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Magnetically recoverable *Ni@C* composites: The synthesis by carbonization and adsorption for Fe^{3+}

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ABSTRACT

Carbon-encapsulated nickel particles (*Ni@C* composites) for removing Fe^{3+} in wastewater have been prepared by the carbonization of phenolic resin mixing with nickel particles. XRD results reveal that the *Ni@C* composites are consisted of C, Ni, and Ni_3S_2. The TG-DTG curves of *Ni@C* composites are almost same as that of phenolic resin. The morphology investigation shows that Ni is distributed randomly on carbon. Based on analysis of N_2 adsorption-desorption isotherm, the surface area and pore volume of *Ni@C* composites are 187.47 m^2 g^{-1} and 0.06900 cm^3 g^{-1} nm^{-1}, respectively. The saturation magnetization values for *Ni@C* composites are 68.99 emu·g^{-1} determined by the Vibrating Sample Magnetometer. *Ni@C* composites exhibit a high adsorption capacity for Fe^{3+}. The adsorption behavior follows the pseudo-second-order kinetic and Langmuir model between the adsorbents and Fe^{3+}. Furthermore, the adsorption capacity of *Ni@C* composites derives from the attractive force between the adsorbed anion and the surface positive charge of *Ni@C* composites, as well as the bond between the adsorbed cation and the COO^- groups. From the above results *Ni@C* composites can be widely applied in wastewater treatment as a new efficiency and excellent recoverable adsorbent.

1. Introduction

Iron and its compounds are contaminants and commonly found in wastewater produced by several industries, including plating, minerals, and cements [1]. Fe^{3+} is toxic and can pose risks to human health such as gastrointestinal disease [2]. It is dreadful even of people just take in a low amount of Fe^{3+} at 60 mg kg^{-1} of body weight [3].

In the past few decades, some processes of removing Fe^{3+} in wastewater, such as flocculation [4], bacterial action [5], reverse osmosis [6], and adsorption [7]. Among them, adsorption is more prone to wider applications in industrial treatment because of its low initial cost and flexibility in design and operation [8]. In particular, carbonaceous materials, such as porous carbon [9], active carbon [10], carbon nanotubes [11], and carbon fibers [12], are common adsorbent materials because of their high specific surface area and good sorption capacity for pollutant [13], and wide availability of precursors [14–19]. Phenolic resin (PR) was usually selected as carbon source because it gives high production yield on account of its ability to polymerize and form complex carbon molecules [20].

Recently, magnetic separation technologies have been attracting more and more attention [21,22]. With the assistance of magnetic force, magnetic matter can be separated from the solution efficiently regardless of its size. Nickel (Ni) has been widely used as a magnetic material because of their excellent magnetic properties. Thus, magnetic *Ni@C* particles are regarded as a promising sorbent for removing heavy metals because of the strong adsorption capacity for metal ion and good magnetic separation performance. Xiao et al. [23] reported that the *Ni@C* composites can be used as adsorbent for heavy metal ions. It has been widely reported *Ni@C* nanocomposites are composed of nickel nanoparticles coated within a layer of thin carbon shell [24–26]. However, small nanoparticles aggregate together easily due to high surface energy [27].

Herein, we proposed to use *Ni@C* composites as sorbent instead of *Ni@C* nanocomposites to resolve the problem of agglomeration.

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Ni@C composites were synthesized by carbonization with nickel powder and PR as the raw materials in the present work. Carbon materials from the pyrolysis of PR are porous and have good adsorption capacity [28,29]. The size of Ni particles is micron-scale rather than nano-scale, so the Ni powder avoids the agglomeration of nanoparticle. Importantly, the metal powder of Ni has stronger magnetism than Ni nanoparticle synthesized from organic compounds. Thus, the magnetism of *Ni@C* composites can be stronger than that of *Ni@C* naonocomposites, attributing to separate sorbents from solution more easily. Besides, the preparation process of *Ni@C* composites is easier than that of *Ni@C* naonocomposites, and the material cost of *Ni@C* composites is cheaper than that of *Ni@C* naonocomposites.

In this study, the microstructure and properties of *Ni@C* composites, such as phase, morphology, specific surface area, pore size, magnetic properties and adsorption capacity for Fe^{3+}, were investigated in details. Moreover, the adsorption kinetics and isotherm for Fe^{3+} from water solution onto *Ni@C* composites, and the adsorption mechanism of Fe^{3+} on *Ni@C* composites were analyzed intensively.

2. Experimental

2.1. Chemicals

Nickel powder (200 mesh, purity of 99.9%), silane coupling agent, and p-toluenesulfonic acid were purchased from Beijing Chemical Works. *PR*, HCl, NaOH, was provided by Jingtong Leitai Chemical Product Co. Ltd. in China. All reagents were used as-received, without further treatment.

2.2. Synthesis of Ni@C composites

In a typical synthesis as shown in Fig. 1, the raw materials of *PR* (10 g), nickel powder (2.31 g), and silane coupling agent (0.77 g) were successively added and then mixed by stirring in a beaker. After stirring for 10 min, p-toluenesufonic acid (2.31 g) was added to the mixture and mixed for 10 min, and the mixture cured naturally for 15 min at room temperature. Then, the composite precursor was put in the furnace (GL-1100M, Siyang Jingmi Shebei Co. Ltd), and the carbonization process took place in the condition of non-oxygen. The samples were heated from room temperature to 850 °C at a heat rate of $2\ ^\circ C\cdot min^{-1}$ and maintained for 2 h at 850 °C. Finally, the samples were cooled down naturally, and *Ni@C* composites were obtained.

2.3. Characterization

The phases of *Ni@C* composites were detected by X-ray diffraction (XRD, Rigaku D/max-RB, Japan) at 40 kV and 120 mA with Cu Kα radiation. The differential thermal analysis and thermogravimetric analysis (TG) were tested on the thermogravimetric analyzer (NETZSCH STA 409 C/CD, Germany) in argon atmosphere. The morphologies and microstructures of *Ni@C* composites were observed by scanning electron microscopy (SEM, JEOL JSM-840A, Japan) at the voltage of 15 kV. Brunauer-Emmett-Teller (BET) surface areas and the pore size distribution of *Ni@C* composites were determined by the Autosorb IQ2 analyzer (Quantachrome Model 2000, USA). The magnetic properties of specimen were investigated by the superconducting quantum interface device (SQUID) magnetometer (Quantum Design PPMS-9). FTIR (Infinity Gold, Thermo Mattson, USA) was used to analyze the difference in surface functional groups of *Ni@C* composites before and after adsorption. Zeta potential of the specimens in various pH value solutions were detected by mütek SZP-04.

2.4. UV–Vis measurement

The adsorption experiments for Fe^{3+} on *Ni@C* composites were carried out by using the water solution of $FeCl_3$ to evaluate the parameters of adsorption. The centrifuge tube containing the solid sample and the solution was shaken at the speed of 160 rpm in the horizontal shaker (HY-5A, Jintan Tianjing Laboratory Instrument) at room temperature for different periods of time as follows: 1, 5, 10, 30, 60, 120 and 180 min. The mass of *Ni@C* composites, the concentration and volume of Fe^{3+} solution used in each experiment were 0.1 g, 3000 mg L^{-1}, and 25 mL, respectively.

The adsorption isotherm for Fe^{3+} on *Ni@C* composites was performed by mixing *Ni@C* composites with Fe^{3+} solution at various initial concentrations of 100, 200, 500, 800, 1200, 2000, 3000, 5000, 6000 and 10000 mg L^{-1}, as well the same parameters of shaking speed (160 rpm) and time (2 h) in the centrifuge tubes on the horizontal shaker.

To investigate the effect of pH value of solution on the adsorption capacity, a changed initial pH value of the mixing solution was used by adjusting the concentration of HCl (1 mol L^{-1} and 0.1 mol L^{-1}) or NaOH (0.01 mol L^{-1} and 0.001 mol L^{-1}) solution while the concentration of Fe^{3+} solution was fixed at 5000 mg L^{-1}. The pH value of solution was measured every 4 h and re-adjusted until the pH value stabilized at the desired final values of 1, 2, 3, and 10. The total mixing time was 12 h.

After a desired period of time, all mixtures were centrifuged for 15 min at 8000 rpm, and the supernatants were filtered through 0.45 μm syringe filters for remaining Fe^{3+} solution after adsorption. The amount of Fe^{3+} adsorbed was determined by the UV–Vis spectroscopy (759S, Shanghai Jingke Co., Ltd) and calculated by the following Equation (1) [30].

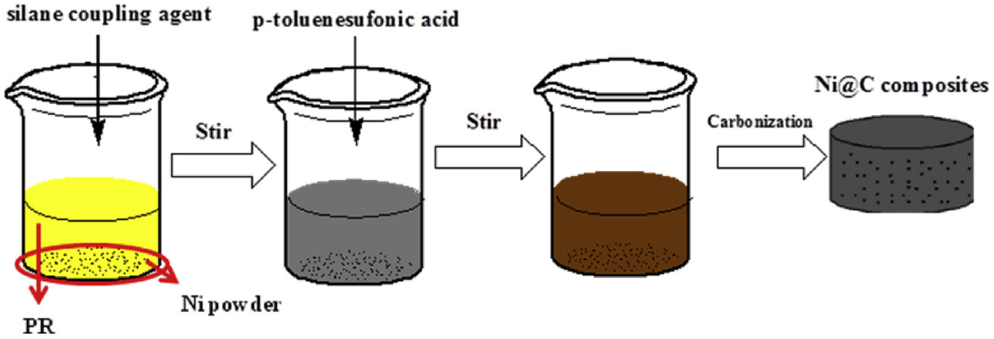

Fig. 1. Schematic illustration of the synthesis of *Ni@C* composites.