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Methanol promoted synthesis of porous hierarchical α-$Ni(OH)_2$ for the removal of Congo red

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ABSTRACT

Porous hierarchical $Ni(OH)_2$ composed of petal-like nanosheets with a mix of α- and β-phase was synthesized via a facile hydrothermal method using urea as precipitating agent. In order to tune the pore properties and optimize phase compositions of $Ni(OH)_2$, different types of alcohols (methanol, ethanol, ethylene glycol and glycerol) were added into the hydrothermal systems. It was found that the addition of methanol would retain the porous hierarchical structure of $Ni(OH)_2$, enlarge the pore size and volume, make the transformation of β phase to α phase. However, other alcohols (ethanol, ethylene glycol and glycerol) would destroy the porous hierarchical structure and have little impact on the phase transformation. Using the as-prepared samples as adsorbents for the removal of Congo red (CR), $Ni(OH)_2$ synthesized in methanol aqueous solution exhibited excellent adsorption performance than other samples. When the volume ratio of methanol to water is 1:1, the as-prepared $Ni(OH)_2$ ($Ni(OH)_2$-m1/1) exhibited best adsorption capacity. The adsorption kinetics fitted well with the pseudo-second-order kinetic model of $Ni(OH)_2$-m1/1. Equilibrium data were best described by Langmuir model. The estimated maximum adsorption capacity of $Ni(OH)_2$-m1/1 for CR was 206.2 mg/g, making it a promising candidate for wastewater treatment.

1. Introduction

As one of typical anionic dyes, Congo red (CR) (1-napthalenesulfonic acid, 3,3′-(4,4′-biphenylene bis(azo)) bis(4-amino-) disodium salt) is a benzidine-based anionic disazo dye, which is acknowledged to metabolize to benzidine, a known human carcinogen [1]. Since it is a common synthetic chemical dye used in many industrial processes, CR containing effluents should be adequately treated before they are discharged into the environment [2]. Various techniques have been applied and adsorption is deemed as one of the most reliable and economical methods due to its simplicity, high efficiency and low energy requirement [3–7]. In order to achieve high adsorption capacity, adsorbents with appropriate physical and chemical properties should be developed. Since dye adsorption processes often occur at the surface of the adsorbents, the full exposure of active sites will greatly enhance the performance of adsorbents. Then rational controlling the structure of adsorbents can be beneficial to the exposure of active sites. Among the various structures, porous hierarchical architecture has aroused great attention due to the unique structure and fantastic properties [8–10]. Porous hierarchical materials integrate multiple levels of porosity and structure and exhibit porous structure on more than one length scale from micro- (<2 nm), meso- (2–50 nm) to macropores (>50 nm) [8]. It is well known that the high surface areas caused by micro/mesopores will make materials exposing more active adsorption sites and the macropores can favor the diffusion of adsorbed molecules [11]. Many adsorbents with porous hierarchical structure have been widely used in the adsorption of CR and exhibit superior adsorption capacity [12–16]. However, not all types of pores are beneficial for CR adsorption. If the pore size is too small to accommodate the CR molecules, the active sites will not be fully contacted with CR molecules. Therefore, tuning the pore properties of hierarchical materials will promote their adsorption performance.

Nickel hydroxide ($Ni(OH)_2$) is an important transition metal hydroxide and has received more and more attention due to its wide applications. Since Ni species has a high affinity for CR molecules, $Ni(OH)_2$ can be a good candidate for CR adsorption [1,6,11]. It is found that materials with different polymorphic modifications will exhibit different properties [17,18]. For $Ni(OH)_2$, it has two polymorphic modifications, namely α and β phases [19]. The α phase is isostructure with a hydrotalcite-like structure, contains stacked positively charged $Ni(OH)_{2-x}$ layers with exchangeable anions and water molecules intercalated into the interlayer space to balance the positive charges. The β phase is structurally brucite-like and consists of an ordered stacking of well-oriented $Ni(OH)_2$ layers without any intercalated species. Due to this distinguishing structure feature, α-$Ni(OH)_2$ and β-$Ni(OH)_2$ exhibit different activities in many fields [20,21]. However, although $Ni(OH)_2$ can be used as adsorbent for the removal of CR in waste water [6,11],

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works referred to the influence of phases on the adsorption performance are rare, so far. Moreover, α-$Ni(OH)_2$ can be easily transformed into β-$Ni(OH)_2$ during the preparation process [20,22]. $Ni(OH)_2$ with mixed phases can be often prepared which may be bad for its performance [23]. Therefore, avoiding the phase transformation is vital for improving the adsorption capacity of $Ni(OH)_2$.

In this work, porous hierarchical $Ni(OH)_2$ with mixed phases is synthesized from $NiSO_4$ and urea via a facile hydrothermal method. In order to tune the porous structure and promote the formation of single phase, different types of alcohols are added into the hydrothermal systems. It is found that the addition of alcohols in the hydrothermal systems has a great impact on the $Ni(OH)_2$ properties. The addition of methanol will retain the porous hierarchical structure, but has great influence on the pore structure and can promote the transformation of β-phase into α-phase. However, other alcohols, such as ethanol, ethylene glycol and glycerol, have no effect on the phase transformation and negative effect on the porous hierarchical structure. Using these prepared samples as adsorbents, $Ni(OH)_2$ synthesized in methanol aqueous solutions shows superior adsorption capacity towards CR.

2. Experimental

2.1. Materials

Congo red was chemical pure (purchased from Beijing Chemical Works), other reagents used in the experiments were in analytical grade (purchased from Sinopharm Chemical Reagent Co., Ltd) without further purification. All solutions were prepared using deionized water.

2.2. Preparation of porous hierarchical $Ni(OH)_2$ samples

In a typical procedure, 1.5 g of $NiSO_4 \cdot 6H_2O$ and 2.0 g of urea were dissolved in 80 mL of alcohol aqueous solution. After stirring for 30 min, the mixture was poured into and sealed in a Teflon-lined stainless steel autoclave of 100 mL capacity. The autoclave was heated and maintained at 120 °C for 12 h. The product was collected by filtration, washed with distilled water and ethanol, and then dried at 60 °C for 12 h. The obtained samples are denoted as $Ni(OH)_2$-mx, $Ni(OH)_2$-ex, $Ni(OH)_2$-egx and $Ni(OH)_2$-gx, where m, e, eg and g represent $Ni(OH)_2$ synthesized in methanol aqueous solution, ethanol aqueous solution, ethylene glycol aqueous solution and glycerol aqueous solution; x represents the volume ratio of alcohol to water. $Ni(OH)_2$ sample synthesized in water is denoted as $Ni(OH)_2$-w.

2.3. Characterizations

$Ni(OH)_2$ samples were characterized by X-ray diffraction (XRD, Rigaku D/Max-2500, Cu Kα radiation), scanning electron microscopy (SEM JSM-7500F). Nitrogen adsorption measurements were determined by Micromeritics ASAP 2020 at −196 °C and the BET surface areas as well as pore size distribution were taken from the isotherms. The redox potential of $Ni(OH)_2$ samples were examined by cyclic voltammetry (CV) tests in 0.5 M NaOH solution. CV tests were performed at 25 °C in a three-electrode cell connected to a LK98II Microcomputer-based Electrochemical System (LANLIKE, Tianjin, China). The working electrode was a glassy carbon disk with an area of 0.071 cm^2. Ag/AgCl and platinum wire served as reference and auxiliary electrodes, respectively. Thin film electrodes for samples were prepared by the following procedure. Simply, the $Ni(OH)_2$ suspension with a concentration of 1.0 mg/mL was obtained with the aid of ultrasonication dispersion, and 10 μL suspension was dropped onto the glassy carbon disk. After evaporating the solvent, 0.5 μL of Nafion (Dupont, 0.5 wt.%) was dropped onto catalyst film to act as binder and proton conductor.

2.4. Adsorption of CR

CR ($C_{32}H_{22}N_6Na_2O_6S_2$) was used as a model dye to investigate the adsorption properties of $Ni(OH)_2$ samples. The adsorption was carried out in an aqueous solution at room temperature. Typically, 50 mg of $Ni(OH)_2$ was added into 100 mL of CR aqueous solutions with a concentration of 50 mg/L in a beaker under stirring at 500 rpm. 3 mL of the dispersion was extracted and subsequently centrifuged to separate $Ni(OH)_2$ and dye solutions at 4000 rpm for 10 min at different intervals. The changes of concentration of the centrifuged solutions were measured at maximum adsorption wavelengths of (493 nm) using UV/vis spectrophotometer. To evaluate the adsorption capacity, the initial concentrations of CR solutions were scaled in the range of 50–250 mg/L, and the dosage of $Ni(OH)_2$ sample was kept at 0.5 g/L. The mixtures were stirred at 500 rpm at room temperature for 12 h, and the concentrations of final CR solutions were measured using UV–vis spectroscopy after centrifugation at 4000 rpm. The amount of CR adsorbed at equilibrium q_e (mg/g) was calculated based on the equations given below:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_0 and C_e (mg/L) are the liquid phase concentration of CR at initial and equilibrium, respectively, V is the volume of the solution (L) and W is the mass of adsorbent used (g).

3. Results and discussion

3.1. Characterization of the $Ni(OH)_2$ samples

As the structure of $Ni(OH)_2$ can be easily influenced when urea is used as neutralizing agent [23], the phase characterization was carried out using XRD technique and the results are shown in Fig. 1. For $Ni(OH)_2$-w, as shown in curve a, it shows a peak at a broad band in the region of diffraction angle 2θ = 32–44°, which may be due to the formation of α-$Ni(OH)_2$ [24]. The other peaks can be corresponding to β-$Ni(OH)_2$ [23]. It is obvious that $Ni(OH)_2$-w exhibits mixed phases of α and β. When methanol is added into the hydrothermal system, the XRD pattern of product is very different from that of $Ni(OH)_2$-w. As shown in curve b, the diffraction angle 2θ = 11.4°, 24.6°, 33.6° and 60.0° can be assigned to (003), (006), (101) and (110) planes of α-$Ni(OH)_2$ for $Ni(OH)_2$-m1/1 (JCPDS card no. 38-0715) [11,25]. No diffraction peak representing β-$Ni(OH)_2$ is observed, suggesting that methanol can promote the formation of α-$Ni(OH)_2$ and make the product be a single phase. Nevertheless, for samples $Ni(OH)_2$-e1/1, $Ni(OH)_2$-eg1/1

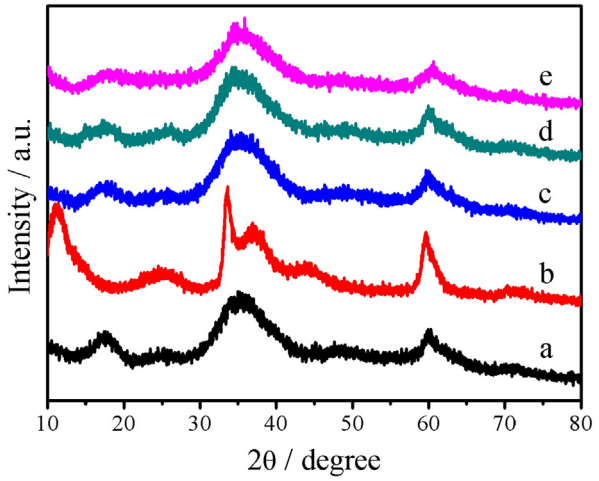

Fig. 1. XRD patterns of $Ni(OH)_2$-w(a), $Ni(OH)_2$-m1/1(b), $Ni(OH)_2$-e1/1(c), $Ni(OH)_2$-eg1/1(d), $Ni(OH)_2$-g1/1(e).