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Removal of nickel(II) from aqueous solutions using iminodiacetic acid functionalized polyglycidyl methacrylate grafted-carbon fibers☆

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ABSTRACT

Iminodiacetic acid functionalized polyglycidyl methacrylate grafted-carbon fibers (PGMA-IDA/CFs) were prepared for Ni(II) removal from aqueous solutions. The effects of solution pH value, temperature and adsorption time were investigated. The maximum adsorption capacity of Ni(II) on PGMA-IDA/CFs is 0.923 mmol·L^{-1} · g^{-1} at pH 5.2 and 50 °C. Kinetic data indicate that the adsorption process matches the pseudo-second-order model and Elovich kinetic model. Thermodynamic data suggest that the adsorption process is endothermic spontaneous reaction.

1. Introduction

Nickel is a common heavy metal pollutant in wastewater from electroplating and metal cleaning industries. Accumulation of nickel in aqueous environment may cause a serious hazard to human health, such as skin allergies, lung fibrosis, different poisoning degrees to kidney and cardiovascular system and stimulation of neoplastic transformation [1,2]. Thus the removal of Ni(II) from wastewater is necessary. Many treatment methods have been investigated, such as chemical precipitation [3], ion exchange [4], electrochemical treatment [5] and adsorption [6]. Adsorption is becoming a popular method due to its convenience and cost-effectiveness.

Carbon fibers have outstanding chemical stability, electric conduction, surface area and adsorption, especially easy operation compared to powder adsorbents. They have been widely used as support materials [7,8] and adsorbents in the removal of heavy metals. For example, Jin *et al.* successfully grafted tetraoxalyl ethylenediamine melamine resin on carbon fibers for separation of Ni(II) from the spent nickel plating baths [7]. Chergui *et al.* grafted cyclam functionalized polyglycidyl methacrylate on carbon fibers, showing excellent uptake towards Cu(II) [8]. The chelating resin, iminodiacetic acid functionalized polyglycidyl methacrylate (PGMA-IDA) was successfully employed in the removal of Ni(II) [9,10]. PGMA-IDA has an excellent adsorption capacity for Ni(II) [7,10]. In this work, PGMA-IDA is grafted on carbon fibers by atom transfer radical polymerization (ATRP) to prepare PGMA-IDA grafted carbon fibers (PGMA-IDA/CFs) for the removal of Ni(II) from aqueous solutions.

2. Experimental

2.1. Apparatus and chemicals

All electrochemical experiments were performed with a CH660 B electrochemical workstation (Chenhua, Shanghai, China). Infrared spectra were measured with IR 200 (Nicolet, America). pH was measured with HI 255 model pH meter (Leici, Shanghai, China). Polyacrylonitrile carbon fibers were obtained from Dingfeng Carbon Fibers Fabrication Company of Yixing (Wuxi, China). One truss carbon fibers have about 3000 branches with a diameter of (7 ± 1) μm and they were snipped to 8 cm long in the experiments. 1-(4-Aminophenyl)-ethanol was purchased from Alfa Aesar. Glycidyl methacrylete (GMA), iminodiacetic acid (IDA), hydrobromic acid and fluoroboric acid were purchased from Aladdin (Shanghai, China). Ethylenediaminetetraacetic acid (EDTA) disodium salt was obtained from Xilong Chemical Co., Ltd. All other chemicals were of analytical grade and deionized distilled water was used throughout.

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2.2. Preparation of PGMA-IDA/CFs

The synthesis processes of PGMA-IDA/CFs adsorbent are divided into four steps and illustrated in Fig. 1.

(i) Synthesis of diazonium salt BF_4^-,$^+N_2$–C_6H_4–$CH(CH_3)$-Br (D1) [11]. 1-(4-Aminophenyl)-ethanol (0.4 g), tetramethylammonium bromide (0.0135 g), and hydrobromic acid (48%, 5 ml) were added into 50 ml a round bottom flask, refluxed at 150 °C for 16 h, and then cooled to 0 °C. Fluoroboric acid (49.5%–50.5%, 3.2 ml) was added into the flask. A solution of sodium nitrite (1.7 mol·L^{-1}, 2 ml) was slowly dripped into the flask then stirred for 30 min in 0 °C ice bath. The precipitated diazonium tetrafluoroborate (BF_4^-,$^+N_2$–C_6H_4–$CH(CH_3)$-Br, D1) was filtered and washed with 5% sodium fluoroborate and methanol, then dried under vacuum.

(ii) Electrochemical treatment of carbon fibers [7]. 0.015 g D1 was added into 30 ml of 0.1 mol·L^{-1} tetrabutylammonium tetrafluoroborate/acetonitrile and reduced on carbon fibers by chronoamperometry for 300 s under nitrogen atmosphere, at a potential of −0.5 V (*versus* saturated calomel electrode). The aryl initiator modified carbon fibers (labeled CF-Br) were washed with acetone and deionized water.

(iii) Surface-initiated ATRP of GMA monomers [7]. ATRP of GMA monomers at the CF-Br surface was carried out in DMF/water mixture (26.6/13.3 in ml) using GMA (3.7 ml), cuprous bromide (0.0065 g), copper(II) bromide (0.039 g), and 2,2′-bipyridine (0.068 g). ATRP was conducted at room temperature under argon atmosphere for 12 h. After polymerization, the carbon fibers (labeled PGMA/CFs) were washed with acetone and deionized water, then dried under vacuum at 40 °C.

(iv) Modification of PGMA/CFs [12]. PGMA/CFs were immersed in 15 ml mixed solution (3.18 g Na_2CO_3 + 0.5 g IDA, pH 12) at 75 °C for 48 h. After modification, carbon fibers (labeled PGMA-IDA/CFs) were washed with acetone and deionized water, then dried under vacuum.

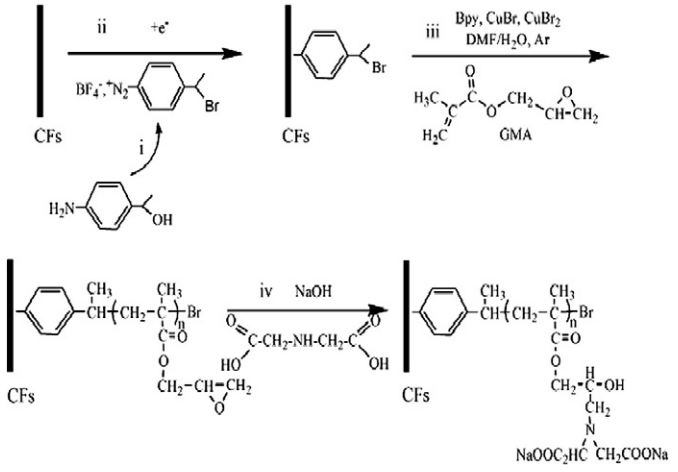

Fig. 1. The preparation process of PGMA-IDA/CF adsorbent.

2.3. Adsorption experiments

Adsorption experiments were carried out by adding 4 trusses PGMA-IDA/CFs into 15 ml Ni(II) solution with initial concentration of 17.09 mmol·L^{-1} in 180 min. Adsorption was studied by varying the variables such as initial pH value of Ni(II) solution, temperature and adsorption time. The initial pH value of Ni(II) solution was varied from 3 to 6 at temperatures from 30 °C to 55 °C. The kinetics was studied in different time intervals and the temperature in thermodynamic study varied from 35 °C to 50 °C. The concentration of Ni(II) was determined *via* titration against 1.5 mmol·L^{-1} EDTA using murexide as an indicator [13]. The adsorption capacity (q, mmol·L^{-1}·g^{-1}) of Ni(II) is calculated by following equation:

$$q = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where c_0 and c_e are the initial and equilibrium concentrations of Ni(II) (mmol·L^{-1}), m is the mass of PGMA-IDA/CFs (g), and V (L) is the volume of Ni(II) solution.

3. Results and Discussion

3.1. IR analysis

IR spectra of materials D1, CF-Br, PGMA/CFs, IDA and PGMA-IDA/CFs are showed in Fig. 2. For CF-Br, the vibration band at 2262 cm^{-1} characteristic of N ≡ N disappears, which is clearly observed in curve a. The vibration band of the aromatic ring stretching at 1510 cm^{-1} (curve a) shifts to 1515 cm^{-1} (curve b). These confirm the electrochemical reduction of D1 and grafting of aryl layer [11]. For PGMA/CFs, the peaks at 1728 cm^{-1} and 906 cm^{-1} correspond to the stretching vibration of ester carbonyl group and the symmetrical stretching of epoxy group, respectively [14]. For IDA and PGMA-IDA/CFs, the peak at 1715 cm^{-1} of stretching vibration of carbonyl group in IDA shifts to lower frequency (1650 cm^{-1} and 1397 cm^{-1}). The peaks at 1650 cm^{-1} and 1397 cm^{-1} match the asymmetric stretching vibration and symmetric stretching vibration of carboxylic acid anion, respectively [15,16]. Thus IDA is successfully introduced onto the PGMA/CFs.

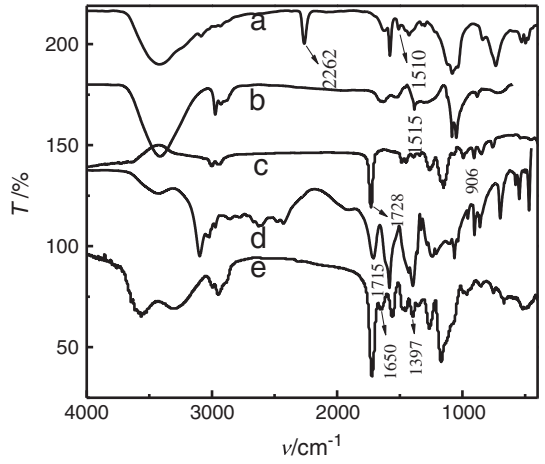

Fig. 2. IR spectra of materials D1 (a), CF-Br (b), PGMA/CFs (c), IDA (d) and PGMA-IDA/CFs (e).

3.2. Effect of pH on adsorption of Ni(II)

The effect of initial pH on adsorption of Ni(II) is showed in Fig. 3. The adsorption capacity of Ni(II) on PGMA-IDA/CFs increases obviously with pH value until reaching a maximum value (0.852 mmol·L^{-1}·g^{-1}) at pH 5.2. The synergy between electrostatic interaction and ligand chelation improves the adsorption capacity of Ni(II) with the increase of pH. The adsorption capacity decreases due to hydrolysis as pH > 5.5 [17].