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Characterization and adsorption performance of Pb(II) on CuO nanorods synthesized by the hydrothermal method

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ABSTRACT

Copper oxide (CuO) nanorods were synthesized by hydrothermal method. The detailed structural, compositional and optical characterization of this material was also evaluated with XRD, FT-IR, EDS, and UV–vis spectroscopy, which confirmed that the obtained nanorods are well-crystallized CuO and possess good optical properties. SEM and TEM studies revealed that the as-synthesized CuO nanorods are uniform with an average diameter of 17 nm. The adsorption activity of the CuO nanostructures was studied. The adsorption results showed that the CuO nanorods are an effective and efficient adsorbent for the removal of Pb(II) ions. The influence of various operational parameters such as the pH of the solution, the contact time and the initial concentrations were also studied and the results were discussed. The estimated maximum lead ion adsorption capacity of the CuO nanorods was found to be 188.67 mg g^{-1} at an optimum pH of 6.

1. Introduction

The synthesis and characterization of transition metal oxides controlling the size, shape, uniform dimension and structure have attracted considerable interest due to their unique physicochemical properties and potential applications in catalysis and photoelectronic devices [1–2]. From all transition metal oxides, copper oxide (CuO) nanomaterials are of great interest due to their novel properties and range of potential applications such as in photocatalysis [3–6], gas sensors, solar energy transformation, field emission (FE) emitters, photovoltaic devices and magnetic storage media [7–11]. Many methods have been used to synthesize CuO nanostructures, with various morphologies, such as the sol–gel method [12], the electrochemical dissolution method [13], the wet chemical method [14], the microwave method [15], the sonochemical method [16], the thermal decomposition method [17] and the hydrothermal route [18–21]. The hydrothermal technique is considered an effective method for synthesizing nanomaterials because it is a simple and reliable method with a low cost.

Heavy metal pollution has recently become the focus of much international attention, mainly due to the great amount of discharge of said metals into the environment from industrial activities. Heavy metals are toxic to ecosystems as well as humans, so their bioaccumulation in the food chain causes serious disorders. From among the contaminating heavy metals, lead is considered an especially hazardous element because it is not biodegradable and tends to accumulate in living organisms causing diseases and disorders [22–23]. Thus, the removal of lead from water is currently one of the most important environmental issues being investigated. The most common methods proposed to remove heavy metal ions from an aqueous medium include solvent extraction, ultra-filtration, reverse osmosis, co-precipitation, nanofiltration, ion exchange and adsorption [24–25]. From these methods, adsorption is the preferred method since it is a highly efficient technique with particularly low operational costs and applicable to a wide range of adsorbents. The materials that are extensively used for the removal of lead from water include activated carbon, ion-exchange resins, red mud, activated alumina, biomass, chitosan, and carbon nanotubes [26–30]. It has become a challenge for researchers to seek cheaper and more effective adsorbents for lead removal. In addition, the use of nanoparticles in water treatment has received substantial attention due to the nanoparticles' high specific surface area, mobility and activity [31–32].

In this work, the CuO nanorods were synthesized by the hydrothermal method and characterized using XRD, SEM, TEM, FT-IR and UV–vis spectroscopy. The ability and analytical efficiency of the CuO nanorods as adsorbents on the selectivity and adsorption capacity of Pb(II) was studied. The selectivity of CuO

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nanorods toward seven metal ions, Pb(II), Ni(II), Au(III), Cd(II), Cr (II), Ag(I), and Al(III), was investigated in order to study the effectiveness of CuO nanorods in the adsorption of selected metal ions. The adsorption capacity of the adsorbent was studied using batch experiments. The impact of the pH, contact time and adsorbent concentrations were all analyzed and the experimental data obtained was evaluated and fitted using adsorbent equilibrium isotherms and kinetic models.

2. Materials and methods

2.1. Materials

1000 mg L^{-1} stock standard solutions of Pb(II), Ni(II), Au(III), Cd (II), Cr(II), Ag(I), and Al(III) were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Double distilled deionized water was also used throughout the study. Copper nitrate and sodium hydroxide was used and purchased from the Sigma–Aldrich Company.

2.2. Preparation of the CuO nanorods

The hydrothermal treatment was performed as follows: 1 mmol of Cu $(NO_3)_2 \cdot 3H_2O$ and 2 mmol of NaOH were treated with 5 mL of water; the medium was kept under vigorous stirring. The pH value was fixed at 11. The reaction mixture was transferred into a 23 mL Teflon-lined autoclave and kept at 120 °C for 3 h. The resulting precipitate was recovered through filtration and washed with distilled water. This sample was dried at 80 °C for 10 h.

2.3. Characterization methods

An X-ray diffraction spectrum (Panalytical X'Pert Pro goniometer with Cu Kα radiation and λ = 1.5406 Å) and a Fourier transform infrared (FTIR) spectrum (recorded on an EQUINOX 55 in the wave number interval 400–4000 cm^{-1}) were recorded. The morphology of the sample was studied using an FEI Quanta 200 Environmental SEM and transmission electron microscopy (TEM). Results were recorded on a JEOL 100CX II electron microscope operated at 200 kV. In order to check the optical properties of the as-synthesized products, UV–vis spectroscopy (PerkinElmer instrument UV/vis-Lambda 45) was carried out at room temperature.

Inductively coupled plasma–optical emission spectrometry (ICP–OES) measurements were obtained with a HORIBA Jobin Yvon ICP–OES spectrometer; model Optima 4100 DV (Waltham, MA, USA). The ICP–OES instrument was optimized daily before measurements were taken and was operated as recommended by the manufacturers. The ICP–OES spectrometer was used with the following parameters: FR power, 1050 W; frequency, 40.68 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 13 L min^{-1}; auxiliary gas (Ar) flow, 0.1 L min^{-1}; nebulizer gas (Ar) flow, 0.75 L min^{-1}; nebulizer pressure, 2.74 bar; glass spray chamber according to Scott (Ryton), sample pump flow rate, 1.4 mL min^{-1}; integration time, 5 s; replicates, 2; wavelength range of monochromator, 165–460 nm.

2.4. Adsorption methods

For the adsorption selectivity study, 4 mg L^{-1} standard solutions of each metal ion were prepared and adjusted to a pH value of 5 with an acetate buffer. Then, each standard solution was individually mixed with 30 mg of CuO nanorods. In this study, a fixed pH value of 5 was chosen for all metal ions in order to avoid any precipitation of other species. Prior to their use, the copper oxide nanorods were oven-dried at 50 °C for 1 h to eliminate moisture traces. Batch adsorption experiments were carried out in 50 mL flasks. 0.05 g of copper oxide nanoadsorbent were added to each flask containing 50 mL of Pb(II) ion solutions with the appropriate concentrations.

All experiments were conducted at room temperature (25 °C) without mechanical agitation. The effect of the pH on the adsorption of lead was studied using sodium acetate and acetic acid to adjust the pH value to 3–6. After 15 min, an aqueous sample

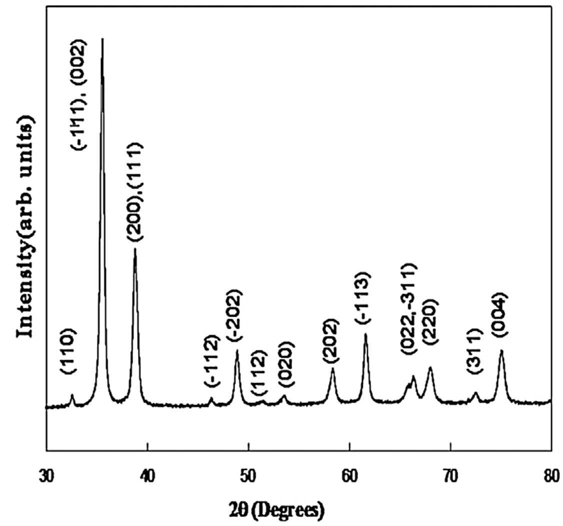
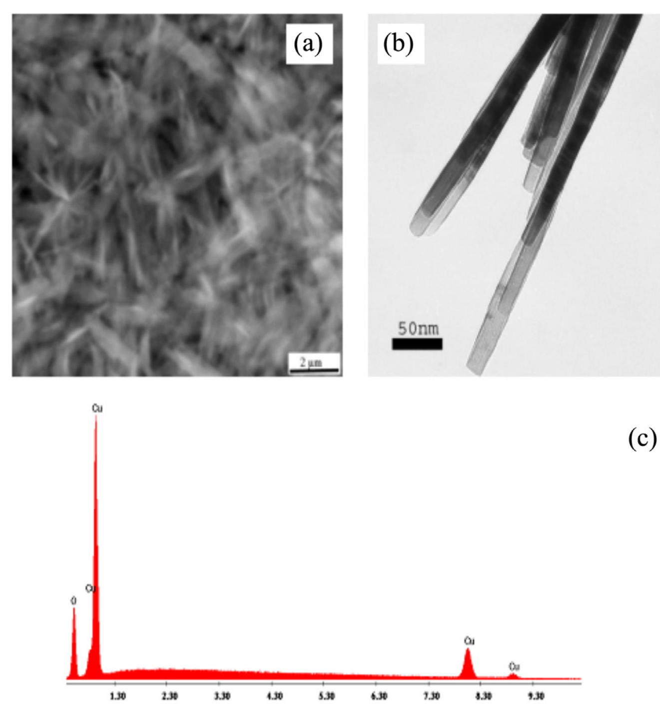


Fig. 1. Powder X-ray diffraction pattern of CuO nanorods.



Elements	Weight %	Atomic %
O k	19.81	49.53
Cu K	80.19	50.47
Total	100.00	100.00

Fig. 2. (a) SEM micrographs of several CuO nanorods, (b) low magnification TEM micrographs of CuO nanorods and (c) EDS study of CuO powder.