In-situ improved phenol adsorption at ions-enrichment interface of porous adsorbent for simultaneous removal of copper ions and phenol

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HIGHLIGHTS

- Simultaneously remove Cu^{2+} and phenol by carboxylic functionalized porous material.
- Adsorption behaviors are compared between in pure and mixed solution.
- The enrichment of Cu^{2+} at interface improves phenol adsorption capacity.
- Effects of Cu^{2+} on phenol adsorption in mixed solution are analyzed.
- Adsorption mechanism of phenol in mixed solution is investigated.

GRAPHICAL ABSTRACT
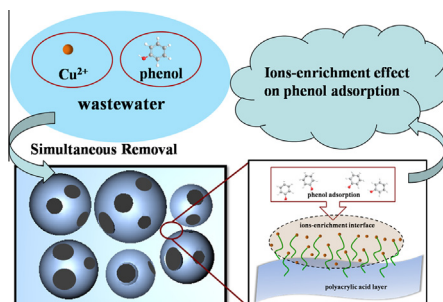
ARTICLE INFO

ABSTRACT

The carboxylic acid functionalized poly (glycidyl methacrylate) (PGMA) porous material was prepared and developed as porous adsorbent for simultaneous removal of copper ions and phenol in aqueous solution. The adsorption capacities of Cu^{2+} and phenol were 37.5 and 36.2 mg/g in their mixed solution, separately. Compared with their adsorption capacities in individual pure solution, it was found that there was no obvious difference on the adsorption behavior of copper ions in mixed solution. What's exciting result was that the adsorption capacity of phenol in mixed solution was improved dramatically. According to the effect of pH value and the relative content of copper ions on the adsorption capacity, the adsorption mechanism of phenol at the presence of copper ions was investigated. Furthermore, the oxygen and copper elemental before and after adsorption in pure and mixed solution were analyzed by X-ray photoelectron spectroscopy in detail. It could be deduced that copper ions in mixed solution were firstly absorbed at the interface of porous monolith and then the ions-enrichment interface layer was benefit for the phenol adsorption. In addition, the adsorption isotherms and kinetics of phenol adsorption were studied, and it was further indicated that the copper ions played important role in improving phenol adsorption capacity.

1. Introduction

With rapid industrialization, water pollution has been one of the major environmental threats observed around the world.

Wastewaters from manufacturing process usually contain multiple pollutants, including toxic organic pollutants phenol or its derivatives [1,2] and heavy metal ions [3,4]. Nowadays, adsorption has been considered as one of the most popular and effective methods for the removal of pollutants from wastewater. Because the adsorption process is interface phenomenon, it has certain qualities, such as fast kinetics, flexibility in design and mild regeneration condition [5].

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Most adsorption materials have been developed by introducing various functional groups for the removal of specific component. In the past few decades, a large number of solid adsorbents were developed to remove heavy metal ions by chemically modifying on the surface of matrixes such as amine-functionalized mesoporous materials [6–8], carboxylic modified magnetic particles [9,10], chitosan [11], and chelating resin [12]. While the removal of phenol and its derivatives had been also studied include activated carbons [13,14], cyclodextrin modified biosorbents [15,16], organic clays [17,18], surface modified zeolites [19] and carboxylic modified resins [20].

In our previous work, polyacrylic acid (PAA) functionalized poly(glycidyl methacrylate) (PGMA) porous monolith with highly interconnected pore network was fabricated by concentrated emulsion polymerization template and applied as porous adsorbent to remove copper ions (Cu^{2+}) component in its individually pure solution [21]. As we knew, the situation in mixed solution would be much more complicated than it in pure solution of single pollutant, and the interaction mechanism of these pollutants were still unclear. Until very recently, there were only a few studies on investigating the mutual interactions of multiple contaminations at simultaneous removal process [22–25]. Chen et al. found that efficiently co-removal of both Cu(II) and *p*-nitrophenol from aqueous solutions was accomplished using polyamine chelating resin and showed additional affinity to Cu(II) and *p*-nitrophenol through coordination as well as hydrogen bonding [26]. Ling et al. used hyper-crosslinked resin to remove organic compounds (acid black 1) and Cu(II), and proved that the coexistence of acid black 1 markedly enhanced the adsorption of Cu(II) [27]. Therefore, it was obvious that the study of the interaction mechanisms was very important for co-adsorption process.

In this study, a novel in-situ improved phenol adsorption at ions-enrichment interface phenomenon was proposed for the simultaneous removal of phenol and heavy metal ions from wastewater using carboxylic functionalized PGMA porous monolith. Compared with removing individually pollutant in their pure solution, it was found that the phenol adsorption capacity increased in mixed solution much more than that in individual pure solution. Therefore, it could be deduced that the co-adsorption method could make copper ions enriched at interface, and this enrichment of copper ions played a positive role on the adsorption properties of phenol. Accordingly, the effect of pH value of solution, relative concentration of copper ions, the kinetics and adsorption isotherm were studied in detail to reveal the adsorption mechanism of phenol. It was clear that the metal ions with strong positive charges could act as the active sites typically linked with phenol to improve the adsorption capacity of phenol. The results indicated that carboxyl groups not only could simultaneously remove metal ions and phenol in their mixed solution, but also had a good effect on phenol adsorption at the presence of Cu^{2+} in mixed solution. As a result, simultaneous removal process of copper ions and phenol was proved to make water treatment more efficient. And the carboxylic acid functionalized adsorbent has a wide and strong application in the treatment of industrial wastewater.

2. Materials and methods

2.1. Materials

Glycidyl methacrylate (GMA), divinylbenzene (DVB), and polyacrylic acid (PAA) (*Mw* = 3000) were supplied by Aladdin Reagent Company. Sorbitanmonooleate (Span80), potassium persulfate ($K_2S_2O_8$), potassium sulfate (K_2SO_4), anhydrous magnesium chloride ($MgCl_2$), *N*,*N*-dimethylformamide (DMF), copper chloride ($CuCl_2 \cdot 2H_2O$), phenol (C_6H_5OH), sodium hydroxide, hydrochloric acid, and anhydrous ethanol were purchased from Beijing Chemical Reagent Research Company. All reagents used in the present investigation were of analytically pure and were used without further purification.

2.2. Preparation of carboxylic functionalized porous monolith

A typical preparation of concentrated emulsion was carried out according to the method described previously [28]. The organic phase contained GMA (3.0 g), DVB (2.0 g), and Span80 (30 wt% based on organic phase) were mixed in flask, and then the aqueous phase consisting of $K_2S_2O_8$ (0.22 wt% to the organic phase) and K_2SO_4 (1.11 wt% to the organic phase) in deionized water (45 ml) was introduced dropwise into organic phase. The obtained milky emulsion was polymerized at 60 °C for 36 h. The product was washed and dried in vacuum.

PAA (1.0 g) was added to 100 ml of DMF, then porous PGMA monolith (3.0 g) and $MgCl_2$ (0.15 g) as catalysts were added. The mixture was stirred for 24 h at 45 °C under vacuum. After cooling to room temperature, the mixture was filtered and washed with ethanol and deionized water twice. Finally, the product was dried at 65 °C.

2.3. Characterization

Fourier transfer infrared spectrometer was recorded by a Nicolet-Nexus 670 spectrophotometer within the frequency range of 500–4000 cm^{-1} by the method of transmission. The morphologies of porous monoliths were characterized by Hitachi-S4700 scanning electron microscopy (SEM, Hitachi, Ltd., Tokyo, Japan). Elemental analysis was performed on Hitachi LtdS-4700 field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive spectrometer (EDS) produced by EDAX Inc. The specific surface areas by N_2 sorption at 77 K were measured using a Micromeritics ASAP 2020 adsorption analyzer. The grafting percentage of PAA was determined from the mass of thoroughly dried PGMA monolith before and after grafting, which were calculated as following [29,30]: PAA grafting percentage = $(W_2 - W_1)/W_1 \times 100\%$; Where W_1 stood for the mass of original PGMA polymer monolith and W_2 denoted the mass of resultant PAA-grafted PGMA polymer monolith.

In a typical adsorption procedure, adsorption experiments were performed at 25 °C. The pure solution was prepared by adding certain amount phenol or copper ions into deionized water, respectively, and the mixed solution was prepared by adding certain amount both phenol and copper ions into deionized water. All batch experiments were carried out by putting 200 ml of solution into glass column (200 mm long, 10 mm internal diameter, pore size 40–50 μm, SIBATA SPC, Japan) which was filled with 0.5 g of dry adsorbent. The amount of phenol (or copper ions) adsorbed at adsorption equilibrium, q_e (mg/g), was calculated according to Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e were the initial and equilibrium phenol (or copper ions) concentrations (mg/L), V was the volume of phenol (or copper ions) solution used in the adsorption experiment (L), and W was the weight of adsorbent (g). Data was representative of at least three experiments, and the standard deviations were less than 3.0%. The concentration of copper ions was determined by atomic absorption spectroscopy (AAS Hitachi Z-8100, Japan) [31], and the concentration of phenol was determined by UV spectrophotometer (Hitachi U-3010) [32]. The absorbance values of phenol were measured according to the maximum UV-absorption at the wavelength of 270 nm.