Journal of Colloid and Interface Science 509 (2018) 245–253

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Nickel nanoparticles encapsulated in porous carbon and carbon nanotube hybrids from bimetallic metal-organic-frameworks for highly efficient adsorption of dyes

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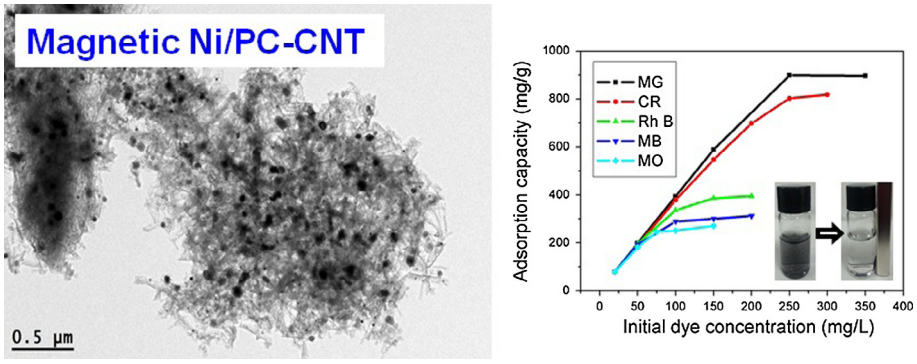
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 June 2017
Revised 27 August 2017
Accepted 1 September 2017
Available online 6 September 2017

Keywords:
Metal-organic framework
Magnetic nanoporous carbon
Adsorption
Dye

ABSTRACT

Nickel nanoparticles encapsulated in porous carbon/carbon nanotube hybrids (Ni/PC-CNT) were successfully prepared by a facile carbonization process using Ni/Zn-MOF as the precursor. Distinct from previous studies, Ni/Zn-MOF precursors were prepared via a direct precipitation method at room temperature for only 5 min. After the carbonization, magnetic Ni nanoparticles were well embedded in the porous carbon and carbon nanotube. The obtained Ni/PC-CNT composites had a high surface area (999 $m^2 g^{-1}$), large pore volume (0.86 $cm^3 g^{-1}$) and well-developed graphitized wall. The Ni/PC-CNT composites showed excellent adsorption capacity for removal of malachite green (MG), congo red (CR), rhodamine B (Rh B), methylene blue (MB) and methyl orange (MO) from aqueous solution. The maximum adsorption capacity of Ni/PC-CNT composites were about 898, 818, 395, 312 and 271 mg/g for MG, CR, RB, MB and MO dyes, respectively, which were much higher than most of the previously reported adsorbents. Moreover, the Ni/PC-CNT composites could be easily regenerated by washing it with ethanol and easy magnetic separation.

1. Introduction

Organic dyes, as one of major pollutants in wastewater, have been found to not only reduce the water quality, but also significantly impact the health of human beings, because most of them are toxic, mutagenic and even carcinogenic [1]. In order to improve the quality of water, the removal of dyes from wastewater is very important.

Up to now, several treatment techniques including photodegradation [2], biological treatment [3], and adsorption [4], have been developed to remove dyes from aqueous pollutants. Among

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http://dx.doi.org/10.1016/j.jcis.2017.09.002
0021-9797/

them, adsorption is the most common treatment technique because of its simplicity, high efficiency and low cost. At present, various adsorbent have been reported to eliminate dyes from industrial or agricultural wastewater, for example, porous carbon [5], zeolites [6], metal oxides [7] and so on. In particularly, porous carbon materials have attracted increased attention due to their high thermal and chemical stability, large surface area and light weight [8]. However, the application of porous carbon materials in water treatment is limited, because they are difficult to be separated from the treated water. To overcome this weakness, unprecedented research efforts have been focused on preparing magnetic porous carbon composites and developing their capable for removing pollutant from aqueous solutions, because magnetic nanoparticles can make the separation easier [9–11].

Although many types of methods have been reported for generating such magnetic carbon composites including CVD synthesis, silica templated etching processes, catalytic method, etc. [12–14], the development of more convenient synthetic methods for the magnetic carbon composites is still of great interest. Recently, metal-organic frameworks (MOFs), which consist of metal ions or clusters and organic ligands, have been recognized as alternative precursors for the synthesis of magnetic porous carbon materials [15–21]. More importantly, some of these magnetic porous carbon materials derived from MOFs exhibit good adsorption properties of organic dyes from aqueous solution. For example, Zhang et al. reported the synthesis of γ-Fe_2O_3/C through the carbonization of MIL-53(Fe) using a microwave-enhanced high-temperature ionothermal method and the obtained γ-Fe_2O_3/C showed high dye adsorption capacity (499 mg g^{-1}, 30 °C) toward malachite green (MG) [16]. Wang et al. prepared magnetic porous carbon composites exhibiting excellent adsorption capacity (183 mg g^{-1}) for the methyl orange (MO) removal [17]. However, the preparation of most of MOF precursors in previous works need time consuming building-up processes, high temperatures and the help of toxic and teratogenic organic solvents such as N,N-dimethylformamide and N,N-diethylformamide (DEF). Therefore, in this regard, the development of high performance magnetic carbon without the use of any toxic solvents and with relatively short reaction time is of great importance.

Generally speaking, the extent of adsorption is proportional to the specific surface area of the adsorbents [22]. However, directly carbonized M-MOF (M = Fe, Co, Ni) usually suffers from low specific surface area and thus mediocre adsorption performance [15–18]. Recently, bimetal-organic frameworks have been used as precursors to prepare metal/carbon composites, such as Co/Zn-MOF, Fe/Zn-MOF. The presence of Zn species can increase the specific surface area of the annealed products due to the evaporation of Zn during pyrolysis [23–25]. In this paper, we report a facile and economical method for synthesis of Nickel nanoparticles encapsulated in porous carbon/carbon nanotube hybrids (Ni/PC-CNT) derived from Ni/Zn-MOF precursors. Distinct from previous studies, Ni/Zn-MOF precursors were prepared rapidly via a direct precipitation method under mild conditions. The obtained Ni/PC-CNT composites possess high surface area and large pore volume, which show excellent adsorption behavior for dye from the aqueous solution and can be easily separated by an external magnetic field during the adsorption and desorption cycles.

2. Experimental

2.1. Preparation of the Ni/PC-CNT composites

All chemicals are of analytical grade and were used without further purification. In a typical experiment, 0.3 mmol of $NiCl_2{\cdot}6H_2O$ and 2.7 mmol of $Zn(Ac)_2$ were dissolved into 25 mL of de-ionized water and 50 mL of ethanol to form a homogeneous solution. 2 mmol of 1,3,5-benzenetricarboxylate acid (H_3BTC) and 6 mmol of NaOH were dissolved to 25 mL of water under continuous magnetic stirring. Then the latter clear solution was added to the former solution. The resulting reaction mixture was stirred at room temperature for 5 min. The as-obtained Ni/Zn-MOF were centrifuged, washed with distilled water and absolute ethanol several times, and dried in vacuum at 60 °C for 5 h. In addition, a calcination process (910 °C for 2 h in nitrogen with a heating rate of 5 °C/min) was performed to transform Ni/Zn-MOF to the Ni/PC-CNT composites.

2.2. Characterization

The products were characterized by powder X-ray diffraction (XRD) on a Rigaku D/max 2500PC diffractometer with graphite monochromator and Cu K_α radiation (λ = 0.15406 nm) at a step width of 0.02°. SEM images of the products were obtained on a field emission scanning electron micro analyzers (JSM-7001F), employing an accelerating voltage of 5 kV. TEM and HRTEM images were obtained on a transmission electron microscopy (JEM-2100 (HR), JEOL). FT-IR spectrum was recorded in the range of 400–4000 cm^{-1} on a ThermoScientific Nicolet iS50FT-IR spectrophotometer using KBr pellets. Raman scattering was collected at room temperature using a DXR Raman spectrometer with 532 nm laser source from an Ar^+ laser. Nitrogen adsorption-desorption isotherms of the samples were measured at liquid nitrogen temperature (77 K) by the instrument of NOVA 2000e. Before testing, samples are degassed at 200 °C for 5 h. The surface area and pore size distribution are determined by the Brunauer-Emmett-Teller (BET) and Density Functional Theory (DFT) methods. The Zeta potential was measured with a Zetasizer Nano Z (Malvern Instruments, UK) at 25 °C.

2.3. Water treatment experiment

Five kinds of dyes, such as malachite green (MG), methylene blue (MB), rhodamine B (Rh B), congo red (CR) and methyl orange (MO), were used in adsorption experiments. In the adsorption kinetics experiment, 5 mg of the as-prepared Ni/PC-CNT hybrids was mixed with 20 mL of aqueous solution of dye with a concentration of 20 mg L^{-1} in a flask reactor (capacity *ca.* 50 mL). The suspension was shaken on a slow-moving platform shaker at room temperature. For a kinetic study, at different time intervals, 2 mL of the solution was pipetted and separated using an external magnet. Ultraviolet–visible (UV–vis) absorption spectra were obtained using a UV–vis spectrophotometer (Mapada, UV-1800PC). For the adsorption capacity study, the initial concentrations of the dye solutions were scaled in the range of 20–350 mg L^{-1}, and the dosage of the Ni/PC-CNT composites was kept at 5 mg. The mixtures were stirred at room temperature for 60 min and separated using an external magnet. The UV–vis absorption spectra of the final dye solutions were obtained using UV–vis spectroscopy after dilution (if necessary).

After the first time it was used, the adsorbent was washed several times, using ethanol and then dried in vacuum at 80 °C for 10 h. The dried Ni/PC-CNT composites were reused for adsorption with a MG or CR concentration of 20 mg L^{-1} for 60 min. After each run, the concentration of MG or CR was determined using UV–vis spectroscopy.

3. Results and discussion

3.1. Characterization of the Ni/Zn-MOF precursors

The SEM images in Fig. 1a and b show that the Ni/Zn-MOF precursors are composed of a great bunch of nanorods and