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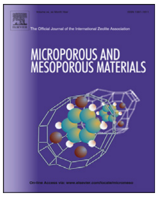

Synthesis of reduced graphene oxide/NiO nanocomposites for the removal of Cr(VI) from aqueous water by adsorption

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ABSTRACT

In this work, we report a room-temperature approach to synthesizing reduced graphene oxide/NiO (RGO/NiO) nanocomposites. The chemical structure of RGO/NiO nanocomposites were investigated by Transmission Electron Microscope (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray power diffraction (XRD). It is shown by the experiment that the RGO/NiO nanocomposites have strong capacity to absorb the hexavalent chromium ion (Cr (VI)), the maximum adsorption capacity of Cr (VI) on RGO/NiO nanocomposites at pH = 4 and T = 25 °C can reach 198 mg g^{-1}, higher than any other currently reported. The adsorption kinetic data were well described by a pseudo-second-order model. Both Freundlich and Langmuir isotherm models were applied to the experimental data analysis, and the latter proved to be a better fit. The pH value markedly affected the adsorption behavior of RGO/NiO nanocomposites, but the effect of temperature was insignificant. The probable mechanism of synergistic adsorption of Cr (VI) ions was considered. These results suggest that RGO/NiO nanocomposites have the potential to be applied in industrial wastewater treatment.

1. Introduction

Heavy metal pollution in groundwater and seawater systems is an important environment problem due to its toxic effects and accumulation throughout the food chain and hence in the human body [1]. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end-products and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic [2,3]. Cr (VI) is very easy to be absorbed by the body, it can invade the human organs through the digestive, respiratory, and mucous membrane. When human have a breath of air contains chromic anhydride, there will be the symptoms of atrophy nasal mucosa. Cr (VI) can cause vomiting and diarrhea through digestive, and cause skin diseases such as hallergicdermatitis and eczema through skin, and may even cause cancer after prolonged exposure. Chromium exists in the aquatic environment mainly in two primary oxidation states: trivalent Cr (III) and hexavalent Cr (VI). Cr (III) is an essential element in humans and is a relatively inactive genetoxic agent [4–6]. The public health consideration of chromium is mostly related to Cr (VI) compounds, which primarily present in the form of hydrogen chromate ($HCrO^{4-}$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$), because they have high solubility and diffusivity in tissue allowing them to cross biological membrane easily [7,8]. Therefore, it is essential to removal them from contaminated water.

During the last decade, numbers of technologies have been adopted to remove Cr (VI) from contaminated water, including low pressure membrane filtration, ion exchange, chemical precipitation, reverse osmosis, and biological treatment, etc [9]. However, these methods show practical limitation to remove Cr (VI), the poor stability of membrane filtration technology has limited its application in industry. Ion exchange and reverse osmosis are not economically attractive because of their high operating costs [10,11]. The reaction speed of chemical precipitation is slow, after the treatment, the water is hardness. Biosorbents often have weak mechanical strength, causing potential secondary pollution in extreme condition.

These drawbacks have hindered the applications for Cr (VI) removal from contaminated water. Adsorption is considered as the most promising approach for the removal of heavy metal ions due to its simplicity, cost-effectiveness, and enabling large-scale application [12]. Various adsorbents have been reported to remove Cr (VI) from wastewater, Potgieter ea.al [13] used South African industrial clay as adsorbent for the removal of Cr(VI) from an aqueous solution, and the adsorption capacity was reached 58.5 mg/g. others are metal oxides and zeolites [14–16]. However,

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the conventional adsorbents often showed a limited adsorption capacity. Therefore, there is an increasing demand for preparing new adsorbents with surface functional groups and high adsorption capacity.

As one of the most important carbon family members, graphene have a large special surface area (with a theoretical value of 2630 m^2 g^{-1} [17]), this makes graphene a potential super adsorbent material. However, graphene composing of carbon atoms only has poorly solubility in water, thus graphene oxide (GO) and reduced graphene oxide (RGO) with abundant oxidized functional groups (epoxy, hydroxyl, and carboxyl groups) on their surfaces are used as adsorbents instead. In recent years, a number of novel metallic oxides have been assembled on the synthesis of graphene-based nanocomposites. By incorporation of nanoparticles into RGO, the aggregation problem of RGO could be minimized or prevented [16]. Besides, the nanocomposites with large surface area show superior properties, compared with bare nanomaterials [18]. Zhou et al. [19] reported a simple solvotermal strategy to prepare RGO-Fe_3O_4 non-nanocomposite for removal of Cr (VI). Chandra et al. [20] have employed magnetite-RGO composites to get rid of arsenic from water, these composites show high capacity for As (III) and As (II). Cao et al. [21] presented a one-pot facile method to produce the RGO- Fe_3O_4 hybrid nanocomposite for removal Pb (II), the maximum adsorption capacities of Pb (II) are 30.68 mg g^{-1}.

Nickel oxide (NiO) is a very important functional material, due to its unique electrical, magnetic, and catalytic properties. It has been widely used in various fields, including battery anode material, electrochemical capacitor, optical materials, gas-sensing material and catalysis [22,23]. There are fewer reports on the environmental applications of NiO for heavy metal removal, Naeem et al. reports NiO as a novel and an efficient adsorbent for the removal of Pb from aqueous solutions [24], Wang et al. reported the synthesis of biomorphous NiO from pine template with impregnation and calcination method, and used for the adsorption of Pb(II) in aqueous solution [25].

In this paper, the RGO/NiO nanocomposites prepared by a facile method were reported. First, we synthesized the GO, and then, a mixed solution of GO and nickel acetate was directly reacted. During preparation, the GO could be partially reduced to RGO sheets and NiO nanograins anchored on RGO sheets formed due to the decomposition of the nickel acetate. The obtained RGO/NiO nanocomposites displayed a greatly absorption property. The maximum adsorption capacity of the nanocomposites can reach 198 mg/g for Cr (VI) ion. The RGO/NiO nanocomposites were characterized and its adsorption performance was systematically studied at various conditions (temperature and pH). The RGO/NiO nanocomposites were demonstrated to possess an excellent absorption capacity for the removal of Cr (VI) ions, which significantly outperformed the other conventional adsorbents.

2. Expermental section

2.1. Chemicals

Graphit (325 mesh) was obtained from Bay Carbon, Inc., Michigan. Nickel chloride, hydrazine hydrate, sodium bicarbonate, sodium carbonate, potassium dichromate and other chemical reagents used in our experiment are commercial products purchased from Beijing Chemical Works. All of the reactants were used without any further purification.

2.2. Preparation of RGO/NiO nanocomposites

Graphene oxide was prepared using the modified Hummers method [26]. 0.2 g prepared GO was mixed with 3.2 g $NiCl_2 \cdot 6H_2O$ and 300 mL of deionized water in a 500 mL three-neck flask equipped. A mixture of 2.3 mL hydrazine hydrate dissolved in 500 mL buffer solution ($pH = 9.5$) is injected continuously into the reaction solution. The mixture was stirred vigorously for 30 min at room temperature to form a homogeneous black solution. The black product was washed with ethanol and deionized water. The preparation process of RGO/NiO nanocomposites is shown in Fig. 1.

2.3. Adsorption experiment

Bath adsorption studies were performed by 10 mg of RGO/NiO nanocomposites with 30 mL of Cr (VI) in a 50 mL plastic tube to reach adsorption equilibrium. The effect of pH on heavy metal ions adsorption on to RGO/NiO nanocomposites was investigated. Standard acid of 0.1 M HCl and base of 0.1 M NaOH solutions were used for pH adjustment. To determine sorption kinetics, the test solution was sampled at various time intervals. For the adsorption isotherm experiments, RGO/NiO nanocomposites were dispersed in different concentration Cr (VI) solution at room temperature.

The concentrations of Cr (VI) ions were determined by using an Inductive Coupled Plasma Emission Spectrometer (ICP). The adsorption capacity at equilibrium (Qe) can be calculated according to equation:

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

where C_0 and C_e are the initial and equilibrium concentrations of Cr (VI) (mg/L), respectively; Q_e is the amount of metal ion adsorbed per unit amount of adsorbents (mg/g); V is the volume of Cr (VI) solution (L), and m is the dry weight of adsorbents (g).

2.4. Characterization

Transmission electron microscopy (TEM) images were taken by using a TECNAI G2 high resolution transmission electron microscope with an accelerating voltage of 200 kV. All TEM samples were created by depositing a drop of diluted suspensions in water on a carbon film-coated copper grid. The X-Ray photoelectron spectrum (XPS) measurements were performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation. X-ray diffraction (XRD) patterns of the samples were collected on a Bruker D&ADVANCE diffractometer (Germany) using Cu Kα(1.5406 Å) radiation. The concentration of metal ions was determined by an Inductive Coupled Plasma Emission Spectrometer (ICP-5000, Juguang, China).

3. Results and discussion

3.1. General characterization of RGO/NiO nanocomposites

The shape, size and morphological characteristics of RGO/NiO nanocomposites were investigated by TEM. Fig. 2 shows the TEM images of the as-synthesized GO and RGO/NiO nanocomposites. As shown in Fig. 2a, it can be clearly seen that the as-prepared GO present the sheet-like structure with smooth surface and wrinkled edge. The obtained GO sheets display layered structures and become very thin. Compared to pure GO, Fig. 2b shows that a large number of nanoparticles were obtained and uniformly dispersed on the surface of RGO sheets. An average particle size of about 2.5 nm was obtained (Fig. 2d). And the HRTEM image (Fig. 2c) shows well-resolved lattice fringes with an interplane distance of 0.21 nm, corresponding to the d-spacing of the (200) planes of NiO (JCPDS [Joint Committee on Powder Diffraction Standards] No.65–5745). This clearly shows the formation of well-textured