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Synthesis of magnetic iron oxide nanoparticles onto fluorinated carbon fabrics for contaminant removal and oil-water separation

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ABSTRACT

The study investigates contaminant removal and oil-water separation efficiencies of magnetic Fe_3O_4 nanoparticle (MNP)-coated fluorinated carbon fabric (CF) membrane. A co-precipitation method was adopted to synthesize spherical MNPs with an average size of 20 nm. The as-prepared MNPs were uniformly dispersed and coated over the CF membrane, forming a two-tier roughened surface. Herein methylene blue (MB) and Cu^{2+} ion serve as adsorbate for evaluating the removal performance of the CF membrane. The MNP-coated CF membrane exhibits superior adsorption ability toward cationic MB molecules and Cu^{2+} ions in liquid phase, attributed to a synergistic effect that combines with porous CFs and Fe_3O_4 magnetite. The capacities for adsorption of MB and Cu^{2+} onto the MNPs are *ca.* 30.1 and 62.5 mg/g, respectively. The hydrophobicity and oleophobicity of the CF membrane were effectively improved by the MNP-coated fluorination approach. The improved repellencies mainly originate from the fact that the decoration of Fe_3O_4 magnetite and the surface fluorination, covering the CF surface, create a two-tier framework against the wetting of liquid droplets. The CF membrane shows fast removal rate of oil drops and excellent efficiency of oil-water separation (>95%). On the basis of the experimental results, the functional CF membrane offers a commercial feasibility for a variety of applications such as environmental protection and wastewater treatment.

1. Introduction

So far, environmental pollutant including air, soil, and water, has become one global concern due to its significant impact on public health. Among the pollutants, improper management of industrial water is one of critical issues, contaminating the environmental ecology in many countries [1]. Industrial wastewater consists of many types of pollutants such as oil, dye and metallic ion. For instance, many industries such as petrochemical and metal finishing, crude oil production and refinery, textile and leather processing, and food and lubricant processing, produce a large amount of oily wastewater [2,3]. The oily wastewater is also contaminated with dye and metal ion, which are so difficult to remove because of their complex composition and poor biodegradability. Thus, industrial oil and dye-laden effluents are an increasingly major concern and required to be efficiently treated before being discharged into the environment to avoid contaminations [4].

In fact, the removal of dye or other organic compounds from aqueous solution has been extensively investigated and various methods such as membrane adsorption [5], coagulation and flocculation [6], photocatalysis [7–9], advance oxidation [10], and adsorption [11–15] have been well developed. Among these methods, adsorption has been regarded as a potential technique due to its simple design, high-efficiency operation, easy maintenance, and low-cost adsorbent usage. Accordingly, the delightful performance has motivated many scientists and researchers to synthesize various porous or nanoscaled adsorbents for the adsorption application. In this regard, magnetic iron oxide nanoparticles (MNPs) have received much attention due to its widespread applications in adsorption of metal ions (e.g., As^{3+} [15], Cr^{6+} [16], Au^{3+} [17], Hg^{2+} [18], and Cu^{2+} [19,20]) and organic compounds [1,4,21–24] from aqueous solution. Several advanced approaches including

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two-precipitation method [25], thermal decomposition of $FeCl_3$ [26], anion-assisted hydrothermal route [27] have been developed to synthesize different types of MNPs. Herein the precipitation is an efficient method in preparing high-quality MNPs as compared to the others. However, there are few reports concerning the deposition of MNPs onto carbon fabrics (CFs) via the precipitation route for adsorption of dye and metal ions in liquid phase.

In order to purify oily wastewater, oil-water separation membrane provides one feasible unit operation because of its high efficiency, high permeability, and excellent effectiveness. The fundamental principle of oil-water separation is based on assembly of functional membranes that possess super water or oil repellency [28]. In some cases, high water repellency imparts the membranes to repel water droplet penetration, whereas superoleophilic property makes the membranes oil permeate freely [2]. Several routes of preparing the functional membranes have revealed their superior oil-water separation efficiencies, such as magnetic polymer-based graphene foam via hydrothermal method [29], Ag nanocluster/nanofiber membranes by electroless plating [30], magnetic foams by pyrolysis of polyurethane (PU) sponge [31], iron oxide/PU/polytetrafluoroethylene foams by surface modification [32], modified cotton fabric via vapor phase deposition [33], and layered double hydroxide functionalized textile [34]. On the basis of previous studies, the design of membranes consists of two critical points: physical (e.g., surface roughness and nanostructure) and chemical factor (e.g., low-surface-energy coating and surface modification [35]). The research achievements direct us at the development of MNP-coated fluorinated CFs for multiple applications including removal of contaminants and water-oil separation.

The aim of the present work is to reveal one possibility for preparing one multiple-functional CF membrane, decorated with MNPs (i.e., Fe_3O_4) and modified by fluorine copolymer. Two kinds of common contaminants, methylene blue (MB) and Cu^{2+}, are used as adsorbates in the present work. MB is a well-known cationic dye, widely used in various applications such as printing, textile, cosmetic and pharmaceuticals [22]. Cu is one heavy metal, which shows widespread applications including conductive wire and cable, integrated circuit and printed circuit boards, dyes and paints [36]. Importantly, copper electroplating technique has been successfully developed in semiconductor applications (e.g., 12″ wafer fab) due to its excellent electrical conductivity. It is recognized that the divalent cation of Cu^{2+} is highly soluble in wastewater, leading to copper toxicity [37]. Accordingly, this work aims at the fabrication of functional CF membrane for (i) separating oily wastewater and (ii) removing the above contaminants from aqueous solution. Such a broad experimentation with high separation efficiency of oil, dye and metal ion from the wastewater using MNPs has not been established well, to the best of our knowledge.

2. Experimental section

2.1. Deposition of MNPs onto fluorinated CF membranes

Nanoscaled magnetic Fe_3O_4 powders were fabricated by the precipitation method, described as follows. In this typical experiment, two Fe-containing salts, $FeCl_3 \cdot 5H_2O$ and $FeSO_4 \cdot 7H_2O$, were dissolved in distilled water by vigorously stirring to form a clear solution. Herein an appropriate mole ratio of Fe^{3+} and Fe^{2+} was set 2:1. Then 3 M KOH was slowly added at room temperature until the pH value of solution reaches 10. The as-prepared solution was vigorously stirred under ambient atmosphere overnight. The Fe_3O_4 precipitate was separated from a filter apparatus and then dried at 105 °C in an oven.

Afterward, the MNPs (0.01 g) were uniformly mixed with a diluted fluoro-containing solution (50 mL), consisted of perfluoroalkyl methacrylic copolymer and distilled water (7/3 in v/v). The dispersion process would take a period of 0.5 h, allowing well dispersion of MNPs in the F-containing solution and partial surface fluorination on the surface of MNPs. The MNPs could not be totally fluorinated by the F-containing copolymer. One piece of CF (Taiwan Carbon Technology Company (Taiwan); thicknesses: 0.55 mm) with an area of $4 \times 4\ cm^2$ was immersed in the slurry. The dispersion process would take a period of 0.5 h, allowing well dispersion of MNPs in the F-containing solution and partial surface fluorination on the surface of MNPs. The commercial CF membrane was composed of microscaled carbon fibers (diameter: 8–10 μm) with a regular arrangement. Herein the F-containing copolymer served as not only a water repellent agent but also a binder for adhesion between the MNPs and CF. The MNP-coated fluorinated CF membrane was then dehydrated at 105 °C in an oven overnight.

2.2. Characterization of MNP-coated fluorinated CF membrane

The microstructural observation of as-prepared CF membrane was carried out by using field-emission scanning electron spectroscope (FE-SEM, JEOL JSM-5600) and high-resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100). An X-ray diffraction (XRD, Shimadzu Labx XRD-6000) spectroscope, equipped with Cu Kα radiation emitter, was employed to examine the crystalline structure of MNPs. Fourier transformed infrared spectroscopy (FT-IR) was adopted to study the surface chemistry of CF composites. The FTIR spectra were collected and recorded by using a FTIR spectrometer (Model: Varian FTS 1000). Herein twenty scans were recorded within 4000–500 cm^{-1} spectral ranges with a resolution of 4 cm^{-1}.

2.3. Magnetic adsorption test of dye and metal ion

An adsorption experiment of MB dye was carried out in which the MNP-coated fluorinated CF sample was added into 50 mL of 20 mg/L MB solution. The suspension was shaken in a thermostated shaker at 30 °C with a rotation speed of 100 rpm. The contact time was set at 10 min. After the adsorption process, the suspension was withdrawn from the shaker and the adsorbed CF sample was separated from the MB solution by applying a magnetic field using neodymium magnets. The MNP-coated CF sample was able to be attracted to the magnets, and the MB molecules were thus separated from the suspension. The residual MB concentration was analyzed by UV–visible absorption spectroscopy (GBC, Cintra 202). Herein the absorbance of the residual MB solution at 664 nm was measured for the estimation of adsorption capacity of MB dye onto the MNPs. One calibration curve of absorbance versus MB concentration, determined from standard MB solutions, was capable of providing the real MB concentration. To clarify the effect of MNPs, a blank experiment for evaluating the adsorption capacity of MB on fresh CF sample was also performed for comparison. Similarly, the adsorption experiment for Cu^{2+} ions onto the MNP-coated fluorinated CF samples was also performed in shaking bath with 100 rpm at 30 °C. The initial Cu^{2+} concentration was approximately 100 mg/L, and the contact period was also set at 10 min. After the adsorption test, the residual concentration of Cu^{2+} ions was determined using the UV–visible spectrometer, with a maximum absorbance wavelength for Cu^{2+} ions at 790 nm.

2.4. Water/oil repellency and separation efficiency

To inspect water and oil repellencies, an optical contact angle (CA) meter (Sindatek Instruments, Model 100SL) was used to measure the CAs of droplets on the CF samples. Herein each droplet (volume: 5 μL) was dropped onto the CF surfaces from a distance

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