



Desorption of Cd(II) from tourmaline at acidic conditions: kinetics, equilibrium and thermodynamics



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ABSTRACT

The effects of different conditions such as time, pH, the initial concentration of the metal ions, temperature and additional cations like Ca(II) and Mg(II) ions on desorption of Cd(II) from tourmaline at acidic conditions were investigated. The results indicated that the desorption of Cd(II) depended significantly on all the above-mentioned parameters. The desorption kinetics closely followed the pseudo-second-order model. And the desorption of Cd(II) followed the Freundlich isotherm model better than Langmuir isotherm model. The maximum desorption capacity of tourmaline for Cd(II), evaluated using a Langmuir equilibrium model, were 2.74 and 13.17 mg/g at an initial pH 4.0 under temperature 25 and 35 °C after the 1440 min equilibrium time, respectively. Thermodynamic parameters indicated that the desorption processes were viable, spontaneous and endothermic in nature. Additionally, Mg(II) and Ca(II) ions can both facilitate the efficiency of desorption, and Mg(II) ions promoted the process of desorption more better than Ca(II) ions. Thus, this study showed that tourmaline was quite an effective adsorbent for the removal of heavy metals in the acidic condition because its desorption capacity was too low to cause secondary pollution. Tourmaline may be used as a stable adsorbent for removing pollutants from environment, especially soil.

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1. Introduction

In recent years, the rapid development of industrialization and urbanization caused serious environment problems that large quantities of heavy metals were released into wastewaters. The toxicity risk of these metals is increased through accumulation in living organisms and following bioamplification in the food chain [1,2], which could result in a long-term toxic effect on human, animals and plants, even at low concentrations. The heavy metals due to their non-biodegradable and polymorphic nature threatened human health and survival.

Among the toxic heavy metals, cadmium is highly toxic and about 80% of global cadmium output is discharged to the environment as a byproduct of zinc smelting process [3]. Most of the cadmium that enters the body causes various diseases and disorders to the kidneys, lungs, bones, and also leads to anemia and sometimes hypertension, neuralgia, nephritis and secretion disorder [4]. USA Environmental Protection Agency has set a limit of only 5 ppb Cd(II) for drinking water [5] due to its carcinogenic

effect on humans. Therefore, it is important to develop a new efficient sorbent that it not only could efficiently remove cadmium ion from wastewater, but also guarantee heavy metals to be adsorbed chronically for wastewater treatment, especially acidic wastewater.

Nowadays, adsorption is an effective method for the removal of heavy metals from the aqueous solutions [6]. The use of natural adsorbents is particularly beneficial for the development of cost-effective processes to remove heavy metals from wastewater [7]. For examples, in recent years, many natural adsorbents like zeolite [8,9], quartz [10], apatites [11], goethite [12], calcite [13], activated sludge [14], dolomite [15], clinoptilolite [16], francolite [17], olive stone [18,19] and volcanic ash [20] have been investigated for the treatment of heavy metal ions from water. Up to now, they have been successfully utilized for the removal of heavy metal ions, both collectively and separately, from aqueous solutions using adsorption techniques [21]. Nevertheless, once the above sorbents were used to adsorb Cd(II), their adsorption capacity for Cd(II) could not be satisfied, especially when the aqueous solutions were stronger acidic conditions (pH < 5.0). For example, the adsorption capacity of surface-functionalized silica-coated Fe₃O₄ nanoparticles for Cd(II) at pH 4.0 was lower than 22.4 mg/g [22], while red mud,

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manganese ore for Cd(II) was 10.6 and 59.2 mg/g at pH 6.0 and 5.5 conditions, respectively [23,24]. Additionally, the detailed study on Cd(II) desorbed from the adsorbents at the acidic condition is relatively scarce. What's more, there were lack of the detailed reports on the capacity of desorption on these natural sorbents for heavy metals at acidic conditions (pH < 5.0). Therefore, it is necessary to assess the desorption properties on the adsorbent for heavy metal.

In our previous studies [25], it was proved that tourmaline had a good capacity for Pb(II) and Cd(II) at acidic condition. For example, 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 [26]. However, tourmaline desorption ability for heavy metals did not investigated. Tourmaline is a special functional material, with unique physical–chemical properties, such as producing an electrostatic field and releasing rare microelements [21]. The most important feature among the electric properties of tourmaline is the possession of spontaneous and permanent poles, which produce an electric dipole, especially in a small granule with a diameter of several micrometers or less [27,28]. The general chemical formula of tourmaline is expressed as $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, where X = Na⁺, K⁺, Ca²⁺ or a vacancy; Y = Li⁺, Fe²⁺, Fe³⁺, Al³⁺, Mg²⁺, Cr³⁺, V³⁺, (Ti⁴⁺); Z = V³⁺, Fe³⁺, Cr³⁺, Al³⁺, Mg²⁺, Fe³⁺; T = Si⁴⁺, Al³⁺, (B³⁺); B = B³⁺, V = [O(3)] = OH⁻, O²⁻; W = [O(1)] = OH⁻, O²⁻, F⁻ and metal ions in parenthesis indicate minor or possible substitutions [29]. Hence, a variety of cation and anion sites in tourmaline provide a great likelihood to adsorption. For these reasons, we speculate that the tourmaline should have great potential to desorb Cd(II) ions from aqueous solutions. To measure whether a new type of adsorbent has high value of practical application, we should not only focus on its adsorption efficiency and performance, but also pay attention to its capacity of desorption to avoid secondary pollution because tourmaline could amend soil contaminated with heavy metals (data not shown). Hence, it is necessary to assess the desorption ability using the experimental data.

Therefore, the objective of the present study was to study the desorption properties of tourmaline at acidic condition with pH 4.0. Different parameters that influencing desorption behavior, such as desorption time, pH, temperature, metal ions like Mg(II) and Ca(II) ions were investigated through kinetic, desorption equilibrium models, and thermodynamic studies. Kinetics data were evaluated according to Lagergren pseudo-first-order and pseudo-second-order models. The desorption capacities of tourmaline were evaluated by both the Langmuir and Freundlich models. To describe the simple desorption mechanism, thermodynamic parameters were also calculated.

2. Materials and methods

2.1. Materials

Iron-rich black tourmaline of 800 nm particle size was purchased from Hongyan Mineral Products Co., Ltd., Tianjin city, China. Tourmaline was produced in Xinjiang province, China. Compositional analysis was performed by an electron microprobe analyzer (EMPA) using a Shimadzu 1600 electron microprobe equipped with four channel wavelength dispersive spectrometers (WDS). The chemical composition of 800 nm particle size tourmaline was as follows: SiO₂, 36.75%; Al₂O₃, 33.62%; Fe₂O₃, 12.19%; TiO₂, 0.57%; B₂O₃, 9.78%; FeO, 1.7%; CaO, 0.4%; MgO, 4.76%; K₂O, 0.14%; Na₂O, 0.74%; P₂O₅, 0.19%; H₂O⁺, 1.0%; MnO, 0.21%. The SEM image of the tourmaline is seen in Fig. 1.

Deionized distilled water (DD-H₂O) was used to prepare all solutions. Besides, cadmium nitrate, MgCl₂, anhydrous CaCl₂ used in the study were of analytical grade and provided by Tianjin Regent Station (Tianjin, China), The 4 mg/L of Mg(II) solution and

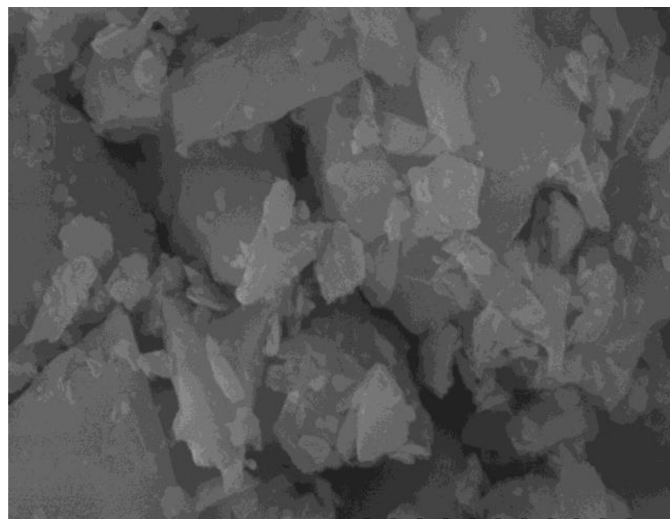


Fig. 1. The SEM image of the iron-rich black tourmaline of 800 nm particle size.

Ca(II) solution was prepared by weighing magnesium chloride and calcium chloride, then adding DD-H₂O and adjusting the volume to 1 L in a volumetric flask, 1 mol/L of NaOH and HCl solutions were prepared to adjusted the pH in desorbent solutions, respectively.

2.2. Cadmium stock solution

The 1 g/L stock solution was prepared by weighing cadmium nitrate, then adding 10 mL of 6 mol/L HNO₃ and adjusting the volume to 1 L in a volumetric flask with DD-H₂O. 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-H₂O, 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.

2.3. Desorption experiments

Desorption experiments was operated after the adsorption experiments, both of them were adopted the same experimental conditions like temperature, pH and reaction time. Batch experiments were conducted in 50 mL plastic polypropylene centrifuge tubes, adding a certain concentration of cadmium nitrate solutions, and a certain dose of tourmaline. Their specific usage amounts were reported in next experimental section. The pH was adjusted using 1 mol/L of NaOH and HCl. 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, retained tourmaline precipitation for the following test and supernatant was discarded. Then, adding DD-H₂O of a certain pH into plastic polypropylene tubes centrifuged, desorption experiments was carried at certain temperature and desorption time.

2.4. Desorption kinetic models

The adsorption were conducted in plastic polypropylene tubes with a 6 g/L of tourmaline and a 100 mg/L of Cd(II) aqueous solution concentration at a temperature of 25 °C and pH 4.0. The adsorption time was 5, 10, 15, 30, 60, 180, 360, 540, 1440 and 2880 min. After plastic polypropylene tubes were centrifuged at 3000 r/min for 15 min, discarded the supernatant and add DD-H₂O

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