



Enhanced adsorption of aqueous copper(II) ions using dedoped poly-N-phenylglycine nanofibers

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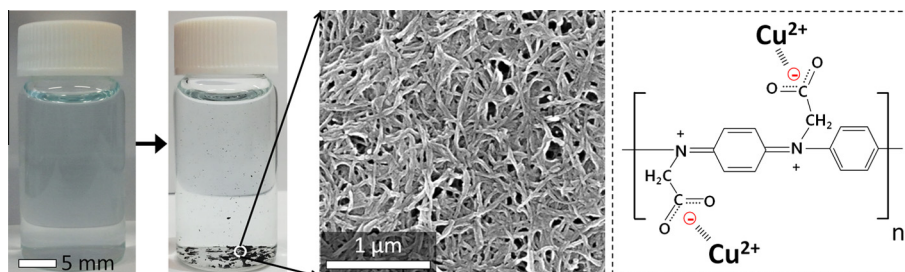
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HIGHLIGHTS

- Poly-N-phenylglycine nanofibers (PPG NFs) were synthesized simply by radical polymerization process.
- High-density functional groups of PPG NFs were exploited for adsorption of aqueous Cu.
- Simple deprotonation process enhanced the Cu adsorption capability of PPG NFs.
- The higher adsorption capacity was found under high pH conditions, owing to spontaneous deprotonation of PPG NFs.

GRAPHICAL ABSTRACT



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ABSTRACT

We report on adsorption of aqueous Cu^{2+} using poly N-phenylglycine (PPG) nanofibers (NFs) prepared by radical polymerization process. The carboxylic acid groups of pristine PPG NFs were deprotonated to form carboxylate groups, resulting in hydrogen-dedoped PPG NFs. The Cu^{2+} -adsorption capability of PPG NFs was markedly increased after the deprotonation, presumably due to high ionic attraction feature of carboxylate in dedoped PPG. We further investigated the pH-dependent adsorption capability of PPG NFs and found much higher Cu^{2+} adsorption capacity under high pH conditions, owing to spontaneous deprotonation by the basic solution. X-ray photoemission confirmed the adsorption of Cu^{2+} on PPG NFs, and Fourier transform infrared spectroscopic analyses confirmed the reduced density of carboxylic acid by deprotonation. The ability of pristine and dedoped PPG NFs to capture aqueous Cu^{2+} is discussed. Our method to improve the adsorption capability using surface modification could be readily applied to many other polymeric or organic nanostructures for metal removal.

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1. Introduction

Adsorption (or filtration) of aqueous metal is an important factor for the purification of water or soil, as well as for mining of rare metal resources from seawater [1–8]. Many studies have

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developed methods for capturing aqueous metals using membrane filtration [4,9], physico- or chemical-sorption [10,11], electrodeposition, bio-sorption [12–15], and so on. Among the many methods studied, the metal adsorption is significantly determined by surface morphology and surface chemical characteristics of the adsorbent materials. For high-efficiency metal adsorption, the adsorbent requires high surface-to-volume (s/v) ratio to increase the area of adsorption, and high-density surface ionic functional groups that strongly attract aqueous metals. The adsorption of aqueous metals has been investigated using many nanomaterials, such as graphene

[9,16] or graphene oxide [17], carbon nanotubes [18–20], nanoparticles [21–23], biosorbents [24], polymers [25,26], and porous- or layer-structured minerals [27–30], all of which exhibited excellent metal removal efficiency due to high *s/v* ratios.

Among the various adsorbent materials used, polymers have several important advantages for use in metal adsorption applications. First, nanostructures with high *s/v* ratios are easily obtained using a controlled polymerization method [31]. Second, specific functional groups that are suitable to attract aqueous metals for adsorption can be inserted in, or connected to, the backbone through the polymerization process [32]. In addition, many polymers are plastically deformable, and can be modified to desirable forms for diverse applications. Since typical polymers can be decomposed with few residues by using oxygen plasma treatment, or some specific solvents, the metal adsorbate can be easily separated by removing the polymers through simple physical or chemical methods. Hence, polymer nanostructures with negatively charged functional groups are thought to be competent for high-efficiency metal adsorption.

Poly-N-phenylglycine (PPG) [33], a well-known conducting polymer, consists of N-phenylglycine (N-PG) monomers with negatively charged carboxylic acid groups. The high-density carboxylic acid groups of PPG can be exploited for collecting positively charged aqueous metals. Since the carboxylic acid groups are deprotonated to carboxylate groups, they have a more negative charge than the carboxylic acid. Therefore, hydrogen-doped PPG is expected to have a higher metal adsorption capacity. In this study we report on the adsorption of aqueous copper (Cu^{2+}) ions using PPG nanofibers (NFs). Specifically, we demonstrate improved adsorption capability of dedoped PPG (d-PPG) NFs prepared by the deprotonation process. We further investigate pH-dependent adsorption capabilities of d-PPG and pristine PPG (p-PPG) NFs.

2. Experimental section

2.1. Synthesis of PPG NFs

PPG NFs were synthesized by polymerization of N-phenylglycine monomers. A mixture of monomer (1 mmol) and N-phenylene-p-phenyldiamine (5 wt.% with respect to the monomer) was dissolved in isopropanol (10 mL) via ultrasonication for 1 h. The oxidation agent was prepared by dissolving ammonium persulfate (APS, 0.25 mmol) in 1.0 M hydrochloric aqueous solution, followed by ultrasonication for 1 h. Then, the prepared oxidation agent was added to the monomer–dimer mixture solution, and this was mixed using a vortex mixer for 15 min. Immediately after mixing, polymerization was performed at a reaction temperature of 4 °C for 48 h using thermostat circulator. The as-synthesized PPG NFs were sufficiently rinsed with dilute hydrochloric aqueous solution and deionized (DI) water. For fabrication of the d-PPG NFs, p-PPG (100 mg) was immersed in NH_4OH aqueous solution (concentration of 25–30%; 100 mL) and stirred for 24 h. The d-PPG NFs were also rinsed with dilute ammonium hydroxide aqueous solution and DI water. To prevent contamination and thermal degradation, the PPG NF powders were lyophilized before the metal adsorption studies were conducted.

2.2. Characterizations

The adsorption of Cu^{2+} ions on PPG NFs was investigated by batch adsorption in aqueous solution at room temperature. The Cu^{2+} aqueous solution was prepared by adding $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ into DI water. Then, the solution was mixed by a vortex mixer. The PPG NFs (2.0 mg) were immersed into the aqueous solution (10 mL) containing Cu^{2+} , and then the suspension was stirred for

the desired time. The removal ratio of Cu^{2+} was characterized by measuring the decoloration of the aqueous solution. The decoloration was measured by measuring absorbance at wavelength of 542 nm (for Cu^{2+}) using a UV–visible double beam spectrophotometer (Biochrom, Libra S70). For the spectrophotometric measurement, the adsorbate/adsorbent was removed via centrifugation at 15,000 rpm for 30 min, and the supernatant was removed using a polyvinylidene fluoride syringe filter with an average pore size of 0.45 μm .

The acetaldehyde–bis(cyclohexanone) oxaldihydrazone (BCO) method was employed to determine Cu^{2+} concentration. First, 0.7-mL triammonium citrate (5.0-g triammonium citrate dissolved in 50-mL DI water), 0.5-mL buffer solution (0.05 M NH_4OH (25–30%) + 0.037 M NH_4Cl dissolved in water), 1.1-mL BCO (0.72 mM), 0.1-mL acetaldehyde (35 wt.%), and 2.1-mL DI water were added to 0.5-mL supernatant and mixed using a vortex mixer [17]. The adsorbed Cu^{2+} content (removal ratio) was calculated by first determining the initial (C_0) and equilibrium (C_e) aqueous Cu^{2+} concentrations using $C = 100(1 - I/I_0)$, where I and I_0 are the integrated absorbance peak intensity of the sample and the control, respectively. The following equation determined the percentage of adsorption:

$$(\text{adsorption } \%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

A linear relationship between the absorbance peak intensity and the dye concentration was confirmed in preliminary studies to be within a metal ion concentration range of 0.01 mM to 1.0 mM, and aqueous metal ion concentrations were controlled within that range.

Aqueous pH was controlled by adding HCl or NH_4OH as necessary. Since there exists possible formation of Cu precipitates or salts at high and low pH conditions, we adjusted the Cu^{2+} amount of various pH solutions to neutral 0.025 mM Cu^{2+} aqueous solution before performing the adsorption experiments: First, HCl and NH_4OH were added to DI water in order to make acidic and basic condition, respectively, followed by mixing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (or $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$) in the solution. After the addition of $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, we simultaneously measured and compared the UV–Vis absorption peak intensities of a series of various pH solutions with that of a control solution (0.025 mM Cu^{2+} aqueous neutral solution). When there existed such salt formation or Cu precipitation (this occurred to strong acidic and basic conditions for pH 2 and 12, respectively), the absorption peaks were lowered than that of a control solution. If so, more $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added to adjust the peak intensities to that of control solution. Also, to remove the salts or precipitates, the solutions were filtered using a common filter paper, and kept the as-filtered solutions overnight. Then, we once more measured and compared the UV–Vis absorption spectra with a control solution. After confirming that the absorption peak did not change, the 0.025 mM Cu^{2+} aqueous solutions with various pH were used for adsorption experiments.

Surface morphology of the PPG NFs was examined by field-emission scanning electron microscopy (FESEM, Hitachi S-4700). The chemical state of PPG NFs and Cu^{2+} -adsorbed PPG NFs were characterized by X-ray photoemission spectroscopy (XPS, Kratos, Axis Ultra DLD) with characteristic X-ray of $\text{MgK}\alpha$. Functional groups of the PPG NFs were confirmed using Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, Spectrum 100). Thermal stability of PPG NFs was characterized by thermogravimetric analyzer (TGA, Mettler Toledo, TGA/DSC 2) at 20–800 °C under ambient nitrogen.

3. Results and discussion

The PPG NFs were synthesized by a radical polymerization process using ammonium persulfate (APS) as an oxidizing agent. As a radical initiator, APS removes one electron from each N-PG

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