

Preparation of Co-conjugate Microporous Polymer Magnetic Tubular Composites and Application in Removal of Phosphate Ions

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Abstract. On the basis of synthesizing tubular conjugated microporous polymer, Co nanoparticles were synthesized in situ on the surface and inside of the tube for the removal of phosphate ions in water. Under the conditions of 24 hours of adsorption, the removal rate of an aqueous solution containing 100 mg L^{-1} of phosphate ion can reach 82.77%, and the requirement for separating contaminants can be achieved by applying a magnetic field. It is proved that the composite material has a good effect of purifying phosphorus-contaminated water sources.

1. Introduction

Since the beginning of the 21st century, with the advancement of science and technology, the pollution of water by many organic pollutants has gradually increased, such as the presence of phosphorus in pesticides, the pollution of aromatic raw materials in industrial production, and so on. Due to the richness of phosphorus, the enrichment of water bodies and lakes is still called an important environmental issue [1-4]. The reduction of phosphorus emissions and the reduction of the impact of these pollutions on water have also become a hot research direction for scientists today.

People have proposed numerous solutions to the above problems. Among the numerous solutions, the adsorption method is widely used due to its unique mechanism [5-6]. In addition, the adsorption method has many advantages such as high efficiency, safety, economy, and simple operation. Finding stable and efficient adsorbents becomes the key to the application of adsorption methods. The characteristics of the adsorption method determine that the adsorbent should have a high specific surface area, excellent stability, and can be recycled and used. The porous material has a large specific surface area, and its unique pore structure makes it widely used in the field of adsorption [7-10].

Organic porous materials have a series of advantages. Due to its unique pore structure, high specific surface area, π - π -conjugated chemical structure, ultra-high thermal and chemical stability, and simple synthesis methods, conjugated microporous polymers are a series of adsorption experiments have been greatly developed [11-13]. In 2015, our project was combined into a unique tubular and porous structure of conjugated microporous polymer [14]. Based on this, this chapter uses tubular conjugated microporous polymer as the carrier to load Co nanoparticles into it. In the

adsorption of phosphate ions has been greatly improved, and can be achieved through the external magnetic field, the effect of rapid separation.

2. Experimental section

2.1. Materials

Solid reagents are 1,3,5-triethynylbenzene, 2-amino-3,5-dibromopyridine, tetrakis (triphenylphosphine) palladium (0), copper (I) iodide, cobalt trichloride hexahydrate, sodium hydroxide. Liquid reagents are toluene, trimethylamine, chloroform, acetone, methanol, hydrated hydrazine, ethanol and all organic solvents were used as received.

2.2. Methods

(1) 337.86 mg 1,3,5-triethynylbenzene, 750.9 mg 2-amino-3,5-dibromopyridine, 150 mg tetrakis (triphenylphosphine) palladium(0), 50 mg copper(I) iodide reacts under nitrogen protection to form tubular-shape conjugated microporous polymers. named CMP. Then the mixture was washed with chloroform, water, acetone, and methanol for several times and named CMP. (2) The magnetic composites were synthesized in 20mL ethanol and 5% sodium hydroxide solution by 0.1g CMP and 0.8g cobalt trichloride hexahydrate. At last, the samples were centrifuged, washed, dried and named Co-CMP.

2.3. Removal of phosphate ions

According to the Lambert-Beer law to configure the aqueous solutions of different concentrations of phosphate ions. Weigh a certain amount of Co-CMP (10 mg) into a glass vial, add 20 mL of an aqueous solution of 100 mg L⁻¹, 300 mg L⁻¹ and 500 mg L⁻¹ phosphate ion, and seal the glass vial and place it in a shaker for 24 h. Adsorption reaches equilibrium.

Under strong acidic conditions, the active phosphate in the water sample reacts with ammonium molybdate to produce pale yellow phosphomolybdate. Phosphomolybdate yellow is reduced by stannous chloride (SnCl) to blue phosphorous molybdenum blue. The blue depth is proportional to the active phosphate content and has a maximum absorption at 710 nm. The colorimetric method can be used to measure the content of active phosphate in the water sample.

After that the absorbance of the supernatant liquids was determined by UV-Vis spectrophotometer, which was described as:

$$\text{Eq. 1: Removal rate} = (A_1 - A_2) / A_1 \cdot 100\%$$

A₁: the initial absorbency of phosphate ions, A₂: the absorbency of phosphate ions within time 24h.

3. Results and discussion

3.1. Analysis of the composites appearance and TEM

As can be seen from the (a) transmission electron microscope, the CMP has a hollow tubular structure and has good dispersibility. From the TEM image of Co-CMP in Figure 1 (b), it can be further seen that Co particles grow not only on the surface of the loaded surface CMP but also in the interior of the tube, indicating that Co particles are in the process of in-situ synthesis. Tube surface load is successful.

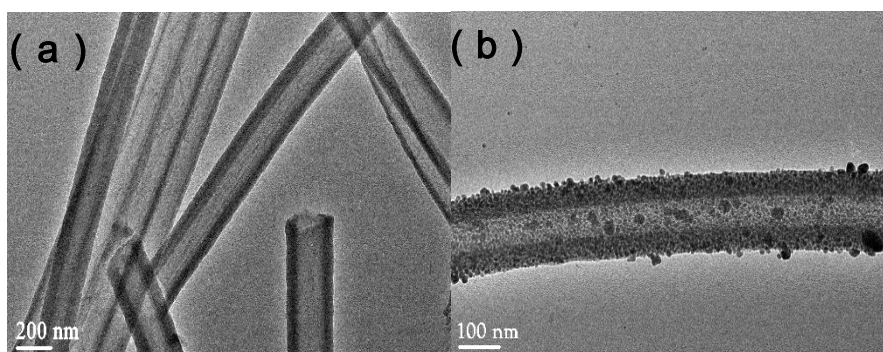


Figure 1. (a) CMP transmission electron microscopy picture, (b) Co-CMP transmission electron microscopy picture.

3.2. Analysis of the composites XRD

The CMP XRD pattern has a large broad peak near 2θ , a broad peak of a typical amorphous polymer, and is amorphous. The X-ray diffraction curves of Co and Co-CMP composites are shown in Figure 2 (b), $2\theta=41.5^\circ$ (100), 44.1° (002), 47.4° (102), 51.22° (200), 75.7° (220), 92.2° (311) are characteristic peaks of Co particles [15]. The XRD pattern of Co-CMP was compared with the XRD pattern of Co. Irregular peaks appeared at 20 - 30° due to the presence of CMP tubes, indicating the synthesis of Co-CMP composites.

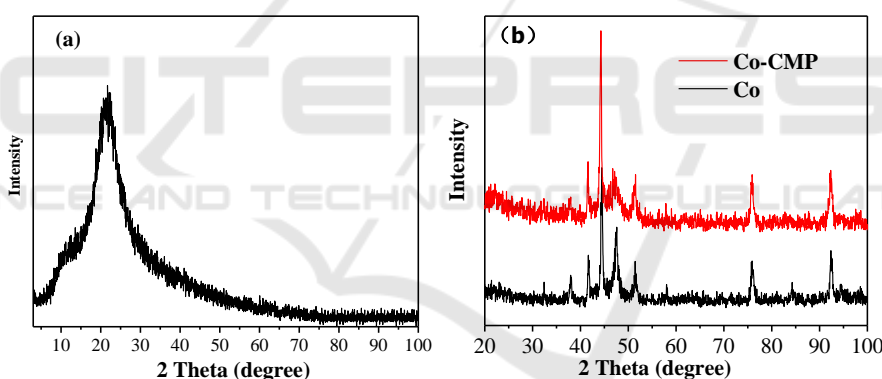


Figure 2. (a) X-Ray Diffraction Curves of CMP, (b) X-Ray Diffraction Curves of Co (Black) and Co-CMP (Red).

3.3. Analysis of the composites materials TGA

The thermal stability analysis of CMP, Co, and Co-CMP is shown in Figure 3 (a). Under the nitrogen protection conditions, the final mass loss of Co particles is about 3 wt%, which is the residual organic matter on the surface of the particles. In CMP, there is basically no mass loss before 300°C . After 300°C , the mass eventually decreases to about 75.5 wt% with increasing temperature. The reason for its good stability is that the CMP structure is composed of a rigid aromatic ring coupled with a relatively strong covalent bond. The figure shows that the final remaining mass of Co-CMP is 91.5 wt%. By the ratio calculation, the CMP content is about 22.4 wt%, and the Co particle content is 75 wt%. CMP provides a good skeletal structure and pore structure, with Co particles loaded on its surface.

3.4. Analysis of the composites materials VSM

Figure 3 (b) shows the hysteresis regression curves of Co and Co-CMP composites at room

temperature (298 K). It shows that both Co and Co-CMP composites have good saturation magnetic field strength at room temperature. The magnetization was 118.1 and 61.3 emu g⁻¹, respectively. Due to the presence of tubular CMP, the resulting polymer is reduced in magnetic properties, but at the same time it maintains good magnetic properties. With the change of CMP quality, the magnetic strength of Co-CMP composites can be controlled to ensure its separation effect.

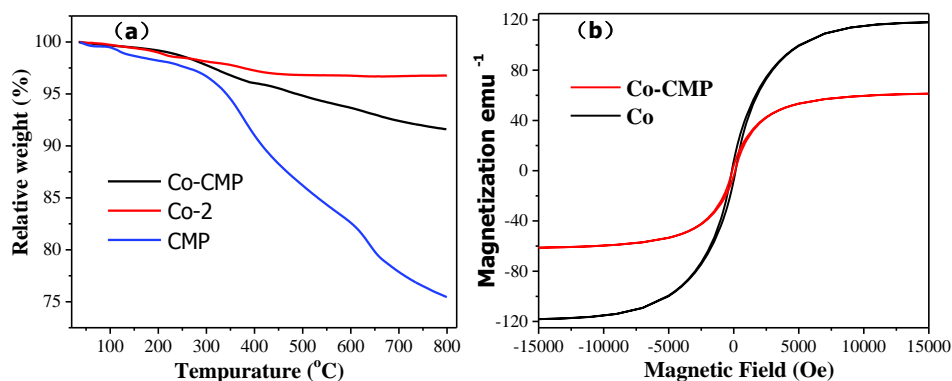


Figure 3. (a) Thermogravimetric analysis of Co-CMP (black), Co-2 (red), CMP (blue) (b) Hysteresis curve of Co (black) and Co-CMP (red).

3.5. UV-vis results for phosphate ion removal

In the 24-hour adsorption experiment, the removal rates of the aqueous solutions containing 100 mg L⁻¹, 300 mg L⁻¹, and 500 mg L⁻¹ of phosphate ions were 21.4%, 24.1%, and 24.64%, respectively. Figure 4 shows the removal rate of Co-CMP was 82.77%, 73.8% and 70.72%. It can be seen that there is a significant increase in the ability of the removal of phosphate ions in Co-CMP compared to CMP.

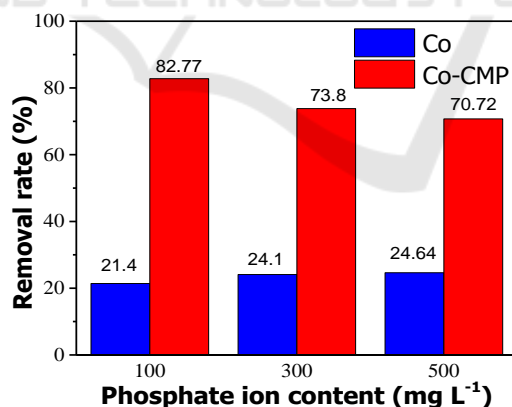


Figure 4. Removal rate of phosphate ion in an aqueous solution by CMP and Co-CMP.

4. Conclusions

A magnetic tubular composite material, Co-CMP, was synthesized and it can effectively adsorb phosphate ions. Phosphorus-polluted water bodies are purified and the contaminants are separated by an external magnetic field. In addition, when the aqueous solution with a phosphate ion content of 100 mg L⁻¹ is treated for 24 hours, the removal rate can reach 82.77%.

Acknowledgement

The authors are grateful to the National Natural Science Foundation of China (Grant No. 51663012, 51462021), Project of Collaborative Innovation Team, Gansu Province, China and Innovation and Entrepreneurship Talent Project of Lanzhou (2017-RC-33).

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