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Adsorption characteristics of copper, lead, zinc and cadmium ions by tourmaline

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Abstract: The adsorption characteristics of heavy metals: Cu(II), Pb(II), Zn(II) and Cd(II) ions on tourmaline were studied. Adsorption equilibrium was established. The adsorption isotherms of all the four metal ions followed well Langmuir equation. Tourmaline was found to remove heavy metal ions efficiently from aqueous solution with selectivity in the order of Pb(II)>Cu(II)>Cd(II)>Zn(II). The adsorption of metal ions by tourmaline increased with the initial concentration of metal ions increasing in the medium. Tourmaline could also increase pH value of metal solution. The maximum heavy metal ions adsorbed by tourmaline was found to be 78.86, 154.08, 67.25, and 66.67 mg/g for Cu(II), Pb(II), Zn(II) and Cd(II), respectively. The temperature (25—55℃) had a small effect on the adsorption capacity of tourmaline. Competitive adsorption of Cu(II), Pb(II), Zn(II) and Cd(II) ions was also studied. The adsorption capacity of tourmaline for single metal decreased in the order of Pb>Cu>Zn >Cd and inhibition dominance observed in two metal systems was Pb>Cu, Pb>Zn, Pb>Cd, Cu>Zn, Cu>Cd, and Cd>Zn.
Keywords: adsorption; heavy metals; Langmuir isotherm; tourmaline

Introduction

Heavy metals are discharged from various industries such as electroplating, metal finishing, textile, storage batteries, mining, ceramic and glass. Some of them are toxic even if their concentration is very low. They pose serious environmental problems and are dangerous to human health (Iqbal and Edyvean, 2004).

A complex mineral, tourmaline, is a potential adsorbing substance. It is also ubiquitous as an accessory of mineral in nature (Bloodaxe, 1999). The general formula of tourmaline may be written as XY_3Z_6 $[T_6O_{18}]$ $[BO_3]V_3W$, where X=Ca, Na, K, [vacancy]; Y=Li, Mg, Fe^{2+}, Mn^{2+}, Al, Cr^{3+}, V^{3+}, Fe^{3+}, (Ti^{4+}); Z=Mg, Al, Fe^{3+}, V^{3+}, Cr^{3+}; T=Si, Al; B=B, [vacancy]; V=OH, O-[O(3)]; and W=OH, F, O-[O(1)] (Yavuz *et al.*, 2002). The tourmaline group of minerals crystallized in space of group R3m. The structure of tourmaline is characterized by a set of boron triangles, a silicate ring of six tetrahedral, three octahedral cation Y sites (arranged trigonally within the tetrahedral rings) and one X site can be looked upon as an island centered around a 3-fold axis, with octahedral cation Z sites (lying between the tetrahedral rings) joining the various "island" to each other around the 3_1 axis. Therefore, there are the wide variety of available cation and anion sites (e.g., trigonal planar, tetrahedral, octahedral, and a large 9-coordinated site) in it. The surface of tourmaline can be considered as alkali group (Yves *et al.*, 2002). For these reasons, tourmaline may possess ability to adsorb heavy metals from aqueous solution.

In recent years, utilizing natural minerals like kaolinite, montmorillonite, apatite, zeolites, sepiolite and clinoptilolite to adsorb heavy metal pollutants from aqueous solutions has widely been studied (Brigatti *et al.*, 1995; Lo *et al.*, 1997; Anne *et al.*, 1999; Garcia *et al.*, 1999; Susane and William, 2000; Chantawong *et al.*, 2003). Although the research on the adsorption of heavy metals with minerals is abundant, a few of them are about tourmaline adsorbing heavy metal. Nakamura and Kubo (1992) investigated the tourmaline crystal reaction with water. The mechanism of applying tourmaline to purify Cu^{2+} wastewater has been studied (Tang *et al.*, 2002).

The objective of this research was to investigate the adsorption characteristics of Cu(II), Pb(II), Zn(II), and Cd(II), as well as their selectivity onto tourmaline. Laboratory batch kinetics isotherm studies were conducted to evaluate the adsorption capacity of tourmaline. The effects of contact time, pH, and temperature were studied.

1 Materials and methods

1.1 Materials

Tourmaline was obtained from Chifeng Mine of China, and its typical analysis is given in Table 1. Adsorbent was produced through crushing tourmaline into micro level fineness. The specific surface areas of adsorbent were determined by N_2 adsorption at 77.4 K with a high-speed gas sorption analyzer(NOVA 4000, USA). The average particle size of adsorbent was measured by a particle counter (Shimadzu, Japan). Metal solutions used in this study were analytical

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grade and in form of nitrate of compound, including $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$.

Table 1 Typical analysis of tourmaline

Composition	Value	Composition	Value
SiO_2, %	45	TiO_2, %	0.49
Al_2O_3, %	20.9	B_2O_3, %	8.98
Fe_2O_3, %	1.78	Na_2O, %	0.98
FeO, %	1.71	K_2O, %	0.06
MnO, %	2.62	Others, %	6.93
CaO, %	6.35	Specific surface areas, m^2/g	8.78
MgO,%	4.74	Average particle size, μm	0.47

1.2 Adsorption isotherm study

The adsorption isotherm of a single-metal on tourmaline was measured by batch technique. Batch experiments were conducted by adding 50 ml of metal solution to a 100-ml polypropylene tube containing 100 mg tourmaline. Their initial solutions were 10—500 mg/L, and the pH was adjusted to 6.0 by HCl or NaOH. The mixture was shaken in a temperature-controlled water bath shaker at (25±2)℃ for 1 h. After shaking, the tube was centrifuged (3000 r/min, 20 min) and a sample was taken from the supernatant. The metal concentration in the supernatant was measured by an atomic absorption spectrometer (VARIAN110, USA).

Data presented are the mean values from three separate experiments. The metal ions adsorbed (Q) for tourmaline was calculated using a mass balance by Eq.(1). The maximum adsorption capacity was determined by applying the Langmuir isotherm Eq.(2).

$$Q = \frac{(C_0 - C)V}{B} \quad (1)$$

$$\frac{C}{Q} = \frac{1}{bq_{max}} + \frac{1}{q_{max}}C \quad (2)$$

where Q is the metal ions adsorbed (mg/g dw), C is residual concentration of metal ions in the solution (mg/L), C_0 is initial concentration of metal ions in the solution (mg/L), V is volume of the solution (ml), and B is the weight of tourmaline (g), q_{max} is the maximum adsorption capacity (mg/g dw). The Langmuir constant b is related to the energy or net enthalpy of adsorption (L/mg; Faust and Aly, 1987).

2 Results and discussion

2.1 Effect of contact time on adsorption

The kinetic profiles of Cu(II), Pb(II), Zn(II), and Cd(II) adsorption by tourmaline at various concentration are shown in Fig.1. The metal uptake was rapid for all concentrations in first 40 min of contact, accounting for 92%, 99%, 88%, and 84% of sorption for Cu(II), Pb(II), Zn(II), and Cd(II), respectively. Time required for attaining equilibrium for all metal ions was about 60 min. The rate of metal uptake during the entire period of adsorption was found to be independent of metal initial concentrations used. The maximum metal uptake capacity of tourmaline at 100 mg/L metal solution was 43.4, 49.4, 28.1, and 23.3 mg/g of tourmaline for Cu(II), Pb(II), Zn(II), and Cd(II) respectively. This difference in maximum level of uptake of various metal ions has been explained in term of their valence and ionic radii (Puls and Bohn, 1988).

2.2 Effect of initial metal ions concentration

Heavy metal ions adsorption capacities of

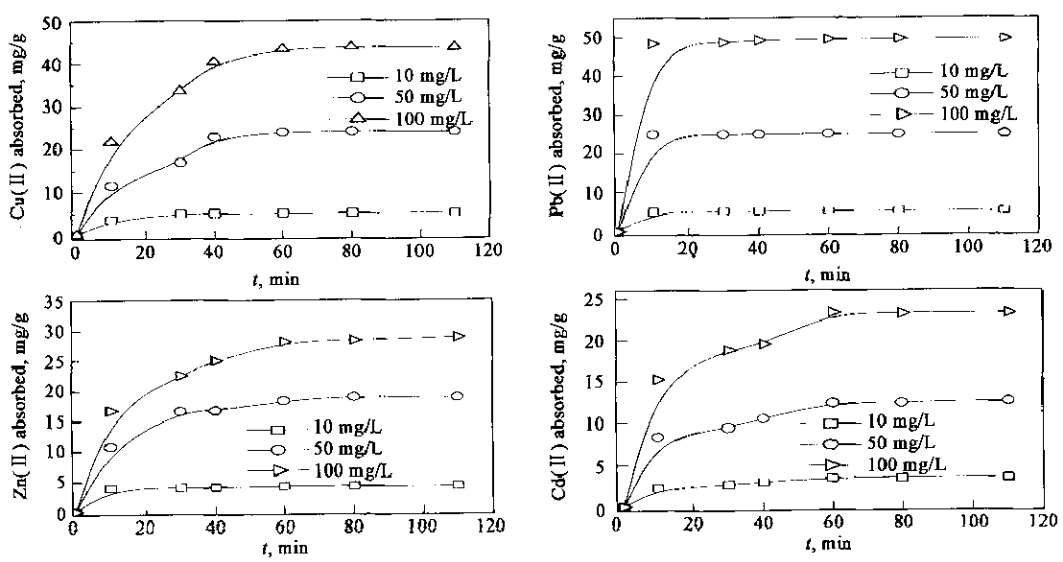

Fig.1 Time-course profiles for Cu(II), Pb(II), Zn(II) and Cd(II) adsorption by tourmaline
50 ml single metal solution (10, 50, and 100 mg/L) was contacted with 100 mg of tourmaline at pH 6.0

tourmaline are present as a function of initial concentration of Cu(II), Pb(II), Zn(II), and Cd(II) ions within aqueous solution in Fig.2. These experiments were performed using single solution (10—500 mg/L) of the metal ions. The amount of metal ions adsorbed per gram of tourmaline increased with the increase of initial metal ions concentration. This increase could be due to an increase in electrostatic interactions (relative to covalent interactions), because the electrostatic field exists in around tourmaline particles (Nakamura and Kubo, 1992). The isotherms for all the four metals were steep at lower concentrations indicating the suitability of tourmaline for the treatment of dilute metal solutions.

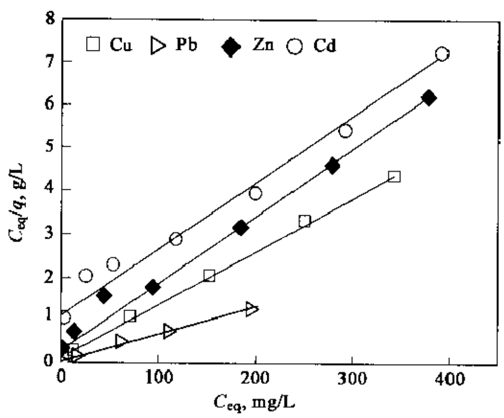

Fig.2 Effect of initial metal concentration on adsorption of Cu (II), Pb (II), Zn(II)and Cd(II) by tourmaline
50 ml single metal solution (10—500 mg/L) was contacted with 100 mg of tourmaline at pH 6.0

Analysis of the equilibrium data is essential to develop an equation which precisely represents the results and which can be used for design purposes. Various isotherm models have been used for the equilibrium modeling of adsorption systems. The Langmuir model is one of the most widely used models to describe the mineral adsorption process. The Langmuir isotherms assume monolayer adsorption. The data fitted this model well (Fig.2). From the linear transformation of the data, values of Langmuir parameters (maximum adsorption capacity q_{max}, isotherm constant b and correlation coefficient R^2) for Cu(II), Pb(II), Zn(II), and Cd(II) were calculated (Table 2). High correlation coefficient (R^2) values (>0.99) obtained with all the four metal ions clearly show that the Langmuir isotherm model is suitable for describing the adsorption equilibrium of these metals by tourmaline in the studied concentration range. Higher q_{max} and b values for Pb (II), as compared with Cu(II), Zn(II), and Cd(II) (Table 2) confirms the stronger bonding affinity of tourmaline to Pb(II) to that of Cu(II), Zn(II), and Cd(II). Adsorption equilibrium and linearized Langmuir isotherms (Figs. 2 and 3) show that metal uptake by tourmaline is a

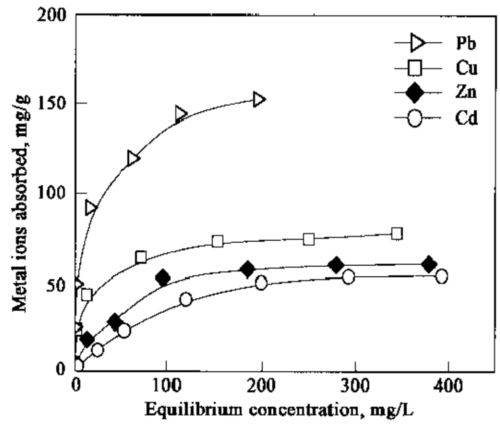

Fig.3 Langmuir adsorption isotherms for Cu(II), Pb(II), Zn(II) and Cd(II) sorption by tourmaline
50 ml single metal solution (10—500 mg/L) was contacted with 100 mg of tourmaline at pH 6.0

chemically equilibrated.

Table 2 shows the adsorption capacity of tourmaline. The q_{max} of tourmaline was 78.86, 154.08, 67.25 and 66.67 mg/g, respectively, for Cu(II), Pb(II), Zn(II), and Cd(II). By contrast, the q_{max} of sepiolite was 6.9 and 5.7 mg/g, respectively, for Cu(II) and Zn(II) (Alastuey *et al.*, 1999). Therefore, the data suggest tourmaline is an effective absorbent for the removal of heavy metal ions.

Table 2 Langmuir constants and correlation coefficient

Metal ion	q_{max}, mg/g	b, mg^{-1}	R^2
Cu(II)	78.86	0.119	0.999
Pb(II)	154.08	0.161	0.994
Zn(II)	67.25	0.028	0.992
Cd(II)	66.67	0.012	0.991

2.3 Effect of pH on metal ion adsorption

Solution pH has been identified as the most important variable factor governing metal adsorption. To study the pH effect on the adsorption of tourmaline, metal uptake was studied at pH ranging from 2.0 to 7.0. Metal uptake was strongly affected by pH of the metal solution (Fig.4). Metal uptake by tourmaline increased with the increase of solution pH. The maximum equilibrium uptake for Cu(II), Pb(II), Zn(II), and Cd(II) ions was 48.4, 49.4, 31.2 and 28.4 mg/g tourmaline at pH 7.0, while at pH 2.0 the adsorption capacity of tourmaline was much low, because large quantities of protons compete with metal cations for the adsorption sites. As the pH of solution increases, the number of protons dissociated from functional groups on the surface of tourmaline increases and thus more negative groups for complexation of metal cations are provided.

The solution pH value of Cu(II), Pb(II), Zn(II), and Cd(II) after contacted with 100 mg tourmaline in

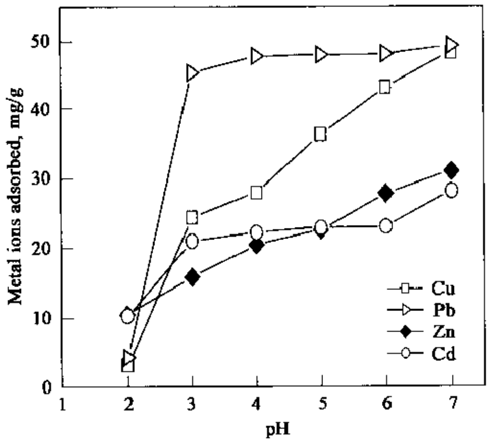

Fig.4 Effect of pH on metal ions adsorption by tourmaline
50 ml single metal solution (100 mg/L) was contacted with 100 mg of tourmaline

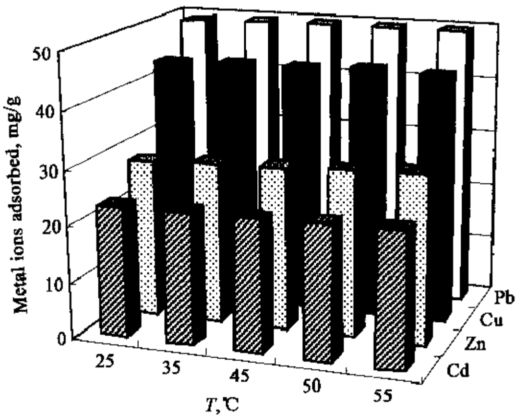

Fig.5 Effect of temperature on metal adsorption of Cu(II), Pb(II), Zn (II) and Cd(II) by tourmaline
50 ml single metal solution (100 mg/L) was contacted with 100 mg of tourmaline for 60 min at pH 6.0

50 ml single metal ions solution (100 mg/L) are shown in Table 3. Solution pH can be increased after metal ions solution contacted with tourmaline. This result may be explained by the alkali group of surface of tourmaline (Yves *et al.*, 2002).

Table 3 Change of pH value of metal solution before and after adsorption on tourmaline

Metal	Cu						Pb					
pH (before contact)	2.1	3.1	4.1	5.1	6.2	7.0	2.1	3.0	4.0	5.2	6.1	7.0
pH (after contact)	2.8	5.8	6.0	6.9	7.4	8.1	2.8	5.9	7.4	7.7	7.9	8.0
Metal	Zn						Cd					
pH (before contact)	2.1	3.0	4.1	5.1	6.0	7.0	2.1	3.0	4.1	5.1	6.0	7.0
pH (after contact)	2.4	6.3	6.6	7.1	7.2	7.5	2.9	6.3	6.9	7.0	7.6	8.0

Note: 50 ml metal solution (100 mg/L) was contacted with 100 mg of tourmaline for 60 min

2.4 Effect of temperature

Results of metal adsorption experiments carried out at different temperatures ranging from 25 to 55℃ are shown in Fig.5. The metal ion uptake capacity of tourmaline showed a small increase with increase in temperature. The maximum metal uptake capacity of tourmaline at 55℃ was 44.19, 49.74, 30.02, and 24.06 mg/g of tourmaline for Cu(II), Pb(II), Zn(II), and Cd (II), respectively, compared with 43.46, 49.35, 28.05 and 23.25 mg/g at 25℃ and 100 mg/L metal solution. The results imply that temperature (25—55℃) has no significant influence on tourmaline adsorption for heavy metal.

3.5 Adsorption in mixed-metal system

Fig.6 shows metal removal percentage obtained with tourmaline in mixed metal solutions. The presence of other metal cations reduced Cu(II), Pb(II), Zn (II), and Cd (II) to the extent of 33.18%, 7.98%, 54.68% and 41.94%, respectively. The lower influence observed for Cu(II), Zn(II), and Cd(II) on Pb(II) adsorption could be due to the greater atomic weight and electronegativity of the later metal (Wong *et al.*, 1993). The observed reduction in the sorption of Cu (II), Zn(II) and Cd(II) in the presence of Pb(II) could be attributed to the difference in their class behaviour on the basis of their covalent indices. (Nieboer and McBryde, 1973). Pb (II) is classified as a class b ions, while Cu (II) and Zn (II) are classified as borderline ions. On the basis of this argument, it is possible to explain clearly the competition effects observed in the present study. Since Pb(II) belongs to a different class of ions (class b), other cations do not exert any effect on its sorption. On the other hand, sorption of Cu (II) and Zn (II) influences each other as they belong to the same class.

4 Conclusions

The results demonstrate that tourmaline is an effective adsorbent and can be successfully used as an adsorbing agent for the removal of heavy metal ions from aqueous solution. Kinetics of Cu(II), Pb(II), Zn (II), and Cd (II) ions adsorption on the tourmaline was found to be dependent on experimental conditions, particularly the medium pH and the initial concentration of the metal ions; moreover, tourmaline can increase the pH value of metal solution after contact. The Langmuir adsorption model was used to represent the experimental data and equilibrium data fitted very well to the Langmuir isotherm model. The adsorption capacity of tourmaline for single metal decreased in the order of Pb>Cu>Zn>Cd and inhibition dominance observed in two metal systems was Pb>Cu, Pb>Zn, Pb>Cd, Cu>Zn, Cu>Cd, and Cd>Zn. Due to this, tourmaline exhibits a net

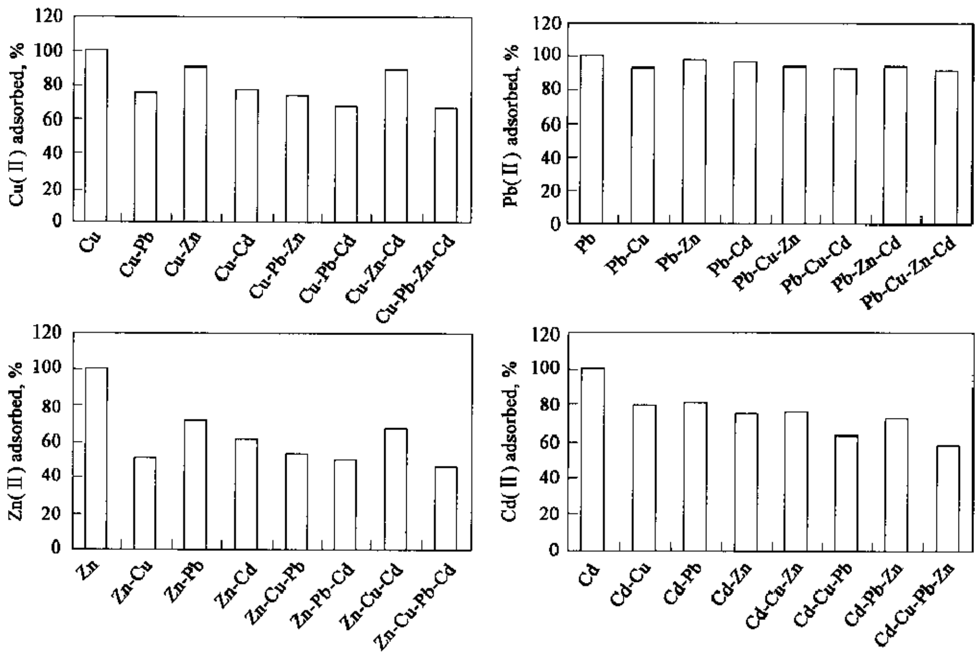

Fig.6 Adsorption of Cu(II), Pb(II), Zn(II)and Cd(II) by tourmaline in single metal or mixed-metal conditions
50 ml metal solution (100 mg/L) was contacted with 100 mg of tourmaline for 60 min at pH 6.0

preference for Pb sorption over Cu, Zn and Cd. The present work shows that tourmaline is a new adsorbent used for treatment of metal-bearing solutions.

References:

Anne M L, Klaus K, Francois M M, 1999. A model for metal adsorption on montmorillonite[J]. Journal of Colloid and Interface Science, 210: 43—54.

Bloodaxe E S, 1999. Links between chemistry and structure in titanites and tourmalines[D]. Ph. D thesis. Department of Geology, Miami University, Oxford Ohio, USA.

Boston G A, Alastuey A, Querol X, 1999. Heavy metal adsorption by different minerals: application to the remediation of polluted soils[J]. The Science of the Total Environment, 42: 179—188.

Brigatti S, Corrodini F, Franchini G *et al.*, 1995. Interaction between montmorillonite and pollutants from industrial wastewaters: exchange of Zn^{2+} and Pb^{2+} from aqueous solutions[J]. Applied Clay Science, 9: 383—395.

Chantawong V, Harvey N W, Bashkin V N, 2003. Comparison of heavy metal adsorptions by Thai kaolin and ballclay[J]. Water Air and Soil Pollution, 148: 111—125.

Faust S D, Aly O M, 1987. Adsorption processes for water treatment [M]. Butterworth Publishers.

Garcia S A, Alastuey A, Querol X, 1999. Heavy metal adsorption by different minerals: application to the remediation of polluted soils[J]. The Science of the Total Environment, 24: 179—188.

Iqbal M, Edyvean R G, 2004. Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of *Phanerochaete chrysosporium*[J]. Minerals and Engineering, 17: 217—223.

Lo B, Mak R, Lee S, 1997. Modified clays for waste containment and pollutant attenuation[J]. Journal of Environmental Engineering, 123: 25—32.

Nakamura T, Kubo T, 1992. Tourmaline group crystals reaction with water[J]. Ferroelectrics, 137: 13—31.

Nieboer E, McBryde W A E, 1973. Free-energy relationships in coordination chemistry. III. A comprehensive index to complex stability[J]. Canadian Journal of Chemistry, 51: 2512—2524.

Puls R W, Bohn H L, 1988. Sorption of cadmium, nickel and zinc by kaolinite and montmorillonite suspensions[J]. Amer J Soil Sci Soc, 52: 1289—1292.

Susanne G, William D J, 2000. Heavy metal-adsorption on micas and clay minerals studied by X-ray photoelectron spectroscopy[J]. Applied Clay Science, 16: 289—299.

Tang Y H, Wu R H, Zhang X H, 2002. Mechanism of applying tourmaline to purifying Cu^{2+}-doped wastewater[J]. Acta Petrologica et Mineralogica, 21(2): 192—196.

Wong P K, Lam K C, So C M, 1993. Removal and recovery of Cu(II) from industrial effluent by immobilized cells of *Pseudomonas putida* II-11[J]. Applied Microbiology and Biotechnology, 39: 127—131.

Yavuz F, Gultekin A H, Karakay M C, 2002. CLASTOUR: a computer program for classification of the minerals of the tourmaline group [J]. Computers & Geosciences, 28: 1017—1036.

Yves F, Martine L, Jorge L, 2002. Oxydation expérimentale de Fe-tourmalines et corrélation avec une déprotonation des groupes hydroxyle[J]. C R Geoscience, 334: 245—249.

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