F^- and metal ions in parenthesis indicate minor or possible substitutions [8]. The variety of atom and ion species at three sites, X, Y and Z, in tourmaline permits a wide range of compositions and colors. Therefore, the unique properties of tourmaline, such as electrical, magnetic and calorific properties, are determined by its structure. Tourmaline adopts the trigonal space group C_{3v}-R3m. The crystal structure consists of $[Si_6O_{18}]$ complex tripartite rings, $[BO_3]$ triangles, and $X–O_5$ (OH) triple octahedra. Within this structure, the corners of the six silicon-oxygen tetrahedra in the $[Si_6O_{18}]$ rings point to the same direction, which results in automatic polarization due to the presence of a permanent electric field [9]. Furthermore, the magnetic property of tourmaline is related to the presence of Fe^{2+} and Fe^{3+} in the Y site in its structure and is also likely to be related to the presence of Fe in the Z site and Mn in the Y and Z sites. In addition, it has been reported that tourmaline is capable of radiating far infrared energy, permanently releasing negative ions, producing an electrostatic field and releasing rare microelements [10]. However, there are few reports on the use of tourmaline in environmental applications. In recent years, the applied research for tourmaline has focused on applications such as purifying water and air, aquiculture, and health care. Of course, these studies have become a hot research topic [11–13]. In China, there have been a small number of reports on the adsorption of Cu^{2+}, Zn^{2+}, Cr^{6+}, and Pb^{2+} ions onto tourmaline [14–18], but only one report presented a detailed study on the behavior and adsorption mechanism of Pb^{2+} ions from strongly acidic wastewater using tourmaline [19].

In the present study, we investigate the adsorption characteristics of Cd(II) onto tourmaline using kinetic, thermodynamic, and isothermal tests under acidic conditions. This study can provide a novel adsorbent and theoretical basis for controlling heavy metal pollution in acidic wastewater.

1 Materials and methods

1.1 Experimental reagents and materials

All chemicals, such as cadmium nitrate, sodium hydroxide and hydrochloric acid, that were used in this study were of analytical grade and provided by the Tianjin Regent Station (Tianjin, China).

Iron-rich black tourmaline with particle sizes of 800 nm was purchased from the Hongyan Mineral Products Co., Ltd, Tianjin city, China. The tourmaline was produced in the Xinjiang province, China. The compositional analysis was performed using an electron microprobe analyzer (EMPA) equipped with a Shimadzu 1600 electron microprobe and a four channel wavelength dispersive spectrometer (WDS). The chemical composition of the tourmaline with 800 nm sized particles was as follows: SiO_2, 36.75%; Al_2O_3, 33.62%; Fe_2O_3, 12.19%; TiO_2, 0.57%; B_2O_3, 9.78%; FeO, 1.7%; CaO, 0.4%; MgO, 4.76%; K_2O, 0.14%; Na_2O, 0.74%; P_2O_5, 0.19%; H_2O^+, 1.0%; and MnO, 0.21%.

1.2 Solution preparation

Deionized distilled water (DD-H_2O) was used to prepare all solutions and suspensions. Stock solutions of Cd(II) metal at concentrations of 1 g/L were prepared using the metal nitrate. The 1 g/L stock solution was prepared by weighing 2.745 g of cadmium nitrate, then adding 10 mL of 1 mol/L HNO_3 and adjusting the volume to 1 L in a volumetric flask with DD-H_2O. 25, 50, 75, 100, 125, 150, 175 and 200 mL samples of this stock were taken and set the volume to 500 mL in a volumetric flask with DD-H_2O, respectively. Finally, the 50, 100, 150, 200, 250, 300, 350 and 400 mg/L cadmium nitrate solutions were obtained. These stock solutions were stored in a refrigerator at 4°C to protect the solutions from light.

1.3 Adsorption experiments

Batch sorption experiments were conducted in acid-washed 50 mL plastic polypropylene centrifuge tubes, each of which contained 20 mL of the 100 mg/L multi-component solutions and tourmaline. The pH was adjusted using 1 mol/L nitric acid and 1 mol/L sodium hydroxide. To accurately control the temperature, the flasks for the batch adsorption experiments were placed into a thermostated container. After adsorption, the above adsorption systems were centrifuged at 3000 r/min for 15 min, and then, 10 mL aliquots of each supernatant were filtered into acid-washed 15 mL plastic polypropylene centrifuge tubes by vacuum filtration through 0.22 μm cellulose filter paper (Millipore Corp.). Afterwards, the residual concentrations of Cd(II) were determined using a WFX-210 atomic absorption spectrophotometer (Beijing, China). Metal solutions that did not contain sorbent served as controls.

1.4 Fourier transform infrared analysis

Fourier transform infrared (FT-IR) spectra of the tourmaline both before and after Cd(II) binding were recorded using a Bruker Tensor 27 FT-IR spectrometer from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. A background spectrum of KBr was recorded to eliminate contributions from the background, such as atmospheric CO_2 and H_2O, which would contaminate the spectra. The samples were packed into a sample holder, their surfaces were smoothed with a glass slide, and they were immediately transferred to a diffuse reflectance cell, which was flushed with N_2 for 10 min to remove water vapor and CO_2.

1.5 Adsorption kinetic models

In this experiment, kinetic models were used to examine the experimental data. The Lagergren pseudo-first-order (eq. (1)) and pseudo-second-order models (eq. (2)) were used.

$$1/Q_t = K_1/(Q_m t) + 1/Q_m, \tag{1}$$

$$t/Q_t = 1/(K_2 Q_m^2) + t/Q_m, \tag{2}$$

where Q_t and Q_m (mg/g) are the metal concentrations at time t and the maximum mass, respectively. The pseudo-first-order constant (K_1), pseudo-second-order constant (K_2) and linear correlation coefficient (R^2) were listed in Table 1.

1.6 Adsorption isotherm models

To quantitatively explain the adsorption capacity of tourmaline for Cd(II), the equilibrium data were analyzed using the Langmuir (eq. (3)) and Freundlich (eq. (4)) models.

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}, \tag{3}$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e, \tag{4}$$

where Q_m and Q_e (mg/g) are the maximum mass and equilibrium mass of metal adsorption, respectively. C_e refers to the equilibrium metal concentrations in the tourmaline and aqueous phases. K_L (L/mg) is the Langmuir isotherm parameter, and K_F is the Freundlich isotherm parameter. n is a heterogeneity parameter of the adsorbent surface.

2 Results and methods

2.1 Adsorption kinetics

To determine the adsorption kinetics behavior for Cd(II) by

tourmaline under acidic conditions, the adsorption studies were conducted at a temperature of 25°C at pH 4.0 with an added adsorbent mass of 6 g/L and a Cd(II) solution concentration of 100 mg/L. The adsorption time was 5, 15, 30 min, 1, 3, 6, 12, 24 and 48 h, and its effects on the adsorption of Cd(II) by tourmaline are illustrated in Figure 1. The complete removal of Cd(II) ions increased rapidly during the first 360 min; thereafter, the adsorption percentage increased slowly and reached equilibrium at 1440 min. This behavior was due to the decrease of adsorption sites on the tourmaline, which gradually interacted with the metal ions. In this study, 59.10% of Cd(II) was adsorbed onto tourmaline under acidic conditions of pH 4.0 with an adsorption time of 2880 min. This result was attributed to the large number of vacant active sites on the tourmaline surface at early time points; Cd(II) can be adsorbed by tourmaline rapidly through electrostatic adsorption. When the adsorption time was prolonged, the adsorption sites on the tourmaline surface were decreased, which resulted in the reduced percentage of adsorption.

To evaluate the mechanisms of adsorption and the potential rate controlling step, kinetic models were used to test experimental data. The Lagergren pseudo-first-order (eq. (1)) and pseudo-second-order models (eq. (2)) were used. The pseudo-first-order constant (K_1), pseudo-second-order constant (K_2), and linear correlation coefficient (R^2) are listed in Table 1. The correlation coefficients for the first-order model were low, and the calculated Q_e values obtained from the first-order kinetic model are not reasonable values. However, the correlation coefficient for the second-order kinetic model are greater than 0.994, and the calculated Q_e values obtained from the second-order kinetic model nearly agree with the experimental Q_e values for the Cd(II) adsorption. Therefore, the pseudo-second-order model appears to be the best for describing the Cd(II) adsorption kinetics. Normally, the Lagergren pseudo-first-order model (eq. (1)) is only suitable for describing the initial stage of adsorption
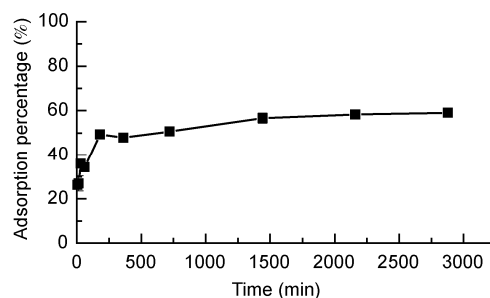
Figure 1 Kinetic study of adsorption of Cd(II) ions by tourmaline: pH 4.0; adsorbent, 0.12 g of tourmaline/20 mL; Cd^{2+}, 100 mg/L; 25°C.

Table 1 Pseudo-first-order and Pseudo-second-order adsorption rate constants of Cd(II) on tourmaline, calculated and experimental Q_e

Models	Model equations	K_1 or K_2	$Q_{m, cal}$ (mg/g)	$Q_{m, exp}$ (mg/g)	R^2
Pseudo-first-order	$1/Q_t = 0.6275/t + 0.1218$	4.70 (min^{-1})	7.94	13.05	0.6581
Pseudo-second-order	$t/Q_t = 0.0989t + 4.2162$	0.0029 (g mg^{-1} min^{-1})	10.2		0.994

kinetics; consequently, this model cannot accurately describe accurately the entire adsorption process [20]. However, the pseudo-second-order model can describe the entire adsorption process, including external diffusion, surface adsorption and internal diffusion [21]; therefore, this model can accurately reflect the adsorption mechanisms of Cd(II) onto tourmaline. When the pseudo-second-order model is the best fit for the experimental data, the sorption mechanism involves chemisorption [22].

2.2   pH effects

The effect of pH on the adsorption of Cd(II) ions using tourmaline was investigated. The experiments were performed at different initial pH values at 25°C. To avoid precipitation of the metal ions, all experimental pH were determined based on heavy metal solubility product constant, K_{sp}. The maximum precipitation of Cd(II) occurred at pH 8.4 with an initial concentration of 100 mg/L. Therefore, to prevent any precipitation occurring before the sorption experiments, the pH was controlled between 2.0–8.0. The initial concentration of heavy metal and the adsorbent dose were fixed at 100 mg/L and 4 g/L, respectively. The equilibrium time was 24 h. The equilibrium concentration of each metal ion was determined at the different pH values. The results are graphically represented in Figure 2. It is evident from Figure 2(a) that when the initial pH of the suspension was less than 4.0, the removal capacity was 12.0% for Cd(II) (Figure 2(a)); when the initial pH ranged from 4.0 to 6.0, the adsorption percentage for Cd(II) ranged from 31% to 49%; when the initial pH was neutral or alkaline, the

adsorption percentage ranged from 55% to 59%. Therefore, tourmaline has a good adsorption capacity for high concentrations of Cd(II) under acidic, neutral and alkaline conditions. Specifically, the removal capacity for Cd(II) was higher under strongly acidic pH values (in contrast to industrial wastewater pH values) compared to that obtained for other types of adsorbents that have been used in the past, such as zeolites [2,23], quartz [3], calcite [24], dolomite [25], kaolinite [26], and different types of clays [27].

The pH influenced the adsorption process for metal ions. This observation was attributed to the surface charge of tourmaline, which could be modified by changing the pH of the solution. It can be observed from Figure 2(b) that the ζ-potential of tourmaline in water became more negative with increasing pH. In addition, at different pH values, the extent of the variation of the ζ-potential of the heavy metal adsorbed by tourmaline was different. At lower pH values (<4.0), the active sites of the adsorbent are less available for the metal ions because of the protonation of the active sites under higher H^+ concentrations, which results in less Cd(II) being adsorbed by tourmaline. At moderate pH values (e.g., 4.0–6.0), linked H^+ is released from the active sites and the adsorbed amounts of the metal ions are increased. Furthermore, the ζ-potential of the Cd(II) adsorbed by tourmaline became less negative than that of tourmaline in water (Figure 2(b)), which indicates that the tourmaline surfaces were covered with heavy metal ions. In this pH range, it was proposed that the ion exchange and electropolar adsorption processes are the major mechanisms for removing single metal ions from the solution [28]. At pH values greater than 6.0, the ζ-potentials of the tourmaline adsorbed Cd(II) became slightly negative. It was suggested that both ion exchange and aqueous metal hydroxide formation (not precipitation) may become significant mechanisms for the metal removal process [28].

2.3   Initial concentration and temperature effects

To obtain the adsorption isotherms and investigate the adsorption thermodynamics, the effect of the initial concentration on the metal ion adsorption capacities of tourmaline was determined by varying the initial concentration of the metal ion solutions. The operating conditions were as follows: the sorbent dose was fixed at 2 g/L and the initial concentrations of the Cd(II) solutions ranged from 50 to 400 mg/L at an initial pH 4.0. The experiments were performed at 15, 25, and 35°C. The results are shown in Figure 3.

From Figure 3, it is seen that the amount of Cd(II) adsorbed per gram of tourmaline gradually increased with increasing initial concentration of the metal ion solutions. When the initial solution was at a low concentration, the ratio between the number of ions and the number of adsorptive sites available is small; consequently, the adsorption depends on the initial concentration. Therefore, as the concentration of ions increases, the adsorption also increases.

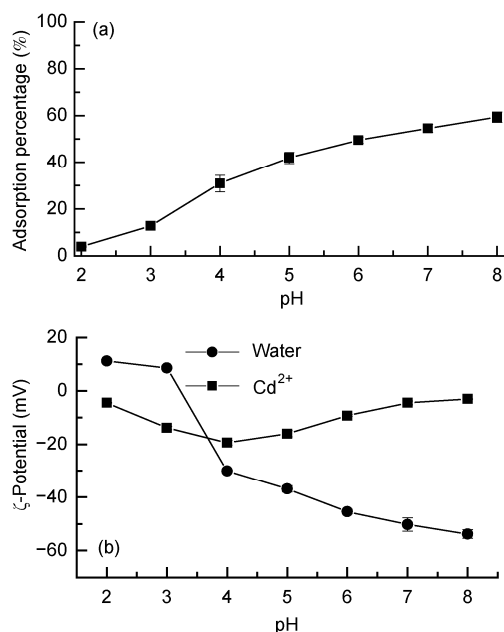**Figure 2**   (a) pH effects on adsorption of Cd(II) ion by tourmaline: adsorbent, 0.4 g of tourmaline/100 mL; Cd²⁺, 100 mg/L; *T*, 25°C. (b) Variation of ζ-potential of tourmaline in water and solutions containing 100 mg/L Cd(II) ion at 25°C, respectively.
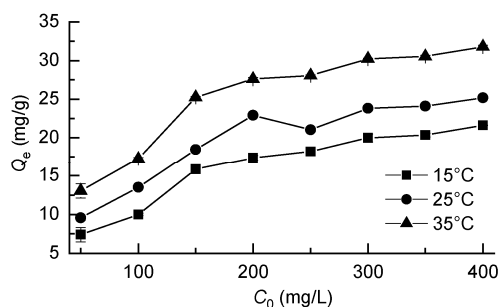
Figure 3 Initial concentration and temperature effects on adsorption of Cd(II) ion by tourmaline: adsorbent, 0.2 g of tourmaline/100 mL; pH 4.0.

At high ion concentrations, each unit mass of adsorbent is subjected to a larger number of ions, which gradually fill the sites. Therefore, the amount of Cd(II) adsorbed per gram of tourmaline was higher.

It was observed that the adsorption of Cd(II) increased with increasing temperature. Because adsorption is an endothermic process, it would be expected that an increase in temperature would help to activate the adsorption sites of the adsorbent. In addition, an increase in temperature involved an increased mobility of the metal ions, which resulted in the metal ions having sufficient energy for interacting with the adsorption sites of the adsorbent. Therefore, the adsorptive capacity of the adsorbent was enhanced [29].

2.4 Adsorption isotherms

The two most commonly employed models are the Langmuir and Freundlich isotherms. The Langmuir isotherms of Cd(II) at different temperatures are shown in Figure 4, and the corresponding parameters are presented in Table 2. The results indicated that that the adsorption of Cd(II) on tourmaline followed the Langmuir isotherm model very well based on the values of R^2 (0.97–0.99) (Table 2); they also fit the Freundlich isotherm model with the values of R^2 (0.93–0.96), but better than the Langmuir isotherm model in general (Table 2).

The Freundlich isotherm parameter was listed in Table 2. The magnitude of $1/n$ quantifies the favorability of adsorption and the degree of heterogeneity of the tourmaline surface. The values of $1/n$ in this study were observed to be less than 1, which indicates that the adsorption for Cd(II) was favorable.

As shown in Table 2, at 15, 25, and 35°C, the values of the Langmuir constant, K_L, were 0.0065, 0.0098 and 0.131

L/mg for Cd(II). The maximum adsorption capacity (Q_m) were 31.77, 33.11 and 40.16 mg/g for Cd(II) (Table 2) at an initial solution pH 4.0, respectively, while the temperature varied from 15 to 35°C. A comparison of the Q_m determined in the present study with that obtained for other types of adsorbents used in the past, such as zeolites [2,23], quartz [3], calcite [24], dolomite [25], kaolinite [26], and different types of clays [27] was made. The removal capacities for Cd(II) using tourmaline in the present study were compared to those of other natural adsorbents, as shown in Table 3. It was observed that tourmaline exhibits very high removal capacities for the Cd(II) ion under acidic conditions, which suggests that the adsorption capacity of tourmaline was very high. Therefore, tourmaline is an effective adsorbent for the removal of heavy metals from wastewater.

2.5 Thermodynamics of adsorption

The thermodynamic parameters, such as the Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$), for the adsorption of Cd(II) were evaluated using the following equations:

$$-\Delta G° = 2.303RT \log K, \qquad (5)$$

$$\Delta G° = \Delta H° - T\Delta S°, \qquad (6)$$

where $\Delta G°$ is the change in free energy (kJ/mol), $\Delta H°$ is the change in enthalpy (kJ/mol), $\Delta S°$ is the change in entropy (kJ/mol), T is the absolute temperature in Kelvin, R is the gas constant (8.314×10^{-3}) and K is the thermodynamic equilibrium constant. The values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the plot between $\ln K$ versus $1/T$.

The thermodynamic parameters for the adsorption of Cd(II) are presented in Table 4. The positive values of $\Delta H°$ indicated the endothermic nature of the adsorption of Cd(II) on tourmaline. Therefore, the metal ion uptake increased with increasing temperature. In addition, enthalpy change data are typically used for distinguishing between physical adsorption and chemical adsorption. When the enthalpy change is greater than 60 kJ/mol, the adsorption is typically associated with chemical adsorption, whereas when the heat of adsorption is less than 40 kJ/mol, the adsorption should be associated with physical adsorption [30]. These experimental enthalpy changes are less than 40 kJ/mol, which implies that physisorption dominates the adsorption of metal ions onto tourmaline. The negative $\Delta G°$ values were predicated to be −15.77, −16.78 and −17.37 kJ/mol for the

Table 2 Different model parameters for adsorption of Cd(II) by tourmaline at different temperatures

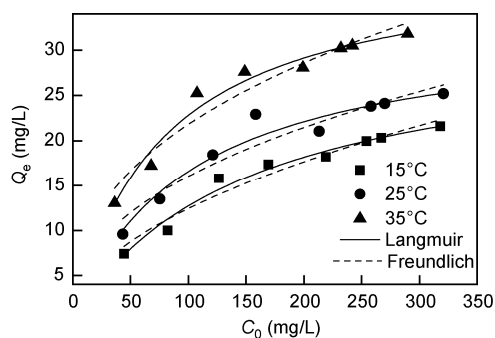| Temperature (°C)	Freundlich model			Langmuir model		
	K_F	$1/n$	R^2	Q_m (mg/g)	K_L (L/mg)	R^2
15	0.9753	0.5568	0.9634	31.77	0.0065	0.9750
25	1.2773	0.4749	0.9359	33.11	0.0098	0.9786
35	1.5900	0.4326	0.9491	40.16	0.0131	0.9909

Figure 4 Adsorption isotherms of Cd(II) ion by tourmaline at different temperatures.

Table 3 Comparison of Cd(II) removal by natural adsorbents (unit of Langmuir capacity is mg/g)

Adsorbents	Cd(II) ion	pH	References
Zeolite	0.1	No listed	[2]
Quartz	9.41	6.8	[3]
Clinoptilolite	4.22	No listed	[23]
Calcite	18.52	5.0–6.0	[24]
Dolomite	1.02		[25]
Kaolinite	9.9	6.0–8.0	[26]
Red mud	10.60	6.0	[27]
Tourmaline	40.16	4.0	This study

Table 4 Thermodynamic parameters of Cd^{2+} ion adsorption on tourmaline

Metal ions	T (°C)	ΔG^{o} (kJ/mol)	ΔH^{o} (kJ/mol)	ΔS^{o} (J/mol)
	15	−15.77	24.69	140.5
Cd^{2+}	25	−16.78	24.69	139.2
	35	−17.37	24.69	136.6

adsorption of Cd(II) ion, which indicated that the adsorption of metal ions on tourmaline is a feasible and spontaneous process and that energy input from outside of the system is required. Generally, the Gibbs free energy change (0~−20 kJ/mol) for physisorption processes are lower than that for chemisorption (−80~−100 kJ/mol) processes [31]. In the present study, the negative ΔG° values were between 0 to −20 kJ/mol for the adsorption of Cd(II), which indicated that the adsorption of the metal ion onto tourmaline is a physisorption process. The positive values of ΔS° indicated that the degrees of freedom increase at the solid-solution interface during the adsorption of the metal ion by tourmaline. Simultaneously, in this study, ΔS° was greater than zero. This observation was attributed to the fact that the ΔS° value depends on the two actions of the dissociation of hydrated ions and the adsorption of free state ions in the adsorption process. The dissociation of hydrated ions can induce increases in ΔS°, whereas the adsorption of free-state ions can result in decreases in ΔS°. When a hydrated cadmium (II) ion dissociates, it can dissociate more than one water molecule. Specifically, the number of dissociating water molecules was higher than that of adsorbing Cd(II) ions, which resulted in the positive value of ΔS° [32].

2.6 Adsorption mechanisms

(1) Water polarized by tourmaline.   The pH value during the Cd(II) adsorption process was measured, and the results are presented in Figure 5. It was observed that when at an initial metal solution pH 4.0, the pH quickly increased to 5.25 within 5 min; thereafter, the pH increased to 6.0 within 30 min and reached equilibrium at 180 min. Furthermore, at different initial pH values of the solution, the pH values were measured when the Cd(II) adsorption by tourmaline reached equilibrium. The results are presented in Figure 6. The overall trend indicated an increase in pH, with the final pH values being higher than the initial levels ranging from pH 2.0 to 6.0, whereas a decrease in pH was observed, with the final pH values being lower than the initial pH values of 7.0 and 8.0 (Figure 6). Additionally, the final pH tended to be approximately 6.0 when the initial pH ranged from 4.0 to 8.0. Therefore, our study confirms that tourmaline can automatically adjust the solution pH because of its spontaneous and permanent poles [9]. When tourmaline was crushed to smaller particle sizes, a large number of mineral cations (such as magnesium, calcium, and sodium) were exposed on the crystal surface along different directions of the crystal fracture. When the tourmaline was then added to aqueous solutions, water was automatically polarized by the tourmaline powder, and hydrogen ions from the polar water molecules pulled these cations from the crystal surface into the water. Finally, the loss of cations on the tourmaline surface increased their negative charge, which resulted in more Cd(II) being adsorbed by tourmaline. This process also caused the pH value to adjust in the solutions that contained added tourmaline [19]. This adsorption mechanism of
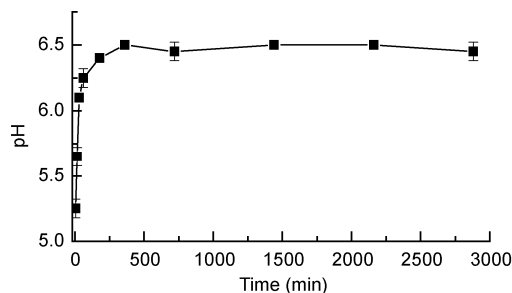

Figure 5 pH change of solution during the adsorption of Cd(II) ion by tourmaline.
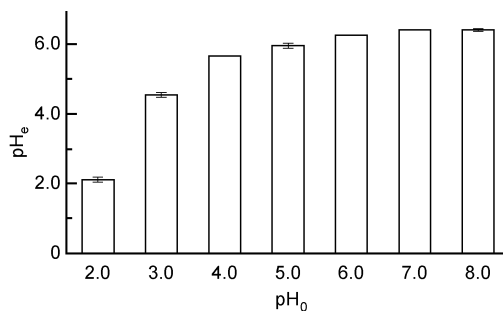

Figure 6 pH change of solution during adsorption equilibrium of Cd(II) ion by tourmaline at different initial pHs of solution.

tourmaline is unique; furthermore, it is obviously different from that of other minerals.

(2) ζ-Potential measurements.　To fully understand the other mechanisms that occur during heavy metal adsorption onto tourmaline, the ζ-potentials of the adsorption system were also measured during the study of the isotherm study system. The measured ζ-potentials of tourmaline were −32 mV at 15°C, −30 mV at 25°C, and 2–9 mV at 3 °C. In the presence of Cd(II), the ζ-potential values increased from −24 to −13 mV at 15°C, from −23 to −8 mV at 25°C, and from −19 to −4 mV at 35°C, at all concentrations (Figure 7). Compared with the ζ-potential of tourmaline, changes in ζ-potential can be explained by mechanisms occurring between the tourmaline particle and a Cd(II) ion. Furthermore, the trend coincides with the adsorption mass of Cd(II) at different temperatures, which is noted in the adsorption isotherms. Therefore, it can be said that the adsorption proceeds through the electrostatic adsorption mechanisms.

(3) Metal ions desorbed and release.　To determine whether other mechanisms occurred between tourmaline and the heavy metals, the desorbed ion concentrations (such as K^+, Ca^{2+} and Mg^{2+}) from the tourmaline were synchronously measured using ion chromatography during the adsorption process in the isotherm studies on the Cd(II) ion. Figure 8 indicates that the total masses of the released Ca^{2+}, Mg^{2+}, and K^+ were low with respect to the masses of the Cd(II) ions adsorbed by tourmaline. It was observed in Figure 8 that there were good linear relationships between the release of the total cations ($R^2 = 0.6010$, 0.9738, and 0.8918) into solutions and that the Cd(II) ion adsorbed onto tourm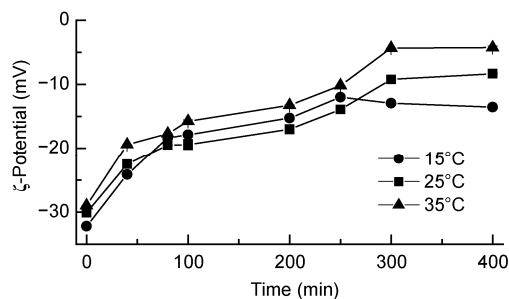aline over heavy metal ion concentrations ranging from 50 to 400 mg/L. These positive correlations confirmed that cation exchange was involved during the removal of heavy metals from acidic solutions. However, the ion exchange mechanism for heavy metals adsorbed onto tourmaline has never been demonstrated.

(4) FT-IR analysis.　FT-IR spectroscopy can not only effectively characterize the surface functional groups in tourmaline but also explore the changes in these functional groups in the presence of metal ions. The tourmalines and their adsorption for Cd(II) at different pH values at 25°C were analyzed using FT-IR spectrophotometry. The comparison of the spectra presented in Figure 9 indicated significant differences in the intensities of the bands between 1161 and 682 cm^{-1} for tourmaline and its adsorption for Cd(II) ions at pH 2.0, 3.0 and 4.0. Noticeable increases in the broad bands (i.e., 1650, 1161−682 cm^{-1}), especially at 1161, 985, 967 and 682 cm^{-1} were observed after the tourmaline reacted with the aqueous Cd(II) ion compared to the spectra of tourmaline. The signals at 1650 cm^{-1} resulted from the presence of tourmaline-water vibrations. The increases in the broad bands at 1161−682 cm^{-1} were due to the internal Si−O−Si and Al−O−Si bridge vibrations in the tetrahedral or alumino- and silico-oxygen bridges and pseudolattice vibrations [19,33,34]. The change in the intensity of the bands in the above ranges can also be an indication of the presence of heavy metals in the tourmaline structure. Therefore, the incorporation of heavy metals into the tourmaline structure changed the degree of ring deformation, which resulted in changes in the signal intensities. This change was attributed to heavy metal bonding through electropolar adsorption and ion exchange due to the mass of cations released from the particle surface. This result supported the notion that physisorption and chemisorption were involved in the absorption of heavy metals by tourmaline.

3　Conclusions

This study demonstrated the effectiveness of tourmaline for removing metal ions from acidic, neutral and alkaline aqueous solutions. Specifically, the removal capacity for

Figure 7　ζ-Potential change during the process of Cd(II) ion adsorption at different initial concentrations at different temperatures.
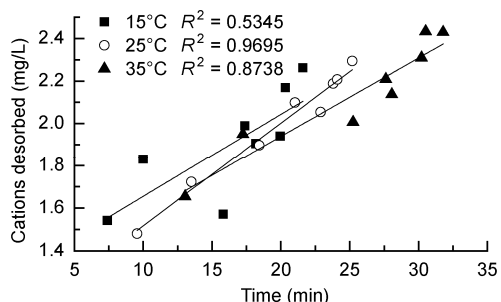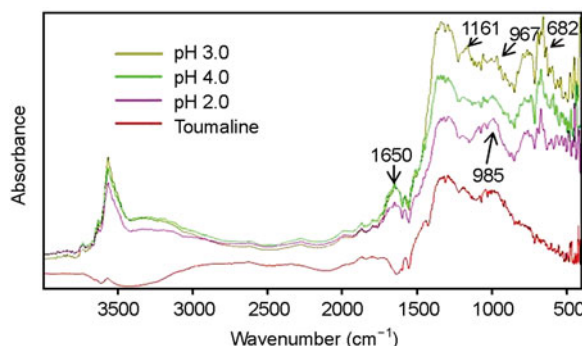
Figure 8　Total amount of K^+, Mg^{2+} and Ca^{2+} cations released into solution versus amount of heavy metal ions adsorbed at different temperature.

Figure 9　FT-IR spectra of tourmaline before and after interaction with Cd(II) ion at initial aqueous pH 2.0, 3.0 and 4.0 at 25°C, respectively.

Cd(II) was higher at strongly acidic pH values (in contrast to industrial wastewater pH values) compared to that obtained for other types of adsorbents. The maximum mass of Cd(II) adsorbed, evaluated using a Langmuir model, was 31.77, 33.11 and 40.16 mg/g on tourmaline at pH 4.0 at 15, 25 and 35°C, respectively. Therefore, the adsorption mass increased with increasing temperature. The kinetics data presented a good correlation with the pseudo-second-order model, which indicated that chemisorption was involved during the absorption of heavy metal by tourmaline. Meanwhile, the thermodynamic parameters and $\Delta G°$ ranged from 0 to −20 kJ/mol, which indicated that the adsorption of heavy metals was feasible, spontaneous, and endothermic, and that physisorption was involved during the adsorption process. Therefore, mechanisms of tourmaline for Cd(II) were involved in physisorption and chemisorption. Furthermore, the FT-IR analysis confirmed that the physisorption and chemisorption mechanisms included water that was automatically polarized by tourmaline, the ion exchange process, and electropolar adsorption. Among these mechanisms, the automatic polarization of water by tourmaline is a unique adsorption mechanism for tourmaline. In general, tourmaline was an effective adsorbent for the removal of heavy metals from wastewater. Tourmaline should be developed as a new material for the removal of pollutants from the environment

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