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In situ growing directional spindle TiO_2 nanocrystals on cellulose fibers for enhanced Pb^{2+} adsorption from water

Yanxiang Li[a], Lixia Cao[a], Lei Li[a,b], Chuanfang Yang[a,*]

[a] *National Key Laboratory of Biochemical Engineering, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China*
[b] *University of Chinese Academy of Sciences, Beijing 100190, China*

HIGHLIGHTS

- Spindle TiO_2 nanocrystals were *in situ* synthesized on cellulose fibers (CF).
- Cellulose acted as a template to direct TiO_2 crystal growth with orientation.
- Minute amount of spindle TiO_2 enhanced Pb^{2+} adsorption capacity.
- Dynamic adsorption with TiO_2/CF membrane outperformed CF membrane significantly.

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ABSTRACT

TiO_2/cellulose nanocomposite was synthesized by *in situ* generation of titanium dioxide (TiO_2) nanocrystals on cellulose fibers (CF) *via* facile hydrolysis of $TiOSO_4$. Cellulose was intended as a scaffold to immobilize TiO_2 nanoparticles (NPs), but turned out surprisingly to be also a chemical template that directed the crystal growth. As a result, spindle rutile TiO_2 crystals were nicely formed on the surface of cellulose. These crystals were further controlled to disperse uniformly without agglomeration for better use of their surface area to adsorb heavy metals. The TiO_2/CF composite showed enhanced adsorption capacity, good regenerability and selectivity for lead (Pb^{2+}) removal. In addition, the composite fibers were readily fabricated into a nonwoven filter bed through which dynamic filtration experiment was conducted. A 12-fold increase in filtered bed volume was achieved for TiO_2/CF bed compared with pure CF bed before breakthrough took place. This work provides a green pathway for fabricating low cost, high efficiency and engineering application possible nanosorbents for water decontamination.

1. Introduction

Heavy metal pollution has always been a concern worldwide because these metals are toxic and nonbiodegradable [1,2]. Their presence in water poses significant threat to environment and public health. Lead (Pb^{2+}) is regarded as one of the most toxic heavy metals. The current allowable maximum contamination level of Pb^{2+} in drinking water set by US EPA is 15 ppb. Chemical precipitation, ion exchange, membrane separation, electrochemical method and adsorption have been used to remove heavy metals from aqueous solutions. Among them, adsorption is a promising method because of its low cost and high efficiency, especially for low-level heavy metal treatment in wastewater. The key to the success of adsorption process lies in the selection of appropriate adsorbents [3,4].

Nanoparticles (NPs) are attractive and promising adsorption materials for application in water treatment due to their high specific surface area, reactivity and mobility [5–7]. Interestingly, the use of TiO_2 for removing heavy metals and other pollutants from water has been extensively studied due to the TiO_2's low-cost, nontoxicity, stability and easy availability [8–11].

However, nanoscale particles, when synthesized, in storage, during transportation or in use, tend to agglomerate and lose a fair amount of surface area which reduces their intended efficiency for target applications. When applied in a fixed bed for adsorption, these particles can cause some practical issues including inevitable particle loss and its induced secondary pollution, as well as high flow resistance [12]. As reported, the mobility of pollutants can often be enhanced or slowed by orders of magnitude because of the presence of colloidal particles in aquatic systems [13,14]. Although

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* Corresponding author. Tel.: +86 10 82544976.
E-mail address: cfyang@ipe.ac.cn (C. Yang).

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TiO_2 is thought to be environmentally benign, its accidental release to aquatic systems could still cause significant environmental risks. An effective approach to overcome the problems is to fabricate hybrid nanocomposite by immobilizing ultrafine particles onto materials orders of magnitude bigger [15].

Cellulose is the most abundant natural polymer on Earth [16,17]. Cellulose and its derivatives have demonstrated adsorption properties for heavy metals, especially when properly modified [18–20]. Cellulose fibers (CF) are soft and easy to process, they can be readily made into a form of filter bed/paper using traditional wet laid technology for practical applications. In addition, the abundant hydroxyl groups on CF surface can act as efficient hydrophilic sites to accelerate nucleation and growth of inorganic particles, thereby controlling the morphology, crystallinity and particle size. As reported elsewhere, such readily available cellulose matrices offered an ideal platform, either as templates or precursors [21–27], for the design and fabrication of hybrid nanocomposite with hierarchical structure. As such, various synthetic strategies have been attempted to anchor nanoTiO_2 onto cellulose matrix, such as dip coating [28,29], self-assembly [30,31], *in situ* hydrolysis [32] and hydrothermal treatment [25,33]. However, most of these TiO_2/cellulose composites are characterized as dense nanoTiO_2 coatings covering the whole cellulose surface, which are not intended for heavy metal removal by design. In this work, we used CF to immobilize TiO_2 NPs for water treatment by taking advantages of not only the adsorption efficiency of the composite material, but also the material' s greenability. We attempted not to compromise the needed surface area of the NPs by purposely controlling particle growth, so a scattered pattern of particle distribution on cellulose was obtained for effective adsorption. Phrased it in other words, we aimed to avoid forming a nanoparticle film on cellulose to sacrifice the surface area of the particles and the flexibility of the composite material in order to further process the material into a form of filter bed, for more convenient applications.

Considering the essential binding strength of nanoTiO_2 on cellulose, which is critical for applying the material under strong hydrodynamic conditions, here we chose a simple method, *in situ* hydrolysis, to synthesize TiO_2/CF composite. Meanwhile, we used a titanium oxysulfate-sulfuric acid complex hydrate ($TiOSO_4 \cdot H_2SO_4 \cdot H_2O$) as the precursor. This material is a low-cost and easy-to-handle chemical as opposed to other titanium salts. The as-synthesized TiO_2/CF nanocomposite showed unique surface morphology, especially for the nanoTiO_2 crystals because of their restrained growth on the cellulose template. More interestingly, the composite exhibited good Pb^{2+} adsorption performance in aqueous solutions in both static batch adsorption experiments and dynamic filtration experiments using a filter bed made of the composite fibers. The composite also showed good selectivity and regenerability for repeated use. And finally, the adsorption mechanism was discussed based on XPS and ATR-IR experiments, as well as surface area measurement of the composite.

2. Experimental

2.1. Materials

TiO_2 (rutile, 35 nm) was obtained from Beijing Dk Nano technology Co., Ltd. Titanium oxysulfate solution ($TiOSO_4 \cdot H_2SO_4 \cdot H_2O$, ~15 wt% in dilute sulfuric acid) was purchased from Aldrich. Cellulose fibers of 10–30 μm diameter were supplied by Beijing Ronel Engineering Materials Co., Ltd., and washed with distilled water before use. The sulphuric acid (H_2SO_4) with a concentration of 95–98% was supplied by Beijing Chemical Works. All other chemicals were analytical grade and used as received.

2.2. Synthesis of TiO_2/cellulose fiber composite

In a typical synthesis, 1.0 g cellulose fibers (CF) was suspended in 150 mL deionized water containing sulphuric acid (2.0 mL) under vigorous stirring, followed by dropwise addition of $TiOSO_4 \cdot H_2SO_4 \cdot H_2O$ (0.7 mL). The mixture was then kept under constant stirring at 70 °C for 4.5 h. The resultant TiO_2/CF composite fibers were collected and further processed by filtering, washing thoroughly with distilled water, and finally drying at 40 °C under vacuum. For comparative studies, pure CF fibers were treated with the same conditions using H_2SO_4 without $TiOSO_4$ addition.

2.3. General characterization

Scanning electron microscope (SEM) images were recorded on a JSM-6700F microscope. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction pattern (SAED) were performed using JEM-2100 TEM operated at 200 kV. To prepare the TEM samples, 10 mg TiO_2/CF composite was dispersed in 5 mL water followed by vigorous sonication (270 W, 24 h) to exfoliate TiO_2 particles from CF. Then a drop of the suspension was deposited on a carbon-coated copper grid and dried in air. The X-ray diffraction (XRD) patterns were observed on an XRD spectrometer (Rigaku Smartlab) with CuKα radiation and operated at 45 kV and 200 mA with a scanning rate of 5°/min. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALAB 250Xi electron spectrometer (Thermo Fisher Scientific). The binding energy scale for final calibration was corrected by the C1s peak corresponding to 284.8 eV. The metal ion concentration was analyzed using atomic absorption spectroscopy (AAS, Hitachi 2000). The detection limit is 0.2 mg/L.

2.4. Adsorption of heavy metal ions

The adsorption experiments were performed on a platform shaker at 150 rpm/min (25 ± 2) °C using 100 mL capped flasks. The effects of pH, initial Pb^{2+} concentration and contact time were investigated. Both 0.1 M HNO_3 and 0.1 M NaOH solution were used to adjust the pH values. The adsorption capacity q_e (mg/g) was calculated with Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 (mg/L) is the initial Pb^{2+} concentration, C_e (mg/L) is the equilibrium Pb^{2+} concentration, V (L) is the volume of the Pb^{2+} solution and m (g) is the mass of adsorbent. The adsorbent dose was kept at 0.4 g/L for all the adsorption experiments. As a comparison, the treated pure CF and commercial rutile TiO_2 were also studied under the same adsorption conditions.

After static adsorption experiment, the Pb^{2+} solution was separated from the solid adsorbents by filtering it through a cellulose acetate membrane of a 0.45 μm pore size. The possible existence of Ti element in the filtrate was checked on an inductively coupled plasma optical emission spectrometer (ICP–OES) (ICAP-6300, Thermo Scientific) at a wavelength of 334.94 nm. The filtrate in dynamic filtration experiments was also checked the same way to determine if TiO_2 falls off the fibers.

For adsorbent regeneration, the used TiO_2/CF composite fibers (0.04 g) were immersed in 0.12 M HCl solution (5 mL) with stirring for 2 h, then filtered and washed with distilled water to neutralize the fibers. The regenerated fibers were used for adsorption again. Such desorption–adsorption process was repeated for three cycles.