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Short communication

Polyacrylonitrile/manganese acetate composite nanofibers and their catalysis performance on chromium (VI) reduction by oxalic acid

Chengcheng Zhang, Xiang Li*, Xiujie Bian, Tian Zheng, Ce Wang*

Jilin University Alan G MacDiarmid Institute, Changchun 130012, China

HIGHLIGHTS

- We have successfully prepared PAN/$Mn(CH_3COO)_2$ composite nanofibers.
- The nanofibers exhibit excellent catalysis performance for Cr(VI) reduction.
- The nanofibers are effective and environment-friendly materials to remove Cr(VI).

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ABSTRACT

Polyacrylonitrile(PAN)/manganese acetate($Mn(CH_3COO)_2$) composite nanofibers have been fabricated by electrospinning, a simple and effective technology. The obtained composite nanofibers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectrometer (FT-IR). The composite nanofibers are amorphous in structure, continuous, even and smooth. At the same time, the reduction performance of Cr(VI) by oxalic acid in the presence of the composite nanofibers is also investigated. The results indicate that the composite nanofibers have exhibited excellent catalysis performance for Cr(VI) reduction from a $Cr_2O_7^{2-}$-containing solution by oxalic acid. And the critical parameters, such as the catalyst dosage, oxalic acid content, chromium concentration, the pH value of the reaction solution and light have important impact on the reduction process. Under the simulated solar light irradiation, after only 60 min, 1.2 mM initial Cr(VI) solution was reduced absolutely in the presence of PAN/$Mn(CH_3COO)_2$ composite nanofibers containing 17.5 wt.% $Mn(CH_3COO)_2$ by 0.3 mL 0.5 M oxalic acid. In light, the reduction of Cr(VI) by oxalic acid is markedly accelerated.

1. Introduction

Chromium (Cr) and chromium compounds are widely used in many industrial processes such as printing inks, leather tanning, textile dyeing, chromium plating, electroplating, paints and pigments as critical industry materials [1,2]. However, with the development of industries, chromium becomes one of the most hazardous heavy metal pollutants in industrial waste water due to improper disposal of wastes and accidental releases. Usually, Cr exists mainly in hexavalent [Cr(VI)] and trivalent [Cr(III)] forms in the natural environment [2,3]. Cr(VI), which is highly soluble and mobile in aquatic systems, is not only highly toxic but also carcinogenic to humans, animals and plants. In contrast, Cr(III) is less toxic and normally precipitates as $Cr(OH)_3$ or $Fe_xCr_{1-x}(OH)_3$ in soil and water [4], and easily adsorbs on the mineral surface. Therefore, the key strategy to remove chromium pollution is to transform the pollutants from Cr(VI) to Cr(III) based on Cr(VI) reduction. As a result, considerable attention has been focused on looking for effective reduction methods for the treatment of chromium pollution. Thus, many reductants such as polyaniline [2], zero-valent iron [5], divalent iron [6] and sulfide [7] have been utilized.

Soil organic matter can effectively reduce Cr(VI) to Cr(III). The reduction of Cr(VI) by various organic matters (citric acid [8], salicylic acid [9], tartaric acid [3] and humic acid [10]) has been the investigation subject of a great many researchers. However, the reaction between Cr(VI) and soluble soil organic substances is slow. Dissolved and surface-bound metal ions could effectively catalyze organic matters to reduce Cr(VI) to Cr(III). Li et al. [4] found that the externally added Mn(II) strongly catalyzed the reduction of Cr(VI) by citrate acid, with the higher initial Mn(II) concentration having higher Cr(VI) reduction rate. Lan et al. pointed out that the role of clay minerals in accelerating the reduction reaction of Cr(VI) by citric acid directly correlated with the amount of adsorbed Mn(II) ions on the surfaces. And the reduction of Cr(VI) by citric acid is increased markedly in illumination in the presence of Fe(III) [11]. However, in the Cr(VI) reduction process, great quantities of

* Corresponding authors. Tel.: +86 431 85168292; fax: +86 431 85168292.
E-mail addresses: xiangli@jlu.edu.cn (X. Li), cwang@jlu.edu.cn (C. Wang).

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metal ions are consumed. Besides, these metal ions also generate secondary waste. Therefore, exploiting an effective, environment-friendly and economical material to remove Cr(VI) fast for practical application is very necessary.

Electrospinning technology is known to be a simple and versatile method to generate nano- to sub-micrometre fibers [12]. The electrospinning technique was first developed for the synthesis of nanofibers since 1934 [13]. It is a process which uses a strong electrostatic force by a high static voltage applied to a polymer solution placed into a container that has a millimetre diameter nozzle. Under the applied electrical force, the polymer solution is ejected from the nozzle. After the solvents evaporate during the course of jet spraying, the nanofibers are collected on a grounded collector [14]. The obtained polymer composite nanofiber films have good orientation, large specific surface area, large aspect ratio, and dimensional stability, which are widely applied in wastewater treatment, such as heavy metal ion or dye adsorption [15,16] and Cr(VI) reduction [17]. It is known that some functional groups (>C=O, –CN, OC–N, etc.) of organic compounds can interact with metal ions. Especially, the nitrile group of polyacrylonitrile (PAN), a common, cheap and non-toxic polymer material used for electrospinning, can form a weak complex with cations, or $CH_2CH(CN)^{-}\cdots M$ ($M = Zn^{2+}$, Fe^{3+}, Fe^{2+}, Li^{+}, Na^{+}, K^{+}) [17–19]. For instance, Lin et al. has fabricated polyacrylonitrile/ferrous chloride composite porous nanofibers and found that the composite nanofibers exhibited excellent performance for Cr-removal from a $Cr_2O_7^{2-}$-containing solution [17]. In the present paper, we prepared PAN/$Mn(CH_3COO)_2$ composite nanofibers and demonstrated that the composite nanofiber membrane can catalyze the reduction of Cr(VI) into Cr(III) rapidly and effectively from a $Cr_2O_7^{2-}$-containing solution by oxalic acid. The Cr-reduction capability is about 187.2 mg Cr/g nanofibers, which is much higher than the previously reported value for other polyacrylonitrile-based materials as PAN/$FeCl_2$ porous nanofibers that give a removal capacity of 11.7 mg Cr/g nanofibers [17], and it is also easier to separate from the solution.

2. Experimental

2.1. Materials

Potassium dichromate ($K_2Cr_2O_7$) and oxalic acid were purchased from Beijing Chemical Factory. N,N-dimethylformamide (DMF) was supplied by Tianjin Tiantai Chemical Factory. Manganese acetate tetrahydrate [$Mn(CH_3COO)_2{\cdot}4H_2O$] was purchased from Tianjin Guangfu Chemical Factory. All the above chemicals were analytical grade and used as received without further purification. Polyacrylonitrile (PAN, $M_w \approx 80{,}000$) was purchased from Jilin Carbon Group.

2.2. Preparation of PAN/$Mn(CH_3COO)_2$ composite nanofibers films

In a typical procedure, 10 g DMF solution of PAN (9 wt.%) containing 0.27 g $Mn(CH_3COO)_2{\cdot}4H_2O$ was delivered to a plastic syringe (inner diameter: about 1 mm). As a high voltage of 15 kV was applied, the solution jet accelerated towards the cathode, which was placed 15 cm from the needle tip, leading to the formation of nanofibers arrays containing 17.5 wt.% $Mn(CH_3COO)_2$ onto the substrate accompanied by partial solvent evaporation. Similarly, pure PAN nanofibers without $Mn(CH_3COO)_2$ and PAN/$Mn(CH_3COO)_2$ composite nanofibers containing 22.0 wt.% $Mn(CH_3COO)_2$ were also prepared under the same conditions.

2.3. Characterization

The morphology of the composite nanofibers was observed by scanning electron microscopy (SEM, SHIMADZU SSX-550). The microstructure of the samples was characterized by X-ray diffraction (XRD) equipment (Siemens D5005 diffractometer using Cu Kα radiation) in the scan range 2θ between 5° and 70°. IR spectra were obtained on a Fourier transform infrared spectrometer (FT-IR, BRUKER VECTOR 22). The concentration of Cr(VI) was analyzed by using a UV-2501 PC Spectrometer. The amounts of Mn(II) ion and the total Cr were determined using an inductive coupled plasma emission spectrometer (ICP, PerkinElmer OPTIMA 3300DV). The pH values of the reaction solutions were measured by using a pH meter (Orion 410A+, Thermo).

2.4. Cr(VI) reduction measurements

The aqueous solutions with different Cr(VI) concentrations were prepared by dissolving analytical grade potassium dichromate ($K_2Cr_2O_7$) in deionized water. Oxalic acid solution was prepared by dissolving appropriate quantity of the solids in deionized water. 30 mL Cr(VI) solution of desired concentration was taken into the 50 mL flask and the pH value of solution was adjusted by 1 M HCl or 1 M NaOH to get the pH value at 3, 6, 9 and 11. The required content of oxalic acid with the concentration of 0.5 M was added. The addition of oxalic acid would reduce the solution pH. After addition of 0.3 mL 0.5 M oxalic acid in the 30 mL 1.2 mM Cr(VI) solution of pH 3, 6, 9 and 11, the solution pH was reduced down to 2.3, 2.5, 2.7, 3.7. After stirring for a moment, the zero time reading was obtained from the mixing solution. Fixed qualities of the composite nanofibers were added to the mixing solutions, and then aliquots of the reaction mixture were removed at definite time intervals. The progress of the reaction was followed at 349 nm by monitoring the changes in absorbance of $K_2Cr_2O_7$ solution on a UV–vis spectrophotometer [20]. The reduction of Cr(VI) could be calculated by $D = C/C_0 = A/A_0$, in which C_0 and A_0 are the initial concentration and absorbency of $K_2Cr_2O_7$ before reaction, while C and A are the equilibrium concentration and absorbency of $K_2Cr_2O_7$ at homologous time. To investigate the influence of the light on the Cr(VI) reduction reaction, we used a 500 W Xenon lamp (CHFXQ500W, 14200 LX) to provide the simulated solar light and visible light with a UV filter to isolate the UV light of wavelengths shorter than 420 nm.

3. Results and discussion

3.1. Morphology and structure

The morphology of the electrospun nanofibers containing different $Mn(CH_3COO)_2$ contents before and after catalytic reaction was examined using SEM. It was found that the $Mn(CH_3COO)_2$ content had a marked influence on the morphology and fiber diameter of the nanofibers. From Fig. 1a, the nanofibers containing 17.5 wt.% $Mn(CH_3COO)_2$ were randomly distributed on the substrate, continuous, uniform and even with diameters between 200 and 350 nm. By contrast, the diameters of the nanofibers containing 22.0 wt.% $Mn(CH_3COO)_2$ were much larger, about 1.1–1.3 μm (Fig. 1b). As shown in Fig. 1c and d, after the catalytic reaction, a well-defined fiber texture kept unchanged for the nanofibers with different $Mn(CH_3COO)_2$ contents.

Furthermore, we also investigated the microstructure of the composite nanofibers containing 22.0 wt.% $Mn(CH_3COO)_2$ in more detail. The XRD spectra of $Mn(CH_3COO)_2{\cdot}4H_2O$ powders, pure PAN nanofibers and the composite nanofibers containing 22.0 wt.% $Mn(CH_3COO)_2$ were shown in Fig. 2A. A crystalline peak (17°) corresponding to the orthorhombic PAN (1 1 0) refection [21], a broad