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Investigation on the room-temperature preparation and application of chain-like iron flower and its ramifications in wastewater purification

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HIGHLIGHTS

- A simple, low-cost and environmental friendly preparation process.
- Chain of flowery Fe and $FeFe_2O_4$ are gained at room temperature for the first time.
- Ferromagnetic powders with high efficient of water-treated capacity.
- High performance achieve in adsorption of heavy metal, organism and sulfonamide.

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ABSTRACT

Here, we are going to report a simple, low-cost and environmental friendly process to prepare catenulate flowery iron (Fe). Magnetite ($FeFe_2O_4$) with similar 3D morphology is gained at room temperature for the first time by aging of iron in water. The saturation magnetizations of these two products are totally high, which are 121.59 emu/g for Fe and 90.2 emu/g for $FeFe_2O_4$. It is not usual for Fe_3O_4 with lamellar structure because magnetic saturation for well defined Fe_3O_4 single crystals is 92 emu/g. Because of the special appearance with large surface area, adsorption experiments of organic dye, sulfonamide and heavy metal ions are carried out in synthetic wastewater. Adsorption rate of two magnetic samples—iron and magnetite—can achieve more than 98% in 5 min. It is worthy to note that, in adsorption experiment of Cr^{VI}, the adsorption rate of Fe can achieve 100% in 5 min. The equilibrium times of all productions can be controlled in a short span of 30 min. Achieve high performance of adsorption in a short time, which perform a great advantage in water treatment applications of such materials. Finally, regeneration experiments of $FeFe_2O_4$ which adsorbed Congo red show that the as prepared sample can be well-regenerated, and after regeneration, the magnetic adsorbents can still show more than 97.6% adsorption capacity.

1. Introduction

The governance of environmental pollution, especially the water pollution control is closely related to people's lives. With the rapid development of industry, waste water from tanneries, chemical plants, stope, battery manufacturing plants and other plants contain a lot of toxic substances, for example, toxic heavy metals. Textile effluent contains organic dye; sewage from hospital contains drug residues, bacteria and viruses; they will form cluster in the organism and cannot be degraded by the organism easily, finally cause different diseases and disorders produce in vivo. Many methods have been developed to remove pollutants from wastewater, such as co-precipitation [1–3], reverse osmosis [4], extraction [5], ion-exchange method [6], biological treatment [7], and catalytic method [8]. However, these methods themselves are costly, and the cost of dealing with residual contaminants is also relatively high [9,10].

Using the magnetic material as adsorbent in sewage treatment has the advantages of high accuracy and simply in post-processing compared to conventional material. In addition, it can be separated from the water by magnetic separation method, and then a suitable stripping agent could be chosen to flaking off the harmful substances adsorbed on the surface of magnetic material, so that both harmful substances and magnetic particles can be re-used. Therefore, in recent years, more and more people research on the use of magnetic materials in wastewater treatment, including the removal of heavy metal ions [11,12], phosphate [13], dye [14–16], fluoride [17] and drugs [18] from wastewater. At present, the main specific to improve absorption efficiency is increase the surface area of magnetic material, for example, prepared porous, nano-scale or hierarchical structure of magnetic materials by controlling the morphology [19,20].

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The Lou's group has synthesis urchin-like α-FeOOH hollow spheres and uses it as an adsorbent in removing the heavy metal ions. The maximal adsorption capacity can reach about 58 mg/g for As^V and 80 mg/g for Pb^{II} [21]. Nevertheless, there are some specific scientific problems requires taking an embedded discussion: primarily, how to simplify the synthesis process of magnetic materials, reduce preparing time and cost is still a challenge. And then, how to reduce the adsorption time and improve the adsorption efficiency is also a long-term subject.

In this contribution, catenulate flowery iron was prepared via a reductive process. Magnetite with similar shape was gained at room temperature (laboratory temperature 13 °C) subsequently by simply immersing iron powders into water. Because of the large surface areas, the simple synthesis process and the derivative product of the as-prepared iron, it was tried to be used as a novel magnetic adsorbent. The adsorption capacities of as-prepared iron and its derivative products—iron hydroxide and magnetite—for heavy metal, organism and sulfonamide were tested respectively. In our work, Cr^{VI}, Congo red (CR) and sulfasalazine (SASP) were chosen as the typical pollutants of heavy metal, organism and sulfonamide. CR, a common azo-dye in the textile industry, was chosen as a typical organic waste in water resources, the efficient removal of them from water is extremely important. SASP is a type of antibacterial sulfa (SA) drugs which are one of the most widely administered groups of antibiotics in animal husbandry as preventive and therapeutic agents for bacterial infective diseases, containing the chemical structure of sulfanillic amide [22–24]. Due to their persistence in the environment and their relatively high mobility, they can enter groundwater and be transported in aquifers and surface waters [25–27]. Perennial ingestion of the SAs can result in serious side effects, such as emiction and hemopoiesis turbulence [28], so it is of great importance to deal with SAs in domestic water. Hexavalent chromium, Cr^{VI}, is a hard oxidant and carcinogen, strong exposure to Cr^{VI} could cause cancer in the digestive tract and lungs, epigastric pain and nausea. Hence, it is urgent to clear Cr^{VI} from effluent to reach the industrial effluent standard before its discharge into the environment [20]. Finally, a simulation experiment of practical application was carried out. In situ synthesis of iron was directly applied to the organic sewage treatment. With strong stirring, iron particles adsorbed the organic contamination fleetly and form iron hydroxide at the same time. When the adsorption equilibrium has been reached, the remaining black powder was separated by magnetic and immerse in water for 1 day, then added into new organic wastewater. After the second adsorption assay, an adsorption rate of 92.58% was got. Coupled with the desorption experiment, it can prove that the new adsorbent can be used in practical application admirably.

2. Experiments

2.1. Chemicals and materials

All chemicals used are analytical grade without further purification. The reagents used for the synthesis are obtained from Beijing Chemicals Co. (Beijing, China). In adsorption experiment, SASP is obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). A standard stock solution (100 mg/L) of SASP is prepared by dissolving appropriate a certain amount of SASP in ethanol. Heavy metal and organic solvents is prepared by dissolving drugs into pure water to form the mother liquors. Working solutions are obtained daily by appropriately diluting the stock solution with pure water.

2.2. Sample preparation

In a typical synthesis process, the samples are synthesized in different processes. Iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) is dissolved in 40 mL pure water (H_2O) to form a transparent solution. During mechanical stir, aqueous solution of $FeSO_4$ is added into a beaker keep $NaBH_4$ in. The reaction is responsive quickly. A black material formed in the bottom of the beaker along with the generating of H_2 gases. After the reaction of hydrogen generation is completed, the black material is magnetically separated to the bottom of the beaker by a magnet and washed twice with deionized water and ethanol. Production obtained is marked as sample one (S1).

S1 is put into pure water with mechanical stirring about 30 min, almost all the S1 particles was oxidized and formed a brown substance, and we marked it as sample two (S2). Additionally, immerse S1 directly in the water after formation reaction for more than one night, and mark the obtained black substance as sample three (S3).

The synthesized samples are subsequently characterized by X-ray diffraction (XRD, Rigaku D/max 2500 pc X-ray diffractometer with Cu K_α radiation, $\lambda = 1.5406$ Å), scanning electron microscope (SEM, Hitachi S-4700), transmission electron microscope (TEM) and selected area electron diffraction (SAED) patterns (Philips Tecnai 20, 200 kV), and high-resolution transmission electron microscope (HRTEM, JEOL-3010, 300 kV). Hysteresis loops are collected on a VSM-7300 vibrating sample magnetometer (VSM) (Lakeshore, USA) in room temperature. The VSM measurements for all the samples are done on the pure and dried powders.

2.3. Absorption experiments

Take the adsorption of the organic dye of CR for example. Standard solution with initial concentrations of 100 mg/L is prepared. Then, adsorbent is added into the above solution under stirring. After a specified time, the solid and liquid are separated by magnet and UV–Vis adsorption spectra (Shimadzu UV-1601PC) is used to measure the concentration in the remaining solutions. Under the same experiment condition, SASP and Cr^{VI} are used as the medicament and the heavy metal pollution. UV–Vis adsorption spectra and Atomic Absorption Spectroscopy (TAS-986) are recorded at different intervals to monitor the adsorption process.

It should be noted that, the preparation and the test of absorption capacity of samples are carried out in room temperature. However the experiments are conducted in winter, and the temperature (about 13 °C) in laboratory is below the true sense of the room temperature (25 °C).

3. Results and discussion

The as-prepared S1 is quickly put on a glass disk and examined by powder XRD which was shown in Fig. 1a. The major diffraction peak in the XRD pattern of the products can be indexed to the iron (JCPDS No. 06-0696). After washing by deionized water and ethanol and drying, the typical Fe^0 particle consists of a Fe^0 core surrounded by an oxide shell composed of maghemite and partly oxidized magnetite [29]. In order to avoid S1 being completely oxidized in air, it is covered by a cling film during the test process. Although the cling film does not have crystal structure, the film and the oxide shell must be the reason of the impurity peaks in XRD pattern. Fig. 1b shows a low-magnification FESEM image of S1. The well-proportioned flower-like particles connect into chains, and each particle diameter is about 500 nm. Inset of Fig. 1b is an individual flower-like structure of the microspheres. It can be clearly seen that petals are composed of flakes with thickness about 20 nm.

TEM is further employed for the crystal structure investigation of the flower-like structure, Fig. 1c shows a typical TEM micrograph of a single chain, which reveals that the thickness of the