

Preparation and Performance Study on Sodalite/Magnetite from Tourmaline

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Abstract. Sodalite/Magnetite was efficiently fabricated by a one-step hydrothermal route using natural tourmaline as a silicon-aluminum source. The obtained products were characterized by X-ray diffraction, field emission scanning electron microscope, and elemental analysis (ICP) and N₂ adsorption-desorption isotherm. In addition, the adsorption characteristics of metal ions (Cu²⁺, Co²⁺, Cr³⁺) on the sodalite were investigated. The results show that sodalite covered by octahedral particles of Fe₃O₄ was successfully obtained under hydrothermal treatment temperature at 300 °C. Nitrogen adsorption studies of sodalities showed the pore size around 0.7 nm and BET surface area over 0.315 m²/g. The adsorption capacities of Cu²⁺, Co²⁺ and Cr³⁺ on sodalite/magnetite were 25.95, 8.90 and 4.1 mg/g.

1. Introduction

The richness of heavy metal resources has been provided China's economic construction and social development with a stable material support. However, the increasing prominence of pollutions issues have caused great harms to humans and ecological environment. Chemical precipitation [1,2], electrochemistry [3], adsorption [4], biological [5] methods were often used to solve the problem of heavy metal pollution. The adsorption method was widely used due to it has high removal efficiency, performance stability.

Sodalite is a framework silicate mineral with the general formula Na₈Al₆Si₆O₂₄ (X) with X =Cl⁻, CO₃²⁻, SO₄²⁻, OH⁻ [6]. It was typically formed under hydrothermal conditions. As a kind of zeolite molecular sieve [7], sodalite has so homogeneous porous, alkali resistant, been characterized by one of the highest thermodynamic stability among all zeolites, that can be used as adsorbents [8], catalysts [9], drug carriers [10] and other functional materials [11]. Unfortunately, sodalite structure is also characterized by one of the smallest sorption capacities [12]. However, the size of channels and cages in this framework allows selective sorption of dozen small ions, such as Ag⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺, S²⁻ or SO₄²⁻ [13, 14]. In the last few years, some researchers have done many works in sodalite crystals synthesized by the hydrothermal process [15, 16].

Tourmaline is a type of granite stone, commonly called electric stone, since it has electrical characteristics. In addition, tourmaline has a very flexible structure, which is able to adjust its composition in response to a wide range of chemical, pressure, and temperature variations [17] as reflected by its complex general chemical formula, XY₃Z₆[T₆O₁₈] (BO₃)₃V₃W [18]. China has very abundant tourmaline mineral resources, that most are schorl, which proven reserves could be more



than million tons [19]. Nevertheless, the fundamental research on the characteristics and comprehensive development and utilization of tourmaline mineral were still in the early stage in China. Moreover, a large number of tourmaline tailings have not been fully utilized. As a naturally aluminosilicate mineral, schorl with the molecular formula $\text{NaFe}_3\text{Al}_6\text{Si}_6(\text{BO}_3)_3\text{OH}_4$ has the same Al: Si ratio (1:1) as sodalite. There has been no report on the hydrothermal fabrication of sodalite using tourmaline as a Si-Al source, so far.

In this study, sodalite which surface supported magnetite was efficiently fabricated by a one-pot hydrothermal route using natural tourmaline as a silicon-aluminum source. Furthermore, N_2 adsorption-desorption isotherms and heavy metal ions were tested in order to investigate the adsorption properties of sodalite.

2. Experimental

2.1. Preparation of sodalite/magnetite

20 g of tourmaline with the size of 15 μm (Ganzhou, Jiangxi, China) and 10 g sodium hydroxide were dispersed into 250 mL deionized water. Subsequently, the mixture was transferred into an autoclave with hastelloy liner and heated at different temperatures for 3, 6, 12 and 48 h. After hydrothermal treatment, the products were collected by filtrating, then washed with deionized water and dried at 70 $^\circ\text{C}$ for 24 h.

2.2. Characterization

Scanning electron microscopy (SEM) images were obtained on SIGMA field emission scanning electron microscope (Carl Zeiss). X-ray powder diffraction (XRD) patterns of the products were collected on a D8-Advance diffractometer (Bruker) using Cu K_α radiation, accelerating voltage of 40 kV and a generator current of 40 mA. The N_2 adsorption-desorption isotherms and pore distribution (Brunauer-Emmett-Teller, BET method) were determined by a Surface area and pore size analyzer (BELSORP-mini II, Japan).

2.3. Adsorption experiments for the removal of metal ions

Sodalite as an adsorbent (0.1 g) was left in contact with 50 mL of heavy metal ion solution in the range of 100 mg/L. The working solutions of CuSO_4 , $\text{Co}(\text{NO}_3)_2$ and CrCl_3 were prepared from their respective stock solutions. All sorption studies with the model solution were carried out in glass bottles with volume capacity of 50 mL. The concentrations of metal ions were determined by Inductive Couple Plasma Emission Spectrometer (IRIS Intrepid II). The heavy metal ions adsorbed on the adsorbent at specified time, q_t (mg/g), were determined by the equation below:

$$q_t = (C_i - C_t)V/m \quad (1)$$

Where C_i is the initial concentrations (mg/L) and C_t is the concentration of metal ions in solution at the specified time, V is the volume of the solution (mL) and m is the mass of adsorbent (g) of batch experiments.

3. Results and discussion

3.1. Phase formation of sodalite/magnetite

Hydrothermal treatment temperature and time is an important factor in synthetic sodalite. Five different temperatures (150, 200, 250, 300 and 350 $^\circ\text{C}$) were heated to investigate the influence of Hydrothermal treatment temperature on sodalite/magnetite synthesized from tourmaline. Hydrothermal time was selected 6, 12, 48h, respectively.

Figure 1a shows the XRD patterns of the synthetic products at the condition of different treatment temperature for 48 h while tourmaline/NaOH mass ratio is 2:1. As can be observed in the XRD profiles, the product is almost tourmaline after hydrothermal treatment temperature at 150 $^\circ\text{C}$, the illustrate tourmaline structure has still not been destroyed. Some very weak peaks appear at 2θ at 24.18 $^\circ$, 31.15 $^\circ$, 34.45 $^\circ$ when heated at 200 $^\circ\text{C}$, which indicated that sodalite was starting been

generated. The appearance of the characteristic peaks of sodalite occurs at 250 to 350 °C with a perfect matching with the characteristic peaks of standard sodalite, and the intensity of the main peaks of sodalites were gradually increased with the hydrothermal temperature (Figure 1b). At the same time, magnetite was formed with sodalite together while the temperature was over 250 °C (Figure 1c). The results of X-ray diffraction shown that tourmaline mineral would transform into sodalite under the condition of high temperature alkaline solutions. Figure 1d shows the product diffraction pattern at 300 °C with hydrothermal time of 6, 12 and 48 h, respectively. It can be seen from the XRD patterns that the reaction of tourmaline with alkali is very rapid, and it has been completely reacted in 6 h. The reaction product phase is sodalite and magnetite. Since then the reaction time was prolonged, the phase did not change, but both the diffraction peak intensities increased, indicating that this is the process of sodalite and magnetite crystal particle growth. The reaction time of 6h or less is a more economical choice.

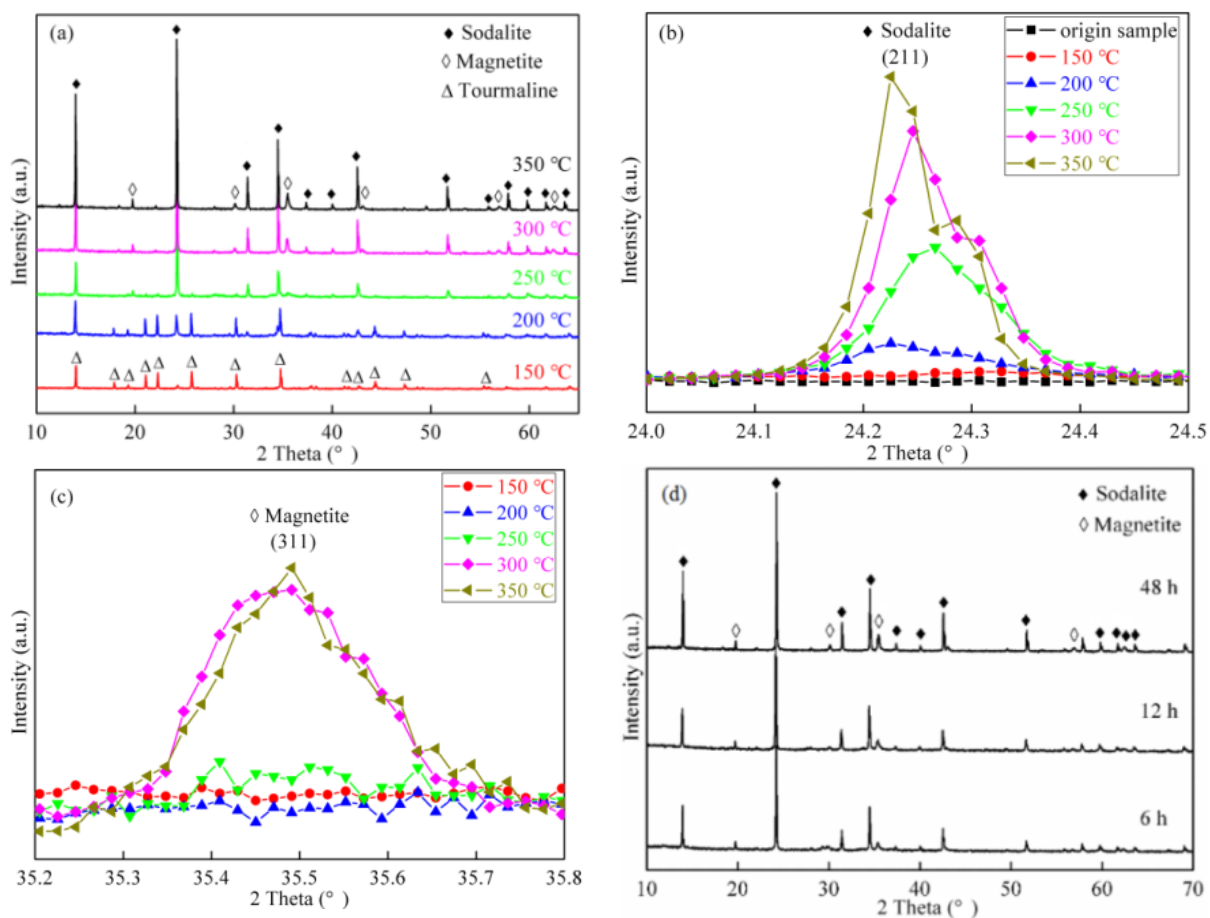


Figure 1. XRD patterns of the products synthesized at different treatment temperature (hydrothermal time of 48 h) and different hydrothermal time.

3.2. Morphology of products

The influence of crystallization temperature on the morphologies of synthetic products was illustrated in Figure 2. The tourmaline crystal morphology was destroyed, after mining and crushing (Figure 2a). When hydrothermally treated at 200 °C, only part of the tourmaline is converted to sodalite (Figure 2b). XRD patterns (Figure 1a) have indicated that almost all the products formed at 250 °C were sodalite, moreover, it was found that sodalite particles were wrapped with smooth slices of sodalite, which would further increase the specific surface area of the products (Figure 2c). In addition, the surface of sodalite was covered by particles of Fe_3O_4 with regular octahedral morphology (Figure 2d) under hydrothermal treatment temperature at 300 °C, and the Fe_3O_4 particles size has been confirmed

from 100 nm to 600 nm. Fe_3O_4 nanoparticles, with magnetism and stability, have been introduced to prepare composited adsorbents. As an adsorbent, sodalite could selectively adsorb of dozen ions, additionally, the generated Fe_3O_4 nanoparticles cause a better ion adsorption property.

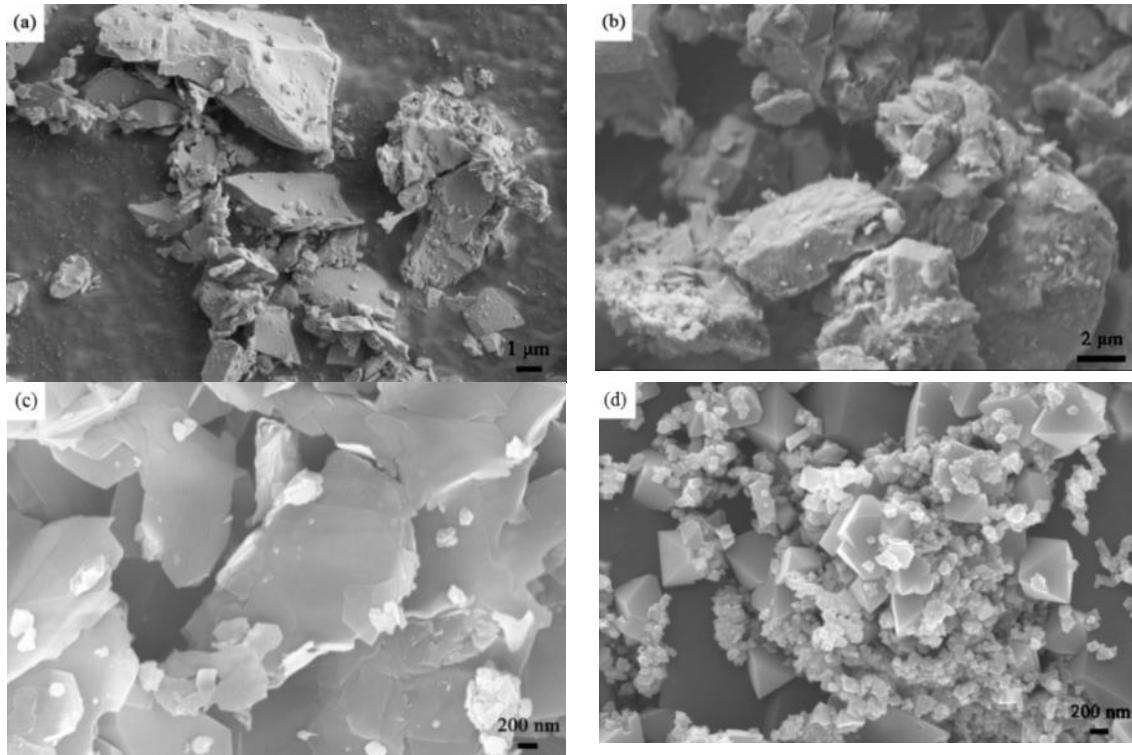


Figure 2. SEM images of the tourmaline (a), tourmaline and sodalite (b), sodalite (c), sodalite/magnetite (d).

3.3. Adsorption properties of products

3.3.1. BET analysis

Figure 3a displayed the N_2 adsorption-desorption isotherms for sodalite/magnetite. It shows a typical reversible curve of physisorption isotherm (type II) according to the IUPAC classification. Pore distribution of sodalite/magnetite appeared multiple peaks, but the microporous of about 0.7 nm was the sharpest peak, which indicated that a large number of holes are distributed in this range. In addition, the BET surface area of samples was calculated to be $0.315 \text{ m}^2/\text{g}$ (Figure 3b).

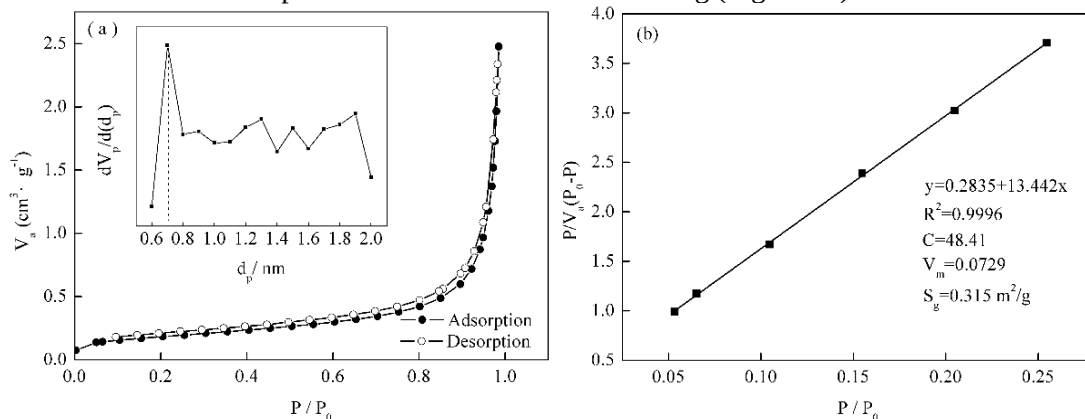


Figure 3. (a) N_2 adsorption-desorption isotherms and pore distribution of sodalite/magnetite, (b) Linear of fit BET and relevant parameters.

3.3.2. Adsorption of heavy metal ions

The adsorption properties of synthetic sodalite and sodalite/magnetite were investigated on the condition that the concentration of 100 mg/L, the temperature of 25 °C (Figure 4). From the results, we could conclude that sodalite and sodalite/magnetite have little difference at adsorption ability of metal ions and it reveals that the maximum sorption capacity was $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+}$. However, sodalite/magnetite shows greater capacity in adsorption than sodalite without magnetite (Figure 4b). The data indicates that there were synergistic effects of sodalite and magnetite on adsorption of heavy metal ions.

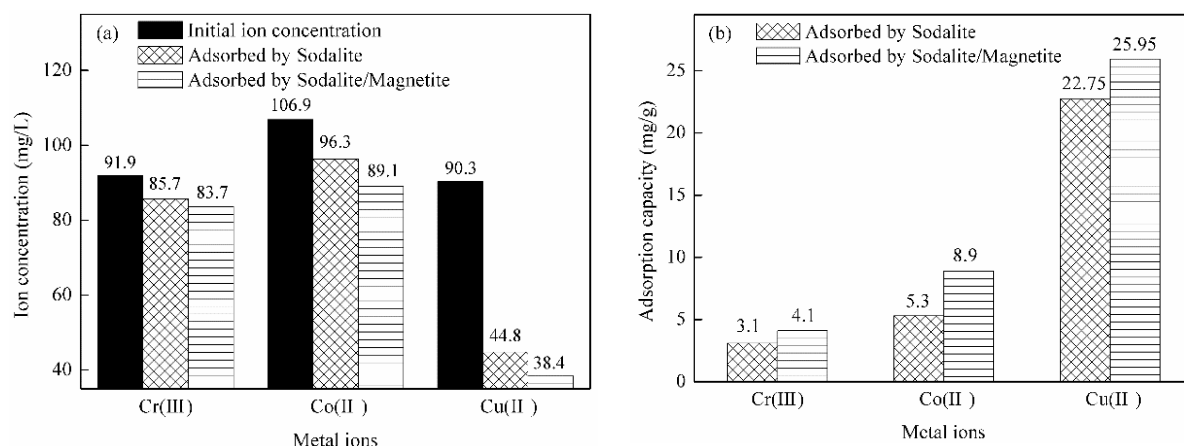


Figure 4. Comparison of adsorption properties of synthetic sodalite and sodalite/magnetite.

4. Conclusions

In this study, sodalite/magnetite adsorbent was synthesized by a hydrothermal process to remove heavy metal ions (Cu^{2+} , Co^{2+} , Cr^{3+}) from solutions. The prepared sodalite/magnetite has satisfactory adsorption capacities. There were synergistic effects of sodalite and magnetite on adsorption of heavy metal ions, the adsorption capacities of Cu^{2+} , Co^{2+} and Cr^{3+} on sodalite/magnetite were 25.95, 8.90 and 4.1 mg/g, which indicated that sodalite/magnetite can be used effectively for removal of metal cations from aqueous solutions.

5. Acknowledgments

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6. Reference

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