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Study of copper ion adsorption from aqueous solution with different nanostructured and microstructured zinc oxides and zinc hydroxide loaded on activated carbon cloth

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ABSTRACT

Microstructured and nanostructured zinc oxides and zinc hydroxide loaded on activated carbon cloth (ACC) were synthesized by microwave-assisted chemical bath deposition (MACBD) at different pH also and hydrothermal methods.

The composition and morphology of samples were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. Deposited sediments on ACC by hydrothermal are dandelion-like structure with nanoneedles of 50 to 200 nm diameter. Deposited samples with MACBD method at pH of 9.8 and 10.8 are flower-like and mixture of flower and rhombic microstructures, respectively. Performance of the synthesized adsorbents (by MACBD and hydrothermal methods) for removal of copper ion was studied by kinetic and equilibrium experiments. The experimental kinetic and equilibrium data have been fitted to different classical and recently developed models. All of the prepared samples behave as super adsorbent for removal of copper ion with maximum adsorption capacity of about 1300 mg/g. Finally, the mechanism off adsorption is presented too.

1. Introduction

Different pollutants are released from industries to the environment and caused serious health problems. Heavy metal ions are one of the main classes of the released pollutants which are released from mine, electroplating, paints, industrial effluents into the environment [1]. Heavy metals are not biodegradable and tend to accumulate in body organs and threat to the health of living organisms. One of the harmful heavy metal ions is copper ion. The presence of copper ion in drinking water causes abdominal pain, nausea, and more. High concentration of copper ion in body damages liver and kidneys and sometimes causes death for children [2,3].

In recent years, numerous studies have been conducted to remove copper ions from aqueous media. There are different methods for removal of copper ion from aqueous solutions such as precipitation, electrolysis, nano-filtration, extraction, adsorption and ion exchange methods [4–8]. Precipitation is a common method to remove copper ion from aqueous solutions. But, due to use of chemicals, the long time process and the possibility of sample contamination the method are not suitable [9–11].

The ion exchange is a suitable method for the removal of copper ion, which makes the recovery of metal ion, but it is expensive and complex [8]. Adsorption is an appropriate method to remove contaminants such as copper ion and it is an economical and environmentally friendly method [12]. In adsorption method, variety absorbents are used, which one of the best adsorbent is nanostructured and microstructured zinc oxides for removal copper ion from aqueous solution [1,13–16]. Zinc oxide can be synthesized with different structures such as: nanoneedles [17], nano-belts [18], nano-wire [19], nano-ring [20], flower-like [1,15,21], dandelion-like [22].

Structure of a crystal can affect on its adsorption properties and therefore study of effect of structure on its adsorption performance is interesting.

In this study, adsorption of copper ion on nanostructured zinc oxides and zinc hydroxide loaded on ACC [23] is investigated. Microstructured and nanostructured zinc oxides and zinc hydroxide loaded on ACC were synthesized by microwave-assisted chemical bath deposition (MACBD) at different pH also and hydrothermal methods. Then their performances as adsorbent for copper ion were investigated at different conditions.

2. Experimental

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http://dx.doi.org/10.1016/j.molliq.2015.11.036 0167-7322/© 2015 Elsevier B.V. All rights reserved. Samples were synthesized based on our recent report by microwave-assisted chemical bath deposition (MACBD) at several pH

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(pH = 9.8 and 10.8) and hydrothermal methods [23]. Briefly for synthesis of adsorbent by hydrothermal method, Zinc acetate (0.035 M), NaOH, (0.75 M), deionized water and a piece of ACC (3 × 1.5 cm) were put in Teflon lined stainless steel autoclave for 24 h at 70 °C. Then the prepared slides were washed with deionized water and dried in oven for 60 min [23].

For synthesis of adsorbent by MACBD method, zinc acetate solution (0.167 M) was stirred and ammonia solution NH₄OH (25–30%) was added to it, till the solution becomes transparent. Then NaOH 0.1 M and/or CH3COOH 0.1 M were used for pH adjustment (pH = 9.8 or pH = 10.8). The ACC (2×2) was added to the solution and the system was heated on microwave oven (Moulinex, MW200130, 2450 MHz) for one to five steps of irradiation (every stage contain 30 s irradiation and 10 s off). Then the prepared slides were washed with deionized water and dried in oven for 60 min [23].

UV/Vis spectroscopy was used to measure the residual concentration of copper ion during adsorption experiments. In this method, zincon was applied as an appropriate indicator in buffer solution at pH = 7 to determine the copper ion spectroscopically [24].

The ability of the synthesized adsorbents (by MACBD and hydrothermal methods) for removal of copper ion was studied by kinetic and equilibrium experiments.

In kinetic studies, the adsorbent (0.015 g) was in contact with 15 ml copper ion solution with specified concentration in a shaker at 25 $^{\circ}$ C and with 70 rpm and sampled at different time intervals.

The amount of adsorbed copper per unit mass of adsorbent, qt (mg/g) at any time was calculated by Eq. (1).

$$q_t = \frac{V(C_0 - C_t)}{W} \tag{1}$$

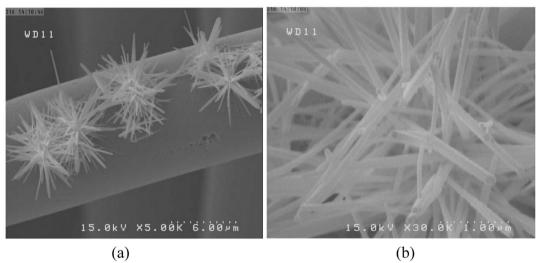
where Ct (ppm) is copper ion residual concentration in solution at time t (min), C0 (ppm), is the initial concentration of copper ion in solution, W (g) is the sediment mass loaded onto activated carbon cloth and V (L) is volume of solution.

For the equilibrium adsorption experiments, a series of solution with different concentrations of copper ion is required. 15 ml of each solution was added to 0.015 g of adsorbent at 25 °C in a shaker with 70 rpm. After 24 (h), the equilibrium concentration of copper ion (Ce) in each sample was determined. The equilibrium amount of Cu^2 + adsorbed per unit mass of adsorbent, qe

(mg/g), was calculated by Eq. (2).

$$q_e = \frac{V(C_0 - C_e)}{W} \tag{2}$$

The point of zero charge pH (pH_{pzc}) was also determined for these adsorbents. For this experiment, NaCl solutions (0.1 M) with different pH were prepared. The adsorbent (0.015 g) was in contact with NaCl solution (0.1 M, 15 ml) at different pH in a shaker at 25 °C and with 70 rpm for 24 h. pHpzc was obtained with measurement of initial and final pH



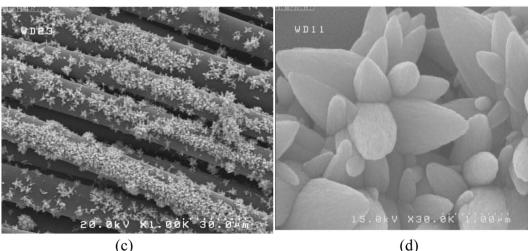


Fig. 1. The SEM micrograph of synthesized sediments (nanostructured and microstructured of ZnO) loaded on ACC by hydrothermal method (a and b) and MACBD method at pH = 9.8 (c and d) with different magnifications.

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