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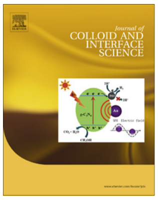

Regular Article

Hierarchical flower-like nickel(II) oxide microspheres with high adsorption capacity of Congo red in water

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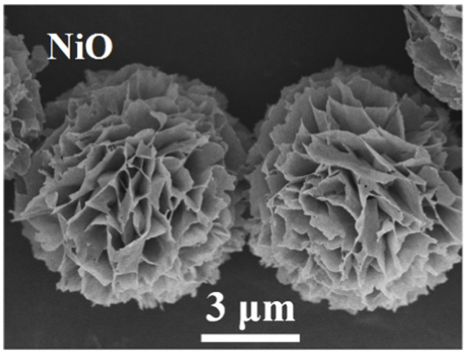
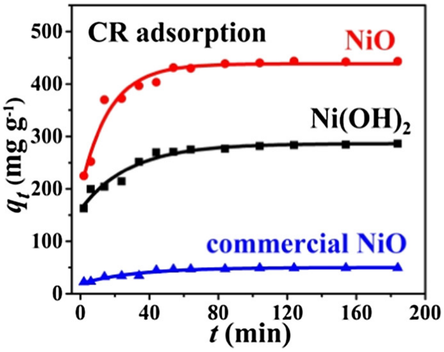
HIGHLIGHTS

- Monodispersed hierarchical flower-like NiO microspheres were synthesized.
- NiO microspheres with hierarchical pore structure and high specific surface area.
- NiO microspheres exhibited high Congo red adsorption capacity of 534.8 mg g^{-1}.
- Adsorption of Congo red onto NiO mainly due to strong electrostatic attraction.

GRAPHICAL ABSTRACT





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ABSTRACT

Monodispersed hierarchical flower-like nickel(II) oxide (NiO) microspheres were fabricated by a facile solvothermal reaction with the assistance of ethanolamine and a subsequent calcination process. The as-synthesized samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, nitrogen adsorption–desorption isotherms, zeta potential measurement and Fourier transform infrared spectroscopy. Flower-like nickel(II) hydroxide microspheres with uniform diameters of approximate 6.3 µm were obtained after the solvothermal reaction. After heat treatment at 350 °C, the crystal phase transformed to NiO, but the hierarchical porous structure was maintained. The as-prepared microspheres exhibited outstanding performance for the adsorption of Congo red (CR), an anionic organic dye, from aqueous solution at circumneutral pH. The pseudo-second-order model can make a good description of the adsorption kinetics, while Langmuir model could well express the adsorption isotherms, with calculated maximum CR adsorption capacity of 534.8 and 384.6 mg g^{-1}, respectively, for NiO and $Ni(OH)_2$. The adsorption mechanism of CR onto the as-synthesized samples can be mainly attributed to electrostatic interaction between the positively charged sample surface and the anionic CR molecules. The as-prepared NiO microspheres are a promising adsorbent for CR removal in water treatment.

1. Introduction

Water is vital for life, and water quality is closely related to human health. However, surface water has been seriously polluted in recent decades with the development of modern manufactory

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and energy industries [1–4]. Synthetic dyes have wide applications in industries such as textile, papermaking, printing and leather tanning [5–7]. Their discharges into the aquatic environment bring risk to human health since many organic dyes are toxic and even carcinogenic [8]. Therefore, it is of great importance to remove the dye pollutants from water.

To eliminate organic dyes from wastewater, various techniques have already been developed, e.g. adsorption [9–11], coagulation [12,13], aerobic or anaerobic treatment [14,15], photodegradation [16–18], chemical oxidation [19], and membrane separation [20]. Compared to other methods, adsorption has remarkable advantages such as simple design and operation, low cost, and high efficiency, thus making it one of the most effective dye removal techniques. Various materials have been applied for the removal of dyes, e.g., activated carbons [21], zeolites [22], fly ash [8], polymer [23], and clay minerals [24]. However, most of these conventional adsorbents still have drawbacks, such as slow adsorption kinetics and low adsorption capacity, as well as low selectivity. Hence, it is indispensable to exploit new adsorbents for removing organic dyes from the wastewater. For this purpose, porous metal oxides have drawn considerable attention based on the advantage of high specific surface area, fast diffusivities as well as excellent adsorption capacity [25].

Nickel(II) oxide (NiO) is an important and promising transition-metal oxide which possesses the advantages of high chemical and thermal stability, environmental compatibility and low cost. It has been widely used in many fields, such as lithium-ion batteries [26], gas sensor [27], supercapacitors [28], and catalysis [29]. Moreover, with an isoelectric point (IEP) of 10.3 [30,31], NiO particles have positive surface charge at circumneutral pH (pH = 6–8), making it suitable to adsorb anionic dyes from aqueous solution. Therefore, besides the above applications, NiO also exhibits excellent performance of adsorption for anionic dye, such as Congo red (CR) and Methyl orange (MO). However, the adsorption ability of these NiO materials for organic dyes are relatively low, and it is imperative to design highly efficient NiO-based adsorbents for organic dye removal from water.

In this work, we synthesized nearly monodispersed flower-like NiO microspheres by a solvothermal method with the aid of ethanolamine, and investigated their performance for CR adsorption in water. The use of ethanolamine in material synthesis reactions could reduce the size of nanocrystals, improve the dispersion properties [32,33], and modify the morphology of the synthesis products. Materials with various morphologies have been successfully prepared with the assistance of ethanolamine, such as flower-like ZnO [34], hierarchical porous β-$Co(OH)_2$ [35] and nanosheet-assembled hierarchical hollow α-Fe_2O_3 microspheres [36]. Herein, flower-like NiO microspheres were successfully synthesized, and showed excellent adsorption capacity for CR, indicating great potential for application in water treatment.

2. Experimental

2.1. Preparation of samples

Nickel chloride ($NiCl_2{\cdot}6H_2O$), urea ($CO(NH_2)_2$), nickel oxide (NiO), ethanolamine ($HOCH_2CH_2NH_2$) and ethanol are obtained from the Shanghai Chemical Industrial Company. The chemicals mentioned above are of analytical grade and used as received without refining. Deionized (DI) water is also employed during the whole fabrication and experimental process.

The monodispersed hierarchical $Ni(OH)_2$ microspheres are prepared by the solvothermal reaction and NiO microspheres are obtained by a subsequent calcination process. Typically, 0.95 g of $NiCl_2{\cdot}6H_2O$ and 0.48 g of urea are added to a 60 mL mixed solvent of ethanol and DI water (2:1, v/v). Subsequently, 8 mL of ethanolamine is mixed into this solution. To form a homogeneous solution, the mixture is stirred continually for 30 min at 25 °C. After stirring, the solution is sealed in a Teflon-line autoclave (100 mL) and then heated to 160 °C and kept for 12 h. After cooling down, the green products are collected by centrifuging and rinsed thoroughly using DI water and ethanol. The abluent precipitates are dried for 8 h at 50 °C by a vacuum oven to collect $Ni(OH)_2$ microspheres. Finally, the NiO microspheres are obtained after calcining the $Ni(OH)_2$ microspheres for 2 h at 350 °C with a 2 °C min^{-1} heating rate. The commercial NiO used for comparison is denoted as NiO-C.

2.2. Characterization

X-ray diffraction (XRD) is conducted on a X-ray diffractometer (D/Max-RB, Rigaku, Japan) using Cu K_α irradiation ($\lambda = 0.15418$ nm). Morphology and microstructure are investigated by a field-emission scanning electron microscope (JSM-7500F, JEOL, Japan) and a transmission electron microscope (JEM-2100F, JEOL). The nitrogen adsorption analyses are operated on a nitrogen adsorption apparatus (ASAP 2020, Micromeritics, USA), the pore size distributions are obtained by the Barrett–Joyner–Halenda (BJH) method [37]. FT-IR spectra are collected on a FT-IR spectrometer (Affinity-1, Shimadzu, Japan).

2.3. Adsorption experiments

The adsorption isotherms are obtained using the batch method with a thermostatic shaker without adjusting pH. The process is as follows: A certain amount of the adsorbent (10 mg) is mixed into a group of conical flasks (250 mL) with 100 mL of dilute CR solutions (20–100 mg L^{-1}) inside. After being sealed, the solutions are incubated in the shaker to reach equilibrium at 30 °C. Subsequently, the suspensions are centrifuged and the CR concentrations left in the supernatant solution are measured with a UV–vis spectrophotometer (UVmini 1240, Shimadzu, Japan). The equilibrium CR adsorption capacity is evaluated by Eq. (1) in Table 1.

For adsorption kinetic experiments, with a fixed initial concentration of 50 mg L^{-1} for CR solutions, the samples are prepared in a similar way to the isotherm experiments. The solutions are sampled and centrifuged at different time intervals and the equilibrium CR concentrations in solution at equilibrium are measured using an identical way to adsorption isotherms study. The CR adsorption uptake at time *t* is measured through Eq. (2) listed in Table 1.

3. Results and discussion

3.1. Crystal phase

XRD patterns for the three samples (NiO, $Ni(OH)_2$ and the commercial NiO-C) are shown in Fig. 1. All the observed peaks in curve (a) correspond to the hexagonal phase β-$Ni(OH)_2$ (JCPDS No.14–0117) [38]. Curve (b) shows five peaks located at 37.2°, 43.3°, 62.8°, 75.4°and 79.4°, which are indexed to the (111), (200), (220), (311), and (222) lattice planes of NiO (JCPDS No.47–1049) with face-centered-cubic (fcc) structure [39]. No other peaks were observed, which indicates pure crystalline NiO can be gained by calcination of the precursor. Compared with curve (b), curve (c) shows the same diffraction patterns but with much sharper diffraction peaks, suggesting the grain size of commercial NiO is much larger.