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# Preparation of new hyper cross-linked chelating resin for adsorption of $Cu^{2+}$ and $Ni^{2+}$ from water

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**Abstract**

The new hyper cross-linked chelating resin NDWJN2 modified with carboxyl groups was prepared for removal of $Cu^{2+}$ and $Ni^{2+}$ from water. NDWJN2 was characterized using BET, SEM and FT-IR spectroscopy. Comparing with commercial resins D113 and IRC84, NDWJN2 could remove $Cu^{2+}$ and $Ni^{2+}$ from water more effectively. Langmuir model could fit adsorption isotherms well.


*Keywords:* Preparation; Hyper cross-linked chelating resin; Adsorption; $Cu^{2+}$; $Ni^{2+}$

$Cu^{2+}$ and $Ni^{2+}$ are mainly employed in electroplating, pesticides, herbicides and tannery industries. The effluents of these industries usually contain $Cu^{2+}$ and $Ni^{2+}$ which can cause environment problems and serious toxicological concerns [1]. The current technologies to remove $Cu^{2+}$ and $Ni^{2+}$ from water/wastewater include chemical precipitation, adsorption and membrane process. Among these technologies, adsorption is the most common approach for removing heavy metal ions from water/wastewater with high efficiency and easy operation. Many solid materials as adsorbents have been investigated, such as activated carbons (AC), polymeric resins and natural bio-adsorbents (NBA). Comparing with AC and NBA, polymeric resins have been used more widely in the removal of heavy metal from water [2,3]. In the present work, a new hyper cross-linked chelating resin NDWJN2 is prepared for removal of $Cu^{2+}$ and $Ni^{2+}$ from water, and its properties are analyzed by using BET, FT-IR spectroscopy and SEM. Furthermore, the adsorption capacity of this new chelating resin for $Cu^{2+}$ and $Ni^{2+}$ is investigated.

## 1. Experimental

Preparation of aqueous phase solution (APS): 8.0 g of hydroxyethyl cellulose and 8.0 g of gelatin was dissolved in 500 mL deionized water, respectively. These two solutions were mixed in 2000 mL round bottomed flask, then 200 mL of 5% NaCl solution was added, and the mixture was used as APS in the following step.

Preparation of low-crosslinked macroporous styrene—divinylbenzene copolymers (LSDC): 100.0 g of styrene, 20.0 g of divinylbenzene, 4 g of dibenzoyl peroxide, and 100.0 g of liquid paraffin were mixed at room temperature in a 2000 mL round bottomed flask. Then APS was added to the flask, stirred at 358 K for 12 h. Then the filtered LSDC was washed by hot water and extracted with acetone for 8 h, and then dried under vacuum at 333 K.

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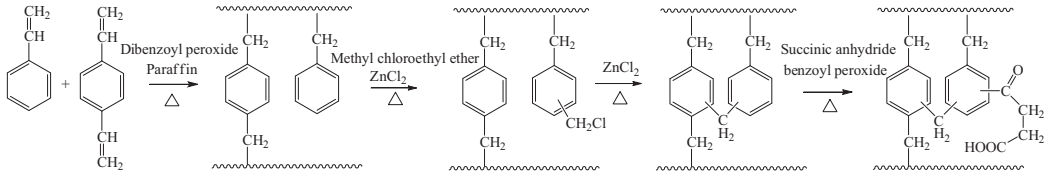


Scheme 1. Schematic presentation for the preparation of NDWJN2.

Preparation of chloromethylation of low-crosslinked macroporous styrene—divinylbenzene copolymer (CLSDC): 100.0 g of LSDC was swollen in 500 mL of methyl chloroethyl, then 40.0 g of $ZnCl_2$ was added and the mixture was stirred at 312 K for 12 h. Then the polymer was filtered and extracted with ethanol for 8 h in a Soxhlet apparatus, and dried under vacuum at 333 K for 8 h.

Preparation of hyper-crosslinked resin (HCR): 50.0 g of CLSDC was swollen in 500 mL of nitrobenzene, 4.0 g $ZnCl_2$ was added, and then the mixture was stirred at 323 K for 4 h, and at 383 K for 4 h. Then, the mixture was poured into an acetone bath containing 1% hydrochloric acid. And the HCR was filtered, and extracted with ethanol in a Soxhlet apparatus for 8 h, and then dried.

Preparation of hyper cross-linked chelating resin (NDWJN2): 50.0 g of HCR was swollen in 250 mL of dimethylformamide (DMF), then benzoyl peroxide, Tween-80 and succinic anhydride were added, and the mixture was stirred continuously at 323 K for 4 h and at 343 K for 8 h. Then, polymer beds were poured into an acetone bath containing 2% hydrochloric acid. Finally, polymeric adsorbent was filtered and then extracted with ethanol for 8 h in a Soxhlet apparatus and then dried under vacuum at 333 K for 8 h (Scheme 1).

The specific surface area and the pore distribution of resin were measured by Micromeritics ASAP-2010 surface area measurement instrument (Micromeritics Instrument, Norcros, USA) following the BET method. Surface morphology was observed by a TEOL JSM-840 scanning electron microscope (SEM). The FT-IR experiments of resin NDWJN2 were performed on a FT-IR spectrometer (MAGNA 560, Nicolet Co.), and the spectra were recorded in the wave number ranging from 400 to 4000 $cm^{-1}$.

Adsorption isotherms of $Cu^{2+}$ and $Ni^{2+}$ on resins were conducted as follows: 0.200 g of resin was introduced into five 250 mL conical flasks, respectively, and then 100 mL of solutions with different concentrations of certain metal ion were added into those flasks, respectively. The flasks were completely sealed and placed in an incubator shaker (120 rpm) at 303 K for 72 h. The concentrations of $Cu^{2+}$ and $Ni^{2+}$ ($c_e$) were determined using atomic adsorption spectrophotometer. Then, $q_e$ (mg/g), the adsorption capacity, was calculated according to Eq. (1)

$$q_e = \frac{V_1 \times (c_0 - c_e)}{W} \tag{1}$$

where $V_1$ is the volume of solution (L) and $W$ is the weight of dry adsorbent (g).

## 2. Results and discussion

Fig. 1 indicates that the pore distribution of NDWJN2 is main micro-pore and macro/meso-pore. In traditional, macro/meso-pore of resin is beneficial to adsorbates entering into resin's pore channels, and micro-pore is advantageous to increasing the adsorption sites. This porous structure of NDWJN2 can be also observed by SEM. As shown in Fig. 2, the SEM photo indicates that NDWJN2 is rough in surface, porous inside the structure. BET surface area of NDWJN2 was 580 $m^2\ g^{-1}$, which was much higher than traditional commercial ion exchange and chelation resin. As shown in Fig. 3, the band near $\delta$ 3400 $cm^{-1}$ is due to the stretching of carboxylic hydroxyl groups, and the band near $\delta$ 1700 $cm^{-1}$ is due to the stretching of carboxylic carbonyl groups [4]. Thus, FT-IR spectra of NDWJN2 indicated that carboxylic hydroxyl groups had been modified on hyper cross-linked resin.

Fig. 4 indicates that the equilibrium adsorption capacities of NDWJN2 for $Cu^{2+}$ and $Ni^{2+}$ are higher than those of IRC84 and D113. The isothermal equilibrium adsorption data are fitted by Freundlich and Langmuir equations [5]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \tag{2}$$

$$\frac{1}{q_e} = \frac{1}{bc_e} + \frac{1}{Q_m} \tag{3}$$