



Removal performance and the underlying mechanisms of plasma-induced CD/MWCNT/iron oxides towards Ni(II)

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HIGHLIGHTS

- Magnetic CD/MWCNT/iron oxides were synthesized by low-temperature plasma technique.
- CD/MWCNT/iron oxides exhibited high physicochemical stability in aqueous solution.
- CD/MWCNT/iron oxides exhibited favorable removal performance towards Ni(II) in the simulated effluent.
- XAFS analysis suggested that Ni(II) was retained on the surface-coated β -CD and the inner iron oxides.
- CD/MWCNT/iron oxides can be repeatedly used for cost-effective purification of Ni(II)-bearing wastewater.

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ABSTRACT

Herein, a novel low-temperature plasma technique was adopted to graft β -cyclodextrin (β -CD) on the surfaces of magnetic MWCNT/iron oxide particles. The as-prepared CD/MWCNT/iron oxides exhibited high saturation magnetization and good physicochemical stability in solution. Batch experiments and X-ray absorption fine structure (XAFS) spectral technique were combined to verify the removal performance and the underlying mechanisms of CD/MWCNT/iron oxides towards Ni(II) from single-solute system and the simulated Ni(II)-bearing effluent. The sorption kinetics of Ni(II) on CD/MWCNT/iron oxides can achieve equilibrium in a time period of 4 h. The surface-coated β -CD improves the dispersion property of CD/MWCNT/iron oxides and therefore enhances its removal performance towards Ni(II). The maximum sorption capacity of Ni(II) on CD/MWCNT/iron oxides is higher than a series of adsorbent materials. XAFS analysis suggests that Ni(II) can bind on the hydroxyl sites on the surface-coated β -CD and also the FeO₆ octahedra of iron oxides in an edge-shared mode, forming strong inner-sphere complexes with high thermodynamic stability. Considering its high physicochemical stability, high removal performance, high separation convenience and favorable regeneration property, the prepared CD/MWCNT/iron oxides can support long-term use as a cost-effective material in the purification of Ni(II)-bearing effluents.

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1. Introduction

Nowadays, the continuous increase of various industrial and agricultural activities discharges a series of inorganic and organic pollutants into the soil and water media. Owing to their non-biodegradable property and biological accumulation effect, the toxic heavy metal ions exhibit adverse, acute and even fatal impacts on ecological safety, aquatic organisms and human health over a long period [1,2]. For instance, the excess intake of heavy metal nickel (Ni(II)) would cause serious diseases such as hepatitis,

hypertension, anemia, muscle cramp, diarrhea and nephritic syndrome [3,4]. In view of this, advanced techniques and adsorbent materials are badly in need for the decontamination of Ni(II) from wastewaters.

Among the current methods for sewage treatment, sorption approach has been widely adopted due to its easy handling, low cost and high efficiency. A series of methods including hydrothermal route, chemical co-precipitation, chemical vapor composition and electrochemical composition have been adopted to synthesize various adsorbents. The derived composites exhibit favorable removal performance towards various heavy metal ions in the aquatic systems [5–9]. In recent years, magnetic composites have been applied in sewage treatment due to their high sorption capacity and high separation convenience [10–12].

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Plasma technique is a novel method to active the substrate material surfaces without altering their bulk properties [13–15]. The activated substrates with high reactivity can be easily decorated by a variety of functionalized polymers and further applied in various research fields. In the present study, magnetic MWCNTs/iron oxides were firstly prepared via the co-precipitation approach. Afterwards, β -cyclodextrin (β -CD) macromolecules were grafted on the surfaces of as-prepared MWCNTs/iron oxides with a novel low-temperature plasma technique. The physicochemical stability of the prepared CD/MWCNT/iron oxides was tested by measuring the amount of Fe leaching into the solution. Batch experiments were conducted to evaluate the removal performance of CD/MWCNT/iron oxides towards heavy metal Ni(II) as a function of various environmental factors. The regeneration property of CD/MWCNT/iron oxides towards Ni(II) removal was tested by multiple sorption/desorption cycles. In addition, X-ray absorption fine structure (XAFS) spectral technique was adopted to identify the underlying mechanisms of Ni(II) sorption on CD/MWCNT/iron oxides. Finally, the environmental significance of the present research findings was further predicted on the basis of the macroscopic and microscopic results.

2. Materials and methods

2.1. Materials

The β -cyclodextrin (β -CD), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were purchased in analytical pure from Sinopharm Chemical Reagent Co. Ltd. (China). The analytical pure $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized water to obtain the Ni(II) stock solution (100 mg/L). The prepared Ni(II) stock solution were diluted to achieve the desired concentrations in the following sorption experiments.

2.2. Synthesis and characterization of CD/MWCNT/iron oxides

The procedures for fabricating the CD/MWCNT/iron oxides consisted the preparation of MWCNT/iron oxides, the activation of MWCNT/iron oxide surfaces by using low-temperature plasma and the grafting of β -CD on surface-activated MWCNT/iron oxides. The specific surface area of CD/MWCNT/iron oxides was measured to be $63.9 \text{ m}^2/\text{g}$ by using the N_2 -BET method. The previous TGA analysis result showed that the grafted amount of β -CD on MWCNT/iron oxides was 16.6 mg/g [16]. The saturation magnetization (M_s) of CD/MWCNT/iron oxides was measured to be 37.8 emu/g . The XRD analysis showed that the chemical co-precipitation procedure, plasma activation and the subsequent decoration of β -CD did not disorganize the basic structure of MWCNTs [17].

2.3. Material stability test

The prepared MWCNT/iron oxides and CD/MWCNT/iron oxides were suspended in a series of solutions with pH 2.0–10.0 to test their physicochemical stability. The solid and aqueous phases were separated by using an external magnet after oscillating the suspensions for a contact time of 24 h. The dissolved Fe contents at different pH values were determined by using the atomic absorption spectrometry.

2.4. Sorption experiments

All the experiments were performed in 10-mL polyethylene centrifuge tubes by using batch technique. Briefly, the CD/MWCNT/iron oxide suspension, NaNO_3 electrolyte solution and

Ni(II) stock solution were added to attain the required concentrations of each constituent. The suspension pH was regulated to the desired values by adding tiny amounts of 0.01 mol/L HNO_3 or NaOH solutions. The centrifuge tubes were gently oscillated for 24 h to achieve sorption equilibrium and then the solid and aqueous phases were separated with a permanent magnet. The concentration of Ni(II) in the supernatant was measured by using atomic absorption spectrophotometry. The sorption percentage ($S\% = ((C_0 - C_e)/C_0) \cdot 100\%$) and sorption amount ($q_e = ((C_0 - C_e) \cdot V/m)$) were derived from the initial Ni(II) concentration (C_0), the final Ni(II) concentration (C_e), the mass of CD/MWCNT/iron oxides (m) and the suspension volume (V).

2.5. XAFS data collection and analysis

The sorption sample for XAFS analysis was prepared in 250 mL vessel by using a similar approach as the batch experiments. Briefly, the Ni(II) stock solution was tardily added in 10–50 μL increments into the CD/MWCNT/iron oxide suspension under constant stirring. The mixture was held steadily at pH 6.5 and shaken on a rotating oscillator for 24 h. The solid and aqueous phases were separated by using an external magnet. The collected wet pastes were then wrapped in a moist paper towel and sealed in a Ziplock bag for the subsequent XAFS data collection.

The Ni K-edge XAFS spectra were collected at the BL14W1 beam line in Shanghai Synchrotron Radiation Facility (SSRF, China) in fluorescence mode for $\text{Ni}(\text{NO}_3)_2(\text{aq})$ reference sample and the sorption sample and in transmission mode for $\text{Ni}(\text{OH})_2(\text{s})$ reference sample. The electron beam energy was 3.5 GeV and the mean stored current was 300 mA. The energy of the X-ray was tuned by using a double-crystal Si (1 1 1) monochromator. The XAFS signals of samples were collected with a multi-element high purity Ge solid-state detector. Each XAFS spectrum was collected in triple and averaged to improve the signal to noise ratio. The energy correction, fluorescence dead time calibration and the subsequent XAFS data fitting were performed by using the Athena and Artemis software. During fitting, the amplitude reduction factor (S_0^2) was fixed to 0.85 for all the samples. The total number of variable parameters did not exceed the maximum limit given by Stern's rule. The accuracies of R and CN values for the first coordination shells were 0.02 Å and 20%, and those for the second coordination shells were 0.03 Å and 40%.

3. Results and discussion

3.1. Material stability

Fig. 1 illustrates the effect of solution pH on the content of Fe leaching from the MWCNT/iron oxides and CD/MWCNT/iron oxides. It is clear that the Fe leaching content decreases with increasing pH values for the two Fe-containing samples. The content of Fe leaching from the CD/MWCNT/iron oxides is much lower than that of Fe leaching from the MWCNT/iron oxides in the acidic pH range, which suggests that the surface-grafted β -CD prevents the dissolution of Fe from the oxidized MWCNT surfaces and therefore improves the physicochemical stability of CD/MWCNT/iron oxides in acidic solution. The high stability supports the use of CD/MWCNT/iron oxides as a potential material for the purification of Ni(II)-bearing wastewater.

3.2. Effect of contact time

Fig. 2 shows the kinetic data of Ni(II) sorption on CD/MWCNT/iron oxides as a function of initial Ni(II) concentration. The sorption amount of Ni(II) increases rapidly during the initial contact time of

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