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Short communication

Controlled synthesis of silkworm cocoon-like α-Fe_2O_3 and its adsorptive properties for organic dyes and Cr(VI)

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ABSTRACT

Industrial wastewater containing both organic and inorganic pollutants is being generated all the time. Efficient materials are highly needed to purify the polluted water. Thus, a hierarchical structured α-Fe_2O_3 with excellent adsorptive property has been synthesized by using a facile hydrothermal method. It can be prepared in macroscopic quantity. The as-synthesized α-Fe_2O_3 with silkworm cocoon-like morphology shows high efficiency in adsorbing Congo red (CR), Methyl orange (MO) and Cr(VI). The removal efficiency of CR, MO and Cr(VI) can reach 99.2%, 83.9% and 100% under appropriate conditions. Besides, this α-Fe_2O_3 shows high adsorptive ability for mixed CR and Cr(VI) in aqueous solution and the final removal rates can reach 94.7% and 97.9%, respectively. The adsorption kinetics fits well with the pseudo-second-order kinetic model. The results indicate that the product may find potential application in purification of wastewater containing both organic and inorganic pollutants.

1. Introduction

Heavy metal ions and toxic dyes do great harm to environment and human health, but they can hardly be degraded naturally [1]. To date, various techniques such as adsorption [2], electrochemical processes [3], photo-catalysis [4], ion-exchange [5] and precipitation [6] are put forward to remove heavy metal ions and dyes from wastewater. Among those techniques, adsorption is a great choice for industrial water treatment owing to its low cost, high efficiency and simplicity of operation [7,8,9]. Nanotechnology contains great potential in wastewater treatment due to high specific surface area and active sites of nanomaterials [10]. There are plenty of nanomaterials used in adsorption such as carbon nanotube [11], metal oxides [12], polymeric nano-adsorbents [13], chitosan-based adsorbents [14] and so on.

Among a variety of nanomaterials, iron oxides are potential materials for removing organic contaminants and inorganic heavy metal ions from wastewater, because it is inexpensive, environmental friendly, stable and sufficient [15,16,17]. For instance, Fe_3O_4 nanoparticles are used in adsorbing Pb(II) [18], Cu(II) [19] and red dye [20]. Maghemite can effectively remove Rose bengal [21] and Cr(VI) [22]. Comparatively, the study on the adsorbents of α-Fe_2O_3 is rather few [23]. This partially due to the unsuitable micro/nano structure since the micro/nano structure may critically affect the performance of the materials. Hierarchical structure possessing high specific surface area, good stability and effective transmission path for the reaction attracts considerable attention in recent years. Because of building hierarchical structure, α-Fe_2O_3 exhibits excellent performance in photo-catalytic degradation [24], lithium ion battery [25], adsorption [26], gas-sensing [27] and so on. Thus, it is necessary for us to synthesize α-Fe_2O_3 with hierarchical structure. However, many synthesis methods are relatively complex and high-cost [28]. Therefore, it can be inferred that an effective hierarchical structured α-Fe_2O_3 built through a facile and low-cost synthesis method is needed and may appear high adsorptive property.

In this paper, a simple hydrothermal method is employed to controllably synthesize nano hierarchical structured α-Fe_2O_3 with high adsorption capacity. This synthesis route can be successfully repeated and the productivity is higher than 50%. Moreover, the nanostructured α-Fe_2O_3 product in this condition shows high removal efficiency in adsorbing both organic dyes like Congo red (CR), Methyl orange (MO) and inorganic heavy metal ion Cr(VI). The maximum adsorption capacities for CR, MO and Cr(VI) are 99.0, 35.4 and 13.4 mg/g, respectively.

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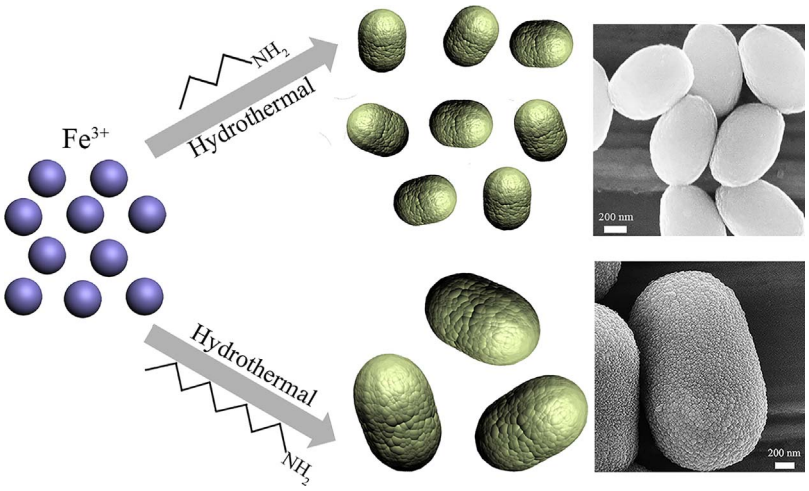

Fig. 1. Schematic diagram of synthetic route.

2. Experimental

2.1. Synthesis of silkworm cocoon-like α-Fe_2O_3

All reagents were analytically pure and used without further purification. $FeCl_3{\cdot}6H_2O$ and *n*-Octylamine were purchased from Aladdin Co., Ltd. (Shanghai, China). *n*-Butylamine was obtained from Xilong Chemical Co., Ltd. (Guangzhou, China). Congo red was supplied by Guangdong Guanghua Science and Technology Co., Ltd. (Guangzhou, China). Methyl orange was bought from Tianjin Jinke Fine Chemical Research Institute (Tianjin, China). $K_2Cr_2O_7$ was purchased from Beijing Chemical Works (Beijing, China).

The silkworm cocoon-like α-Fe_2O_3 was synthesized using a simple hydrothermal method. In a typical procedure, 25 mmol of $FeCl_3{\cdot}6H_2O$ were dissolved in 25 mL of deionized water under magnetic stirring, and then 3 mL of *n*-Butylamine were added to this solution. After a 20-min' stir, the mixture was put into a 50 mL Teflon-lined stainless-steel autoclave and then heated at 150 °C for 2 h. When the system was cooled down naturally to room temperature, the obtained substance was centrifuged and washed with deionized water and absolute ethanol alternately for 6 times, and then dried in air at 60 °C.

2.2. Characterization

The purity and phases of the products were characterized by means of X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.5418 Å). A field emission scanning electron microscope (LEO1530) was used to observe the morphology of the obtained α-Fe_2O_3. The nitrogen adsorption-desorption isotherms were carried out using a Quantachrome Instruments AUTOSOR8-1C Powders Adsorption Analyzer. The residual concentrations of chromium and organic dyes were measured by using UV–vis spectroscopy and ICP-AES.

2.3. Removal of the anionic dyes

Two anionic dyes (Congo red (CR) and Methyl orange (MO)) were selected to test the adsorption property of the as-synthesized product. CR and MO are both azo dyes commonly used in the textile industry [29]. To study the influence of initial concentration and reaction time, 0.1 g of the obtained α-Fe_2O_3 was added into 100 mL of CR and MO solutions at different initial concentrations (20, 30 and 50 mg/L) respectively. In the study of reaction time, 5 mL of the supernatant was taken at some time points, and UV–vis spectroscopy was used to measure the residual concentrations of CR and MO solutions.

2.4. Removal of Cr(VI)

$K_2Cr_2O_7$ [30] was used to prepare different concentrations of Cr(VI) solutions (20,40 and 60 mg/L). To study the influence of initial concentration and reaction time, 0.24 g of the obtained α-Fe_2O_3 was put into 60 mL of the above solutions separately. The effect of adsorbent dosage was researched by adding 2 g/L, 4 g/L and 5 g/L of α-Fe_2O_3 to 40mg/L of Cr(VI) solution. All the residual concentrations of Cr(VI) solution were detected by UV–vis spectroscopy.

2.5. Removal of both CR and Cr(VI)from the mixed solution

40 mg/L of CR and 40 mg/L of Cr(VI) were mixed at volume ratio 1:1 and stirred till fully mixed. Then 0.2 g of the obtained α-Fe_2O_3 was put into 100 mL of the above solution under constant stirring. The residual concentrations of CR were measured by using UV–vis spectroscopy and the residual concentrations of Cr(VI) were detected by means ofb ICP-AES.

3. Results and discussion

3.1. Synthesis

Different reagents, temperature and reaction time had great influence on the synthesis of α-Fe_2O_3. *n*-Octylamine and *n*-butylamine were used in the synthesis and played the role of structure-directing agent. When *n*-octylamine was used, the primary particles were relatively big and a preliminary attempt showed that the adsorption ability for organic dye and/or Cr(VI) was not good. When *n*-octylamine was changed to *n*-butylamine, the particles became much smaller and revealed better performance in adsorption. We assumed that different space structure and size of the two kinds of amines led to that result. Besides, while other conditions kept the same, the particles got smaller when their action time became shorter or reaction temperature became lower. So the α-Fe_2O_3 produced at 150 °C for 2 h by using *n*-butylamine as the structure-directing agent (sample 6) was chosen for all the adsorptive functional tests in this article. The schematic diagram of synthetic route is showed in Fig.1. All the detailed reaction conditions are listed at Table S1 (Supplementary material).

3.2. Characterizations of the obtained α-Fe_2O_3

Fig.2 shows the XRD pattern of the obtained substance. All of the confirmed peaks indicated that the obtained substance was hexagonal structure of α-Fe_2O_3 compared with the PDF card 33–664.Fig. 3 displays SEM images and Table S2 (Supplementary material) exhibits the