



Full Length Article

Performance and mechanism of simultaneous removal of Cd(II) and Congo red from aqueous solution by hierarchical vaterite spherulites

Yuan-Yuan Chen^a, Sheng-Hui Yu^a, Hao-Fan Jiang^a, Qi-Zhi Yao^{b,*}, Sheng-Quan Fu^c, Gen-Tao Zhou^{a,*}^a CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, PR China^b School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, PR China^c Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, PR China

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ABSTRACT

Hierarchical vaterite spherulites, synthesized by a simple injection-precipitation method at room temperature, were applied for the simultaneous removal of heavy metal Cd(II) and dye Congo red (CR) from aqueous solution. Batch experiments reveal that the maximum removal capacities of as-prepared vaterite spherulites to Cd(II) and CR are 984.5 and 89.0 mg/g, respectively, showing excellent removal performance for Cd(II) and CR. Furthermore, in the binary Cd(II)-CR system, the removal capacity of vaterite to Cd(II) is significantly enhanced at lower CR concentration (<100 mg/L), but inhibited at higher CR concentration (>100 mg/L). In contrast, the concurrent Cd(II) shows negligible effect on the CR removal. The simultaneous removal mechanism was investigated by FESEM, EDX, XRD, FT-IR and XPS techniques. The simultaneous removal of Cd(II) and CR in the binary system is shown to be a multistep process, involving the preferential adsorption of dye CR, stabilization of CR to vaterite, coordination of the adsorbed CR molecules with Cd(II), and transformation of vaterite into otavite. Given the facile and green synthesis procedure, and effective removal of Cd(II) and CR in the binary system, the obtained vaterite spherulites have considerable practical interest in integrative treatment of wastewater contaminated by heavy metals and dyes.

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1. Introduction

Recently, combined pollution has been an increasingly hot topic in environmental studies. In particular, heavy metals and dyes often coexist in the effluents of textile, leather, cosmetic and papermaking industries because of the wide application of heavy metals (e.g., cadmium, copper and aluminum) in the dyeing process as mordant [1–3]. Both heavy metals and dyes could cause serious damages to human health due to their strong toxicity, environmental persistence and bioaccumulation [4,5]. For example, cadmium is a common hypertoxic contaminant [6]. Cadmium exposure can cause many diseases, such as emphysema, hypertension, diabetes mellitus and skeletal malformation due to the lack of homeostatic control for cadmium in the human body [7]. Congo Red (CR), one of the most widely used anionic disazo dyes, can be metabolized to cancerigenic benzidine in aquatic environment [8,9]. Currently, numerous conventional techniques are mainly focused on the removal of a single class of contaminants

(either heavy metals or dyes) [10–13]. However, the different physicochemical properties of heavy metals and dyes make the treatment of wastewater more challenging [14]. Growing evidence also suggested that the combined toxicities of heavy metal ions and dyes are generally larger than the simple adduct of their individual toxicity [15,16]. Therefore, developing facile and environmentally benign materials to simultaneously remove heavy metals and dyes from wastewater is urgent and crucial.

Calcium carbonate, occurring geologically as one of the main mineral constituents of sedimentary rocks and biologically as inorganic components in the skeletons of many mineralizing organisms [17,18], is one of the most abundant minerals in nature. It exists in three anhydrous crystal polymorphs: rhombohedral calcite, orthorhombic aragonite, and hexagonal vaterite [19]. Among them, calcite is the stable form under ambient conditions, aragonite is the high-pressure polymorph, while vaterite is thermodynamically unstable [20]. Calcium carbonate has important industrial applications in the areas of plastics, rubbers, papermaking, biomedical implant and drug delivery [21,22]. In recent years, numerous investigations have demonstrated that calcium carbonate could act as a cost-effective green material to remove heavy

* Corresponding authors.

E-mail address: gtzhou@ustc.edu.cn (G.-T. Zhou).

metals from wastewater [23–31]. For example, waste calcite sludge, an industrial waste material, could be used for the removal of Cd(II), Cu(II), Pb(II), and Zn(II) from aqueous solution [24]. Biogenic aragonite and calcite mollusk shells also exhibited high sorption capacities to Pb(II), Cd(II) and Zn(II) from contaminated water [27]. Hybrid calcite-pepsin hemispheres prepared by vapor-diffused method were applied to the removal of Cu(II) and Pb(II) [28]. Compared with calcite and aragonite, vaterite usually has high specific surface area, high dispersion and small specific gravity [32]. Additionally, the solubility product of vaterite is reported to be $10^{-7.91}$ at 25 °C [33], which is higher than that of calcite ($10^{-8.48}$), aragonite ($10^{-8.34}$), and most heavy metal carbonates like otavite ($10^{-12.10}$), cerussite ($10^{-13.13}$) and smithsonite ($10^{-9.87}$) [23,34,35]. Thermodynamically, hexagonal vaterite is the most unstable phase relative to rhombohedral calcite, otavite, cerussite and smithsonite, as well as orthorhombic aragonite [19]. This fact may facilitate the transformation of vaterite into a heavy metal-rich carbonate in the presence of a solution containing these elements in a similar way to what has been observed for calcite and aragonite [36], enhancing the removal capacity of vaterite to heavy metal ions. Moreover, vaterite-based nanomaterials also exhibit excellent removal performance for dyes [31,37]. Therefore, vaterite may have potential application in the simultaneous removal of heavy metals and dyes from aqueous solution. However, to the best of our knowledge, no research has been reported on the simultaneous removal of heavy metals and dyes by calcium carbonate, especially by vaterite.

In this study, Cd(II) and CR were selected as model pollutants because Cd(II) and CR are typical pollutants in the dye wastewater. For instance, a study from an industrial estate of Mumbai, India suggested that the concentration of Cd(II) is up to 31.0 mg/L in dyes and textile effluents [38]. In addition, Congo red (CR) is reported to be one of the commonest disazo dyes in the wastewaters of textiles, printing, dyeing, paper, rubber and plastics industries [8,9]. Herein, the hierarchical vaterite spherulites, synthesized by a facile injection-precipitation method at room temperature, were applied for simultaneous removal of Cd(II) and CR. The mutual effect between the copollutants in the binary system and the removal mechanism were systematically investigated.

2. Materials and methods

2.1. Materials

All chemical reagents were of analytic reagent grade and used as received without any further purification. CaCl_2 , Na_2CO_3 , CdCl_2 , Congo red (CR), HCl and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water purchased from Blue Science and Trade Co., Ltd (Anhui, China) was used in all the experiments.

2.2. Preparation of hierarchical vaterite spherulites

Vaterite synthesis experiments were carried out at room temperature by using an injection-precipitation method developed from our previous work [39]. Typically, 0.02 mol of CaCl_2 was dissolved in 220 ml of deionized water in a 250 ml beaker to obtain a homogeneous solution (0.09 mol/L CaCl_2). Then 20 ml of Na_2CO_3 solution (0.5 M) was quickly injected into the CaCl_2 solution under magnetic stirring to form a white precipitate. After being continuously stirred for 2 min, the white precipitate was harvested by filtration, washed with deionized water and absolute ethanol several times, and finally dried in vacuum at room temperature for 12 h.

2.3. Characterization

Several analytical techniques were used to characterize the synthesized products. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Japan Map AHF X-ray diffractometer equipped with graphite monochromatized Cu $K\alpha$ irradiation ($\lambda = 1.5418 \text{ \AA}$), employing a scanning rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range of $10\text{--}70^\circ$. FT-IR spectra were measured on a Nicolet Magna IR-750 spectrophotometer from 4000 to 400 cm^{-1} at room temperature. The morphology and microstructure of the products were observed by JEOL JSM-6700F field-emission scanning electron microscopy (FESEM) equipped with X-MAX^N energy dispersed X-ray spectroscopy (EDX, Oxford Instruments). Before the FESEM observation, the samples were loaded on a Cu foil, and then sprayed by Au. X-ray photoelectron spectra (XPS) were taken on a Thermo ESCALAB 250 X-ray photoelectron spectrometer with Al K α radiation. All spectra were calibrated with graphitic carbon as the reference at a binding energy of 284.6 eV to compensate for the surface charging effects. The XPSPEAK 4.1 software was used to fit the XPS spectra of each relevant element into subcomponents. The zeta potential of the materials was determined with NanoBrook Omni Zeta Potential Analyzer (Brookhaven Instruments Corporation, America).

2.4. Removal experiments

The removal behavior of the vaterite spherulites to Cd(II) or CR was firstly investigated individually. All removal experiments were conducted by mixing 0.05 g of the scavenger (vaterite spherulites) with 50 mL of Cd(II) ($C_{\text{Cd(II), initial}} = 500 \text{ mg/L}$) or CR ($C_{\text{CR, initial}} = 20 \text{ mg/L}$) solution at room temperature. To determine the optimal pH condition for the removal, the effect of pH on the removal ability of the scavenger was studied in a pH range of 3.0–7.0 for Cd(II) solution because Cd(OH)_2 can precipitate out of the solution when pH exceeds 8.0 ($K_{\text{sp, Cd(OH)}_2} = 10^{-15.00}$ [40]). A pH range of 3.0–11.0 was adopted for CR solution. The kinetics experiments of Cd(II) or CR sorption by the vaterite spherulites were carried out at 5–150 min. After the established contact time, the precipitate was separated from the mixture by centrifugation at 10,000 rpm for 10 min. The residual concentration of Cd(II) in the supernatant was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 7300 DV). Inductively coupled plasma mass spectrometry (ICP-MS, Plasma Quad3) was used when the concentration of Cd(II) was below 0.1 mg/L. The Ca(II) concentration released from the vaterite was also measured by the same techniques as the Cd(II). Residual dye CR concentration in the supernatant was determined by UV–vis spectrometry (TU-1901, Beijing Purkinje General Instrument Co., Ltd.) at a wavelength of the maximum absorbance of CR ($\lambda_{\text{max}} = 497 \text{ nm}$). In addition, to understand the mutual effect of the concurrent Cd(II) and CR on their removal by vaterite, a series of binary sorption experiments were performed by varying Cd(II) (0–1800 mg/L) or CR (0–300 mg/L) concentration with another one fixed at pH 6.0. All removal experiments were run in triplicate, and averaged values were reported. The removal capacity q_e (mg/g) and removal percentage $W\%$ was calculated according to following equations, respectively:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$W\% = \frac{(C_i - C_t)100\%}{C_i} \quad (2)$$

where C_i (mg/L), C_e (mg/L) and C_t (mg/L) are the liquid phase concentration of Cd(II) or CR at initial, equilibrium and any time t , respectively. V is the volume of the solution (L), and m is the mass of vaterite spherulites added (g).

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