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Efficient removal of cesium from aqueous solution with vermiculite of enhanced adsorption property through surface modification by ethylamine

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ABSTRACT

Ethylamine modified vermiculite (Ethyl-VER) with high specific surface area and excellent pore structure was prepared to remove cesium from aqueous solution. The physic-chemical properties of the pristine and modified vermiculite were analyzed by X-ray diffraction (XRD), Fourier-transform infrared (FTIR), specific surface area (BET) and scanning electron microscopy/energy disperse spectroscopy (SEM/EDS). The corroding effect of ethylamine increased the specific surface area of vermiculite from 4.35 to 15.59 $m^2\ g^{-1}$, and the average pore diameter decreased from 6.8 to 5.34 nm. Batch adsorption experiments were conducted as a function of pH, initial Cs^+ concentration, contact time, coexisting cations (K^+, Na^+, Ca^{2+}) and low-molecular-weight organic acids (acetic acid, oxalic acid, citric acid) to illustrate the adsorption behavior. The study found that the adsorption capacity of cesium in aqueous solution was improved from 56.92 to 78.17 mg g^{-1} after modification. The formation of micropores and mesopores and the increased surface area played a critical role in the enhancement of cesium adsorption. Kinetic experiments indicated that the adsorption process can be simulated well with a pseudo-second-order model. The presence of cations or low-molecular-weight organic acids inhibited cesium adsorption in different degrees. On the basis of our results, Ethyl-VER with good surface characteristics and high adsorption capacity is a suitable adsorbent for cesium removal from aqueous solution.

1. Introduction

The nuclide ^{137}Cs with a half-life of 30.4 years is a radioactive contaminant of concern in environment [1]. It has been introduced into the environment via various events, notably fallout from the atmospheric weapons testing and accidental release [2]. As an important source of radioactivity in the radioactive waste, cesium has posed serious environmental threats because of its high solubility and ability to move with aqueous media in the subsurface. Furthermore, as its chemical similarity to potassium, cesium is readily assimilated by terrestrial and aquatic organisms [3].

The removal of Cs^+ from water can be achieved through chemical precipitation and conventional coagulation. However, these approaches cannot reach the emission standards imposed for radioactive wastewater and even generate a large amount of sludge difficult to handle [4]. More effective purification methods such as membrane process and ion-exchange column are costly and unsuitable for industrial processing. The adsorption technique has been found to be effective and practical in application for the radioactive wastewater treatment because of its simplicity, high efficiency, and the availability of a wide range of adsorbents [5–7]. Among the adsorbents, clay minerals are the commonly used adsorbents for their abundance, low cost and environment-friendly nature [8].

Vermiculite is a clay mineral composed of octahedral alumina or magnesia sandwiched between two tetrahedral silicate sheets [9]. It possesses a high cation exchange capacity due to surface and interlayer ion exchange process, as well as isomorphic substitution. The properties of swelling capacity, chemical and mechanical stability have made vermiculite an efficient adsorbent for radioactive waste [10]. However, considering the limited affinity for some radionuclides, different methods have been tried to enhance the adsorption capacity of natural clay minerals. Inorganic acid activation can significantly improve the specific surface

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area and porosity of vermiculite [11]. While, as noted by previous studies, the loss of exchangeable cations and the collapse of layer structure may exert adverse impacts on the adsorptive property of acid clays [12]. Currently, many researches are interested in organically modified clays (organoclay). Various organoclays have been proven effective in removing heavy metals and radionuclides [13–16]. And ion exchange with alkyllammonium ions is a well-known method for the preparation of organoclays [17,18]. However, organic modifiers especially the long-chain alkyl organic cations can also block the pore channels of clay, leading to a significant decrease in the specific surface area and pore volume [19]. There is a great demand for developing novel modifiers to solve these problems. Most researches prefer to choose ionic surfactants as modifying agents. The research about clay's modifications formed with organic neutral molecules is still limited. Amines acted as neutral molecules, may enhance clay's adsorption capacity towards heavy metals because of the free pair of electrons present on nitrogen atoms. Several studies of lamellar compounds modified with different kinds of amine such as secondary, tertiary, cyclic, or aromatic amines have been reported [20]. In our previous study, ethylamine modified montmorillonite was prepared and the Cs^+ adsorption capacity of montmorillonite was increased by ethylamine. Moreover, the results revealed that the adsorption of ethylamine modified montmorillonite was regulated by ion exchange and the coordination of $-NH_2$ [21]. In order to further study the corrosion of ethylamine on clay surface, ethylamine was selected as a modifying agent to treat with vermiculite in this research.

So the focus of this study is to prepare ethylamine modified vermiculite with larger surface area and abundant pore structure for efficient Cs^+ removal from aqueous solution. The adsorption performance of pristine vermiculite and ethylamine modified vermiculite were investigated with respect to Cs^+ removal from aqueous solution. The adsorption equilibrium, kinetics and the effect of pH, coexisting cations and low-molecular-weight organic acids are discussed in detail. Structure and surface properties of Ethyl-VER and VER were analyzed with XRD, FTIR, BET and SEM/EDS to support our findings.

2. Experimental methods

2.1. Materials

The vermiculite sample, supplied by Sigma–Aldrich, has a cation exchange capacity (CEC) of 0.85 meq g^{-1}. Ethylamine (68.0–72.0% in H_2O) and CsCl were purchased from Aladdin Chemistry Co. Ltd. The chemicals adopted in the study including KCl, NaCl, $CaCl_2 \cdot 2H_2O$, acetic acid, oxalic acid, citric acid, HCl and NaOH which are of analytical reagent grade, were provided by Guangzhou Chemical Reagent Factory (Guangdong Province, China).

2.2. Preparation of modified vermiculite

Vermiculite samples were thoroughly washed with distillated water to remove impurities. The modified vermiculite was prepared by mixing ethylamine with 5% washed vermiculite suspension until the ratio of $n_{\mathrm{ethylamine}}/m_{\mathrm{vermiculite}}$ was 2.55 mmol/g. The mixed suspension was shaken in a water bath oscillator at 30 °C for 24 h. Thereafter, the modified clay was centrifuged and washed three times with distilled water to remove excess ethylamine, oven-dried at 60 °C until constant weight. The final product was named Ethyl-VER and grinded to pass through a 200-mesh sieve before use.

2.3. Instruments and methods of analysis

The XRD patterns of the samples were measured with a Bruker D8 ADVANCE diffractometer equipped with Cu Kα radiation at 40 kV and 40 mA, using a step size of 0.02°, a rate of 17.7 s $step^{-1}$, a range of 3–40°. The samples were over dried for 24 h at 60 °C, pulverized to pass through a 200-mesh sieve, and sealed in bottles for the next step.

The FTIR spectra were recorded using the KBr pellet technique on a PerkinElmer 1725X FTIR spectrometer, over the spectral range of 4000–400 cm^{-1} with 4 cm^{-1} resolution.

The BET surface area and pore size distribution were determined by N_2 adsorption–desorption isotherm measured by a specific surface area analyzer (Micromeritics, ASPA 2020). The samples were degassed at 80 °C for 12 h.

The SEM images of adsorbents were recorded by a field emission scanning electron microscope (Carl Zeiss EVO LS10). Coarse elemental analysis was performed with energy dispersive X-ray spectroscopy (IE250X Max50) equipped on the scanning electron microscope. The samples were disposed under about 30 min ultrasound by dispersing approximately 0.2 g powder with 15 mL ethanol. Dispersion was added to a carbon platform with solid surface, and excess solution was blotted off by a filter paper.

2.4. Adsorption study

Stock Cs^+ solution was prepared by dissolving CsCl in distilled water and used to prepare the adsorbate solution with appropriate dilution. The pH of the solution was measured by a pH meter (PHS-2, Three Letters Instrument Factory, Shanghai) and adjusted with negligible volume of 0.1 M HCl and NaOH. Batch adsorption experiments were conducted at 30 ± 1 °C. Briefly, 0.05 g adsorbent and 25 mL Cs^+ solution were added in 50 mL erlenmeyer flask. The suspension was shaken for a fixed period of 2 h in a rotary shaker and then centrifuged at 12,000 rpm for 2 min. The supernatant was filtered preliminarily through a 0.45 μm fiber membrane. Quantitative analysis of Cs^+ in solution was made by Hitachi Z-2000 Zeeman Atomic Absorption Spectrophotometer with air-acetylene flame. Besides, the effect of pH (1–12), initial concentration (20–200 mg L^{-1}), contact time (2–240 min), coexisting cations (0.01–0.1 M K^+, Na^+ and Ca^{2+}) and low-molecular-weight organic acids (0.001–0.008 M acetic acid, oxalic acid and citric acid) were conducted in the similar manner to find out the appropriate adsorption condition. All experiments were performed in duplicate.

The amount of adsorbed Cs^+, q (mg g^{-1}) is obtained by the differences between initial and equilibrium Cs^+.

$$q = \frac{(C_0 - C)V}{W}$$

where C_0 (mg L^{-1}) and C (mg L^{-1}) are initial and equilibrium Cs^+ concentration in solution, respectively; V (L) is the volume of solution and W (g) is the weight of adsorbent.

3. Results and discussion

3.1. Materials characteristics

3.1.1. XRD analysis

Fig. 1 illustrates the XRD patterns of VER and Ethyl-VER. The characteristic diffraction peak (001) of VER is found at 6.1° with the characteristic basal spacing (d_{001}) of 1.49 nm. The peaks at 7.4° and 10.5° correspond to the impurity of mica mineral in vermiculite [22], while a peak at 17.62° is due to low amount with octahedral iron [9]. After leaching of ethylamine solution, the peak