

# Fabrication of copper coated polymer foam and their application for hexavalent chromium removal



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## ABSTRACT

The polymer foam coated with zero-valent copper ( $\text{Cu}^0$ ) was designed and prepared for the removal of hexavalent chromium ( $\text{Cr(VI)}$ ) in water. Firstly, porous poly(tert-butyl acrylate) was fabricated by concentrated emulsion polymerization and then acrylic acid groups were generated on the surface of foam by hydrolysis reaction. Secondly, with the help of the large amount reactive carboxylic acid groups, polyethyleneimine (PEI) were chemically grafted onto the surface by the reaction between amine group and acrylic acid group. Finally, zero-valent copper was reduced by sodium borohydride ( $\text{NaBH}_4$ ) and coated on the surface of polymer foam. Thus the copper functionalized porous adsorbent ( $\text{Cu}^0\text{-PEI-PAA}$ ) was constructed, and then applied for removing  $\text{Cr(VI)}$  from aqueous solution. The removal mechanism of  $\text{Cr(VI)}$  involved redox reaction by zero-valent copper and adsorption by amine groups, simultaneously. As a result, 99.5% of  $\text{Cr(VI)}$  could be removed within 2 h, and the maximum removal capacity for  $\text{Cr(VI)}$  of  $\text{Cu}^0\text{-PEI(1800)-PAA}$  was 9.16 mg/g. Furthermore, the effect of initial concentration of  $\text{Cr(VI)}$ , pH value, and temperature on the  $\text{Cr(VI)}$  removal was investigated. Therefore, the as-prepared zero-valent copper-loaded polymer foam could be an efficient and promising remediation material to remove  $\text{Cr(VI)}$  from wastewater.

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## 1. Introduction

Due to the advantages of low density and high specific surface area, polymer foam materials show their attractive applications as a supporter in separation [1,2], adsorption [3], chemical reduction and catalysis [4]. The foam-supported functional substances generally include organic groups, inorganic salts, metal oxides, and zero-valent metals, which provide the materials unique properties. Zero-valent metals are particularly commendable option to remove heavy metal, nitrate and chlorinate aliphatic organic compounds from waste-water due to the superior catalytic and reduction properties. Zero-valent iron ( $\text{Fe}^0$ ) was the most applied reactive metal [5], however, drastic oxidation in air or water and agglomeration from high surface energies constitute the obstacles in the application [6]. Therefore, zero-valent metal with smaller size, especially zero-valent copper, shows quicker and more completed effects [7].

In recent years, technologies on using porous materials as support medium to enhance the dispersibility and stabilisation of metals have been developed. For example, the nanoscale zero-

valent iron supported by kaolin or clinoptilolite was synthesized to remove heavy metal, nitrates, hexachloro benzene and dyes [8–12]. Recently, some studies indicated that nanoscale zero-valent copper could avoid undesired competitive reactions because of the stability in water [13]. Therefore, zero-valent copper ( $\text{Cu}^0$ ) was tried to be loaded onto porous organic materials such as cellulose, chitosan [14], cation resin and other specially designed polymer foam to enhance the dispersibility. Such kind of composite materials offered higher mechanical strength, catalysis performance and avoid agglomeration effectively [15].

Flexible polymeric foam with the controllable pore space could protect unstable zero valent metal particles, and the specific functional groups on the matrix could load particles chemically and selectively. Concentrated emulsion template [16] is one of the best approaches to fabricate polymeric foam with open-cell porous structure. In this study, the polymer foam coated with zero-valent copper ( $\text{Cu}^0\text{-PEI-PAA}$  foam) was fabricated for the removal of hexavalent chromium ( $\text{Cr(VI)}$ ) in water, and the amino functional groups were used to complex with copper particles and enhance the capability of  $\text{Cr(VI)}$  removal, simultaneously. Firstly, the polymer foam containing plenty of amino functional groups with strong selectivity and chelating properties to copper ions was designed and prepared [17]. Secondly, the nanoscale zero-valent

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copper ( $\text{Cu}^0$ ) was reduced and dispersed onto the polymeric foam support. Finally, a large number of  $\text{Cu}^0$  was loaded on the high specific surface area of foam materials, which could provide more contact area to reduce chromium ( $\text{Cr(VI)}$ ). At a same time, the remaining amino groups on the surface of polymer foam make further efforts on the adsorption of  $\text{Cr(VI)}$ . Therefore, the obtained metal/polymer nanocomposite could exhibit the better removal capacity of  $\text{Cr(VI)}$ . The preparation scheme of  $\text{Cu}^0$ -PEI-PAA foam is illustrated in Fig. 1. The embedding of zero-valent copper into the porous support could avoid the oxidation of metal and increase the efficiency and stability of zero valent metal, which was seldom reported. As a result, the improved adsorption properties of the adsorbent could be achieved.

## 2. Experimental

### 2.1. Materials

Tert-butyl acrylate (tBA) and divinyl benzene (DVB) were purchased from Aladdin reagent Co., China. Sorbitanmonooleate (Span80), potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), and potassium sulfate ( $\text{K}_2\text{SO}_4$ ) were supplied by Beijing Chemical Reagent Co., China. Trifluoroacetic acid (TFA), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), dimethyl Sulfoxide (DMSO), polyethylenimine (PEI, Mw = 400 or 1800 g/mol), dicyclohexyl-carbodiimide (DCC), and 4-dimethylaminopyridine (DMAP) were obtained from Vas Chemical Co., China.

### 2.2. Preparation of PEI-PAA polymer foam

A mixture of tBA 8 mL, DVB 2 mL, and Span80 2 mL was firstly introduced into a flask as the continuous phase. An aqueous solution of  $\text{K}_2\text{S}_2\text{O}_8$  0.2 g and  $\text{K}_2\text{SO}_4$  0.5 g in 90 mL water was added dropwise as the dispersed phase to the continuous phase with vigorous stirring at room temperature, and a concentrated emulsion with a volume fraction of 90% was obtained. The system was heated to 65 °C for 24 h and PTBA foam was obtained. The obtained foam was washed with water and methanol, and then dried in a convection oven at 60 °C for 24 h.

PTBA foam was immersed in 250 mL aqueous solution containing TFA 10 mL and  $\text{CH}_2\text{Cl}_2$  100 mL at room temperature for 48 h [18], and a vacuum condition was applied to help the solution permeate into the micro-pores. Poly (acrylic acid) (PAA) foam was generated during the hydrolysis (the reaction was shown in Fig. 2), and then washed in  $\text{CH}_2\text{Cl}_2$  (50 mL) at 60 °C with constant stirring for 48 h.

PAA foam was immersed in 500 mL of DMSO solution containing 10 g PEI, 0.05 g DMAP, and 1 g DCC at room temperature for 72 h. A vacuum condition was applied to help the solution permeate into the micro-pores. Then, the whole system was transferred into a sealed glass vessel and heated to 70 °C for 24 h. Finally, PEI functionalized PAA foam (denoted as PEI-PAA foam) was obtained [19].

### 2.3. Synthesis of $\text{Cu}^0$ -PEI-PAA foam

PEI-PAA foam was added in 0.4 M  $\text{Cu(II)}$  solution at 35 °C for 12 h.  $\text{NaBH}_4$  aqueous solution of 0.4 M was gradually dropped into. After the reduction, copper-PEI-PAA foam ( $\text{Cu}^0$ -PEI-PAA) was filtered and quickly rinsed with deionized water. The product was dried in vacuum and then stored in a dry cabinet.

### 2.4. Characterization

The pore size and morphology on cryogenic fracture surfaces of the foam were characterized using scanning electron microscope (SEM, Japan, Hitachi Lt dS-4700) with a voltage of 20 kV and a current of 10  $\mu\text{A}$ . Specimens were coated with gold for 30 s in SEM-coating equipment. The pore size was measured through SEM using Image J as a software tool providing the number distribution of the pores. In each measurement more than 100 pores were taken into account. The functional groups of the materials were detected using Fourier transfer infrared spectrometer (FT-IR, Thermo, Nicolet-Nexus 670) in the wavenumber range of 500–4000  $\text{cm}^{-1}$  under ambient condition by the method of transmission. The surface area of the foams was measured by Brunauer-Emmett-Teller (BET) method. The total pore volume was determined according to the Gurvitch rule. The open-cell rate was measured by automatic opening/obdurate rate measurement instrument (Ultra foam, Quanta chrome USA). The organic elemental analysis (vario ELcube) was used to detect the nitrogen content of the PEI grafted PAA. The elemental composition was monitored by Energy Dispersive Spectrometer (EDS, S-4700, Hitachi). The content of copper loaded on  $\text{Cu}^0$ -PEI-PAA foam was determined by thermogravimetry analysis (TGA, TG209c, Netzsch) performed in nitrogen atmosphere at a heating rate of 10 °C/min. The samples were heated from 25 to 700 °C. The concentration change of  $\text{Cr(VI)}$  in the solution was characterized by direct colorimetric measurement (UV-VIS, Varian Cary 50) with the wavelength of 540 nm. In acid condition, hexavalent chromium and diphenylcarbazide complexed into purple compound. Powder X-ray diffraction (XRD) patterns were recorded on X-ray diffractometer (Rigaku D/Max2400, Japan) operated at 40 kV and 30 mA at a wavelength of  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ). The composition and valence state of copper and the chromium ions were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, ThermoFisher Scientific) using monochromatised  $\text{Al K}\alpha$  ( $\lambda = 0.83 \text{ nm}$ ,  $h\nu = 1486.7 \text{ eV}$ ) X-ray source operated at 2 kV and 20 mA.

## 3. Results and discussion

### 3.1. Preparation of PEI-PAA foam

The PEI-PAA foam was synthesized in three steps: (a) synthesis of PTBA monolith by concentrated emulsion template, (b) surface modification to generate acrylic acid by hydrolysis reaction, and (c) grafting polyethylene polyamine (PEI) on the surface of foam.

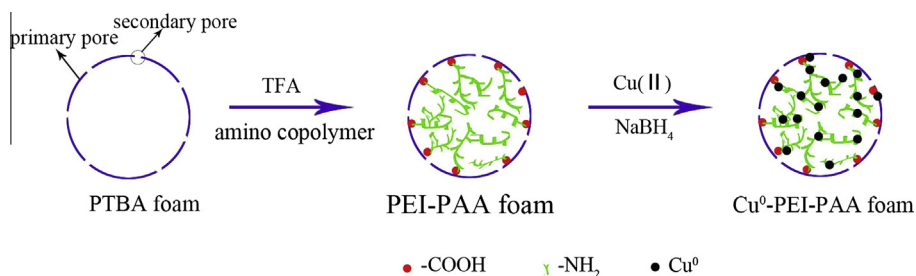


Fig. 1. The preparation process of  $\text{Cu}^0$ -PEI-PAA foam.

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