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Thermal activation of serpentine for adsorption of cadmium

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HIGHLIGHTS

- Thermal activated serpentine was prepared by changing heated temperature.
- Thermal activated serpentine exhibited excellent adsorption behavior for cadmium.
- The adsorption mechanisms could be explained as formation of $CdCO_3$ and $Cd(OH)_2$.
- The adsorption obeyed Langmuir model and pseudo second order kinetics model.

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ABSTRACT

Thermal activated serpentine with high adsorption capacity for heavy metals was prepared. The batch experiment studies were conducted to evaluate the adsorption performance of Cd^{2+} in aqueous solution using thermal activated serpentine as adsorbent. These samples before and after adsorption were characterized by XRD, FT-IR, SEM, XPS, and N_2 adsorption-desorption at low temperature. It was found that serpentine with layered structure transformed to forsterite with amorphous structure after thermal treatment at over 700 °C, while the surface area of the samples was increased with activated temperature and the serpentine activated at 700 °C (S-700) presented the largest surface area. The pH of solution after adsorption was increased in different degrees due to hydrolysis of MgO in serpentine, resulting in enhancing adsorption of Cd^{2+}. The S-700 exhibited the maximum equilibrium adsorption capacity (15.21 mg/g), which was 2 times more than pristine serpentine. Langmuir isotherm was proved to describe the equilibrium adsorption data better than Freundlich isotherm and pseudo second order kinetics model could fit the adsorption kinetics processes well. Based on the results of characterization with XPS and XRD, the adsorption mechanisms could be explained as primarily formation of $CdCO_3$ and $Cd(OH)_2$ precipitation on the surface of serpentine.

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1. Instruction

Cadmium (Cd) is recognized as one of the most harmful heavy metal pollutants in the environment due to its toxicity, non-degradability, bioaccumulation and mobility in natural water and soil ecosystems. It could cause a high carcinogenicity and an endocrine disorders, as well as renal dysfunction and bone fracture [1–3]. Cadmium pollution mainly derives from electroplating, paint pigments, plastics, silver-cadmium and nickel-cadmium battery industry and smelter operations [4]. With the rapid development of industry, a large wastewater containing cadmium drainage had not only polluted water environment but also resulted in continuous increase in soil pollution. The area of Cd-contaminated agricultural soil reached about 1.3×10^7 hm^2 covering 25 regions of 11 provinces in China [5]. Cadmium pollution becomes increasingly serious and badly affects human lives and health. Therefore, it has been generated great attention of researchers to remediation of Cd-polluted soil and water.

Classical techniques used for remediation and cleanup of heavy metal from polluted environment included precipitation, coagulation, ultrafiltration, reverse osmosis, electrodialysis, ion exchanges and adsorption [6–13]. Among these methods, adsorption was considered as one of the most prospective process due to low-cost, simplicity of application and efficiency. For the adsorption process, the adsorbent was the key parameter. The use of relative low cost and efficient materials as potential adsorbent for immobilization and elimination of heavy metals from soil and wastewater has always been the focus of attention. These cost-effective materials

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Table 1
The composition and content of serpentine.

Composition	SiO_2	MgO	CaO	Al_2O_3	Fe_2O_3
Content (wt.%)	51.00	47.32	0.92	0.38	0.38

as adsorbents for heavy metal included industrial by-products or waste, such as bauxite residue, slag gravel sludge and waste rubber tires [14–16], agricultural products such as rice straw and coconut husks [17,18], organic matter, such as farmyard manure and compost [19,20], and some of natural materials like clay and zeolite [8,21,22].

The natural clays and zeolite have been more and more used to adsorption heavy metal ions due to their unique properties of high surface area, high cation exchange capacities, low cost and the ubiquitous occurrence in most soil. In the last few decades, extensive researches have been conducted on heavy metal adsorption by natural clay minerals such as montmorillonite, sepiolite, and palygorskite, all of which had great potential to be applied in treatment of heavy metals in environment [8,23–25].

Serpentine is a 1:1 layered hydrated magnesium silicate mineral with a regular pore structure, and strong surface activity [26–28]. The basis crystal structure of the serpentine is a silicate layer connected to a layer of $[MgO_2(OH)_4]$ octahedral. This composite layer is linked to the corresponding layers by weak bonds. The serpentine group includes three closely related minerals: antigorite, lizardite and chrysotile [29]. Previous studies showed serpentine, especially thermal activated serpentine exhibited better adsorption performance for heavy metals in the soil [28]. However, there are very few reports about the adsorption properties and mechanism of heavy metals on serpentine.

Based on these understanding, in current work, the effect of thermal activation on the structural and textural proprieties of the serpentine, and the adsorption of Cd^{2+} on natural serpentine and thermal activated serpentine samples were systematically investigated. Batch experiments were conducted to investigate the adsorption affinity, kinetics and isotherm. X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermogravimetric and differential scanning calorimetry (TG-DSC), and X-ray photoelectron spectroscopy (XPS) were employed to investigate the effect of thermal activation on the structure of serpentine and the detailed mechanism of adsorption. The results of this work would provide insights to the mechanisms underlying the adsorption of Cd^{2+} with serpentine, which will be helpful for the application of serpentine in treating heavy metal ions in environment.

2. Materials and methods

2.1. Test materials

The serpentine was obtained from Xiuyan County, Anshan City, Liaoning Province, China, the content and composition of which were determined by XRF and shown in Table 1. The serpentine was spread in a porcelain crucible, and the crucible was then placed in the center of the muffle furnace. The furnace was heated to a given temperature for 2 h by increasing the temperature at a heating rate of 2 °C min^{-1}. After temperature dropped to room temperature, the crucible was then removed. The thermal activated serpentine was obtained, and abbreviated as S-T, where T was the heated temperature. All the reagents used in this study were of analytical reagent grade. An aqueous stock solution (1000 mg/L) of Cd^{2+} ions was prepared by dissolving a known amount of cadmium chloride ($CdCl_2{\cdot}2.5H_2O$) salt in deionized water.

2.2. Characterization of sample

XRD patterns were conducted at 25 °C in a Bruker D8 Advance X-ray diffractometer using monochromatised Cu/Kα radiation (40 kV, 40 mA). The samples were scanned with a step size of 0.02° and a counting time of 0.2 s per step.

FT-IR analysis was conducted on a Bruker Tensor 27 spectrometer. FT-IR spectra in the transmittance mode were recorded in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} using the KBr pressed disk technique.

N_2 adsorption-desorption isotherms were measured with BelSorp-Max (Bel Japan Inc.) at −196 °C. The samples (ca. 150 mg) were previously outgassed at 150 °C for 5 h. The surface area was estimated by the Brunauer Emmett Teller (BET) method.

XPS analyses were performed with an Axis Ultra spectrometer (Kratos Analytical Ltd.) using Al monochromatic X-ray source (Al Ka = 1486.6 eV) at 25 °C in a high vacuum environment (approximately 5×10^{-9} torr). All the binding energies were calibrated by using containment carbon the C 1s (284.8 eV).

TG-DSC was performed on a Netzsch STA449F5 instrument (German). The samples were heated from 30 to 900 °C with a heating rate of 10 °C min^{-1} under air atmosphere.

SEM images were recorded on a Philips-FEI model Quanta 200. X-ray fluorescence (XRF) spectra were recorded on a Philips MagiX X-ray fluorescence spectrometer.

2.3. Adsorption experiments

Adsorption kinetics experiments were performed in a group of 50 mL centrifugal tubes which contained 20 mL Cd^{2+} solution (160 mg/L) and 0.2 g adsorbent, and the pH of solution was adjusted to 6. The centrifugal tubes were shaken on a constant temperature oscillator at 25 °C by varying the contact time from 10 min to 24 h. After centrifuging, the Cd^{2+} concentration of the supernatant was measured by atomic absorption spectrometer (WYS2200, Wanyi, Anhu). The adsorption capacity (q_t) was calculated by the following equation:

$$q_t = (C_0 - C_t)V/m \tag{1}$$

where C_0 and C_t (mg/L) were the initial and remaining Cd^{2+} concentrations, respectively; V (L) was the volume of the suspension; and m (g) was the mass of adsorbent.

The most used kinetics models to fit experimental data were pseudo-first-order and pseudo-second-order models, whose mathematical expressions were as follows.

$$\text{Pseudo-first-order kinetics model}: \quad q_t = q_e(1\text{-}e^{-k_1 t}) \tag{2}$$

$$\text{Pseudo-second-order kinetics model}: \quad q_t = \frac{q_e{}^2 k_2 t}{1 + q_e k_2 t} \tag{3}$$

Where q_e and q_t were the amounts of Cd adsorbed (mg/g) at equilibrium and at any time t (min), respectively, k_1 was the pseudo-first-order kinetics model rate constant (min^{-1}), k_2 was the pseudo-second-order kinetics model rate constant ($g\,mg^{-1}\,min^{-1}$).

Adsorption isotherms of Cd^{2+} on adsorbent were carried out by a batch equilibration technique. Adsorbent (0.2 g) was added to 50 mL centrifugal tubes, which was then filled with 20 mL of $CdCl_2$ solution with different Cd^{2+} concentrations (40, 80, 120, 160, and 200 mg/L) and the pH was adjusted to 6. The centrifugal tubes were shaken for 24 h at 25 °C in a constant temperature oscillator. The suspensions were then centrifuged, and the resulting supernatants were collected to determine the equilibrium Cd^{2+} concentrations. The equilibrium adsorption capacity (q_e) was calculated according to Eq. (1). To investigate the adsorption equilibrium of Cd^{2+} onto serpentine, the adsorption equilibrium results were fitted to the Langmuir and Freundlich, which were the most frequently used

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