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Synthesis and characterization of polyamidoxime chelating resin for adsorption of Cu(II), Mn(II) and Ni(II) by batch and column study

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ABSTRACT

New polyamidoxime chelating resin (PAO-AN) was prepared by copolymerization of acrylonitrile (AN) with *N*,*N*′-methylenebisacrylamide (MBA) followed by amidoximation reaction with hydroxyl amine under alkaline conditions. The composition, properties and morphology of the resulting chelating resin have been characterized by Fourier transform infrared spectroscopy, thermal gravimetric analysis, scanning electron microscopy, surface area measurements and water regain. Batch technique was employed to examine the effects of different parameters such as solution pH, concentration of metal ions, contact time and medium temperature on metal ion uptake. The results indicated that the new chelating resin (PAO-AN) had high affinity towards heavy metal ions such as Cu(II), Ni(II) and Mn(II) which showed the maximum uptake of the chelating resin of 2.62, 2.21 and 1.42 mmol/g resin, respectively. The adsorption data have been perfectly described by Langmuir isotherm rather than other isotherms such as Freundlich and Temkin. Kinetics data have been analyzed using pseudo-first order, pseudo-second order, and intra-particle diffusion equations. However, pseudo-second-order kinetic model was best fit with the obtained data. Thermodynamic data proved the spontaneity of sorption process. Furthermore, the removal of metal ions using amidoxime resin (PAO-AN) has been studied using column technique as well. Regeneration was effectively performed using nitric acid and the chelating resin could be used repetitively for five times with little decrease (≈1–10%) in sorption of metal ions.

1. Introduction

Due to their high toxicity, recently, heavy metal ions removal from drinking water and industrial wastewater attracts strong concerns [1,2]. Industrial wastewater contain heavy metal ions such as Ni(II), Cu(II), Pb(II) and Mn(II) [3,4]. Many separation techniques such as membrane process, chemical precipitation, reverse osmosis and chelating resins were employed for the removal of these metal ions [5–7]. Among these treatment techniques, the adsorption of metal ions using chelating resins is favored due to their high adsorption capacities, low costs, selectivity and durability [8–10].

Chelating resins were extensively used for the removal of heavy metals from aqueous medium and wastewater streams [8–14]. The chelating resins are a kind of crosslinked functional polymeric materials containing many specific functional groups such as amine, hydrazine, iminoacetate, carbamate and amidoxime, etc., which have chelating ability toward metal ions [11–18]. Most studies of preparation of chelating resins containing amidoxime group are derived from conversion of nitrile groups of polyacrylonitrile into amidoxime groups by treatment with solution of hydroxylamine in strong basic medium [19–23]. Wang et al. prepared a novel chelating resin containing amidoxime–guanidine functional group from the reaction of chloromethylated poly (styrene–divinylbenzene) resin with dicyandiamide. The nitrile group in the resin was converted into amidoxime group by treatment with hydroxylamine [24]. Chen et al. prepared two types of amidoxime adsorbents for removal of mercury [25]. In our recent report, poly(acrylamide-co-*N*,*N*′-methylenebisacrylamide) supported acrylonitrile group was amidoximated with hydroxyl amine hydrochloride to prepare new chelating resin for the removal of metal ions [26].

The aim of this work is to prepare new amidoxime chelating resin via two steps reaction and use it for the removal of Cu(II), Ni (II) and Mn(II) from aqueous solution using column technique. The effects of different parameter such as pH value, metal ion concentration, contact time and temperature on adsorption capacity of chelating resin for metal ions will be examined using

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batch method and will be investigated using Langmuir, Freundlich and Temkin isotherms. Kinetic and thermodynamic parameters of heavy metals removal were also estimated.

2. Materials and methods

2.1. Materials

Acrylonitrile (AN) and *N,N′*-methylenebisacrylamide (MBA) were pure grade products of Merck Co., Germany. 2,2-Azobis (isobutyronitrile) (AIBN) and hydroxylamine hydrochloride were purchased from Sigma–Aldrich Co., USA. Metal salts $CuSO_4{\cdot}5H_2O$, $Mn(CH_3COO)_2{\cdot}4H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ were used as sources for Cu(II), Mn(II) and Ni(II), respectively. All other chemicals and solvents were used as received.

2.2. Synthesis of amidoxime chelating resin

2.2.1. Synthesis of crosslinked polyacrylonitrile (CPN)

According to our previous report [16], CPN beads were prepared by suspension polymerization method using round bottom flask fitted with a reflux condenser and an over head mechanical stirrer. A polymerization mixture comprised of 9.5 g AN, 0.5 g MBA and the initiator 0.2 g of AIBN were suspended into toluene (50 mL). The reaction mixture was heated at 75–80 °C for 3 h. The solution was degassed by purging with nitrogen for 10 min. After cooling, the resin was filtered off, washed (with distilled water and methanol), and then dried in air. The 150–250 μm fraction was used for further synthesis with a yield of 73%.

2.2.2. Amidoxime modification of CPN

A suspension of CPN (6 g) and $NH_2OH{\cdot}HCl$ (5 g) in 100 ml of methanolic solution (methanol/water 5:1) was added to a flask fitted with reflux condenser and a magnetic stirrer. The reaction mixture was stirred for 30 min at room temperature. Sodium hydroxide solution (6 M) was added to the reaction mixture and the pH was maintained at pH 8 to neutralize $NH_2OH.HCl$. The above mixture was allowed to react at 70 °C for 24 h with continuous stirring under nitrogen atmosphere. The collected beads (PAO-AN) were filtered out, washed (with distilled water and methanol) and finally left to dry in air.

2.3. Characterization of the resins

IR spectra of the prepared resin samples were obtained with an FTIR spectrometer (Shimadzu 8201 PC) in the 400–4000 cm^{-1} range.

Water regain factor (*W*%) indicates the amount of water absorbed by one gram of the chelating resin. Water regain was estimated according to the previously reported procedure [26]. Swollen chelating resin (1 g) was placed in an appropriate size column (column weight = W_1). The column was centrifuged for 5 min at 3000 rpm to remove excess water in the resin. The weight of the column containing centrifuged resin was estimated as (W_2). The swollen resin weight (W_w) can be calculated as ($W_2 - W_1$). The chelating resin has been dried overnight at 80 °C then the weight of the column containing dried resin was determined (W_3). The dried resin weight (W_d) can be calculated as ($W_3 - W_1$). Eq. (1) was used to calculate water regain factor (*W*) as follows:

$$W\% = \frac{(W_w - W_d)}{W_w} \times 100 \quad (1)$$

The surface morphology of the chelating resin and its metal complexes were carried out using FEI QUANTA 250 FEG scanning electron microscope (SEM) after gold coating at 20 kV and 20,000 magnifications.

The thermal degradation analysis for the prepared chelating resin was determined using SDT Q600 TA instrument, USA. The experiment was performed under nitrogen atmosphere from room temperature to 700 °C with heating rate of 10 °C/min.

The surface texture measurements of the chelating resin were measured by nitrogen adsorption–desorption method at 77 K using a model NOVA 3200 automated gas sorption system (Quantachrome, USA).

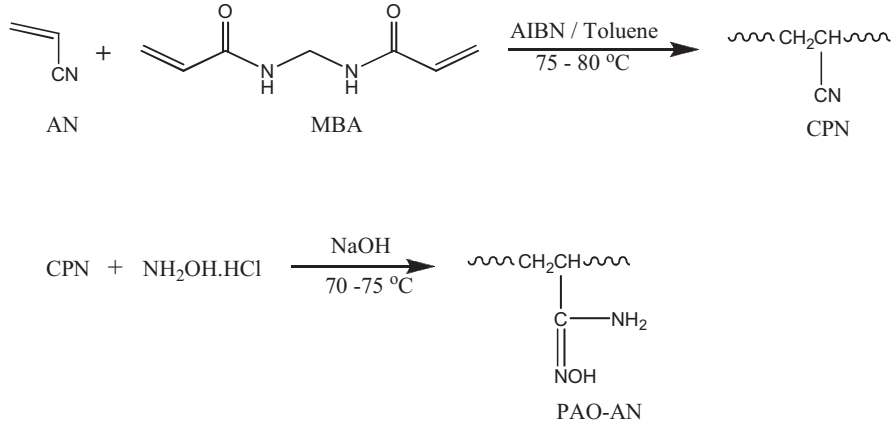
2.4. Adsorption of metal ions

2.4.1. Uptake of metal ions using batch method

All batch adsorption experiments were carried out using 0.1 g resin. A sample of 100 mL of the metal ion solution was placed in 250 mL erlenmeyer flask in thermostated shaker rotating at a speed of 250 rpm. All experiments were performed at 25 °C unless otherwise stated. The desired pH was adjusted by either HNO_3 or NaOH solution. The residual concentration of metal ions in the solution was detected using Hitachi atomic absorption Z-6100 polarized Zeeman. Experiments were performed in triplicate for the sake of accuracy. The adsorption capacity of the chelating resin was calculated according to Eq. (2).

$$q = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where *q* is the adsorption capacity (mmol/g), C_0 and C_e are the initial and the final concentrations of metal ions in solution



Scheme 1. Schematic illustration of preparation process of PAO-AN chelating resin.