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Efficient removal of pentachlorophenol from wastewater by novel hydrophobically modified thermo-sensitive hydrogels

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ABSTRACT

Poly (*N*-isopropyl acrylamide-*co*-butyl acrylate) (PNIPAM-BA) hydrogels were synthesized by copolymerization of *N*-isopropyl acrylamide (NIPAM) with butyl acrylate (BA), which have been proposed as adsorbents for the efficient removal of hydrophobic organic pollutants, *e.g.* pentachlorophenol (PCP). Adsorption experiments showed high removal efficiencies of PCP. The isotherm experimental data of PCP fitted Langmuir model, and the adsorption capacity of PNIPAM-11% BA hydrogel was greater than that of the original PNIPAM hydrogel. It is possibly due to the enhanced interaction between the hydrophobically modified hydrogels and PCP. Moreover, the PNIPAM-BA hydrogels could be easily recycled by the desorption process at 323 K in solution.

Introduction

Hydrophobic organic compounds (HOCs) are generally produced from various kinds of industrial manufacturing processes [1], and they have been reported to cause allergies, irritation, dermatitis, cancer, and mutation to human [1,2]. HOCs can be adsorbed by adipose tissue due to their high octanol-water partition coefficient (k_{ow}), thus resulting in high biological concentration in fish and mammal with the accumulation in food chains [2]. Moreover, HOCs can migrate for long distances and exist in environment for a long time, their properties of highly accumulative and toxic cause adverse health effects in fish, wildlife, and humans [2]. Thus, it is necessary to remove HOCs from wastewater before they are discharged into the natural water bodies. A number of approaches have been developed for the removal of HOCs, such as adsorption, flocculation, oxidation, microbial degradation, and so forth [3–5]. However, due to the low water-solubility of HOCs, they cannot be efficiently removed by the above traditional physical and chemical methods [3]. On the other hand, the biotechnological treatments such as microbial degradation are hard for stable operation because of the low bioavailability and toxicity of HOCs [3]. Therefore, the adsorption process is considered as a relatively efficient method for the removal of HOCs [4,6]. Many kinds of adsorbents including activated carbon, bentonite, and carbon nanotubes [3,4,6] have been used for the removal of HOCs, but the regeneration of these adsorbents are difficult [7].

In recent years, the smart hydrogels have attracted much attention as a promising adsorbent. Smart hydrogels are environmental stimuli-sensitive, with unique and good sensitivity to temperature [8–10], pH [11,12], magnetic field [13], and light [14], etc. They can quickly adsorb pollutants, and are easily to be recycled by changing the environmental conditions. Among the smart hydrogels, poly(*N*-isopropyl acrylamide) (PNIPAM) is a typical thermo-sensitive polymer, which exhibits the lower critical solution temperature (LCST, 303–308 K) in water [15]. Below LCST, the hydrogel will be swollen, hydrated and hydrophilic; whereas above the LCST, the hydrogels will shrink forming a dehydrated and hydrophobic state [16]. The reversibility of the hydrogel has many potential applications, such as the controlled release and delivery of drugs [8,17,18], separations [19,20], preparation of molecular switch [21,22], and so on. Kabiri et al. found that super adsorbent hydrogels were efficient for the adsorption of water-soluble contamination such as dye and metal ions [23]. Yildiz et al. [24] and Ju et al. [25] synthesized several kinds of hydrogels to remove heavy-metal ions, such as Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+}, the adsorption-desorption can be easily achieved by changing the environmental conditions. Zhou et al. [26] applied cellulose-based

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hydrogels to remove the methylene blue dyes from wastewater. However, to our knowledge, the application of PNIPAM hydrogels for the removal of HOCs was rarely reported.

Pentachlorophenol (PCP) is one of the typical HOCs, because its high octanol-water partition coefficient (log k_{ow}) is 5.25. In order to remove PCP in aqueous solution, we synthesized a novel hydrophobically modified thermo-sensitive hydrogel (PNIPAM-BA). The PNIPAM-BA hydrogel was comprised of NIPAM and hydrophobic monomer butyl acrylate (BA), and the hydrophobic surface was well documented to enhance the interaction between the adsorbent and pollutants [27–29]. So, it was expected that the surface of the hydrogel becomes hydrophobic, the hydrophobic organic pollutants could be efficiently adsorbed. Moreover, the hydrogel could be easily regenerated by changing the temperature of reaction condition due to its thermosensitivity.

In this study, the PNIPAM-BA hydrogels with different BA contents have been synthesized. The adsorption and desorption kinetics of PCP on the hydrogels were systematically investigated. The interactions between the hydrogels and PCP were discussed to reveal the adsorption mechanism of PCP on hydrophobically modified hydrogels.

Materials and methods

Materials

N-Isopropyl acrylamide (NIPAM) (99%, Aladdin Co., Ltd, Shanghai, China) was purified by recrystallization twice from *n*-hexane and dried under vacuum at room temperature. Butyl acrylate (BA) (99%, Tianjin Yongda Co., Ltd, China) was distilled under reduced pressure (30 Torr) to remove inhibitor. *N*, *N*-methylenebis (acrylamide) (BIS), *N*, *N*, *N*′, *N*′-tetramethylenediamine (TEMED), ammonium persulfate (APS), sodium dodecyl benzene sulfonate (SDBS) and other reagents were all of analytical grade, and used without further purification.

Synthesis of PNIPAM-BA and PNIPAM hydrogels

Poly (*N*-isopropyl acrylamide-*co*-butyl acrylate) (PNIPAM-BA) and poly (*N*-isopropyl acrylamide) (PNIPAM) hydrogels were synthesized *via* the aqueous micellar polymerization. A fixed molar ratio of NIPAM (1.0 g) and BIS (20:1) was dissolved in 9 mL deionized water in the test tube, and then different amounts of BA (3–20 mol% of NIPAM) were injected into the mixture with a micropipette. The solution was then degassed by bubbling nitrogen for 15 min. Then, sodium dodecyl benzene sulfonate (SDBS, 3 wt% of water) was added to the water medium, and the hydrophobic monomer was solubilized within the surfactant micelles, whereas butyl acrylate (BA) is dissolved in the aqueous continuous medium. After the addition of APS and TEMED as a redox pair to initiate the polymerization, the tube was then blocked with stopper. The polymerization proceeded in a water bath thermostat at 323 K for 24 h. The prepared hydrogels were then taken out and sliced into disks with the thickness of 0.5 cm and the diameter of 1 cm. Then, the disks were immersed in ethanol for 24 h and in deionized water for 5 days (replaced water every 12 h) to thoroughly leach out unreacted monomers and other impurities. The process for preparing the PNIPAM hydrogel was exactly the same as that for PNIPAM-BA except that only NIPAM was used as the monomer. The dried hydrogels were obtained by vacuum drying to constant weight under 323 K.

Adsorption experiments

The batch adsorption experiments were carried out by adding the dried adsorbent (PNIPAM-BA hydrogels and PNIPAM hydrogel) into a simulated wastewater contacting a certain amount of PCP at 298 K, and an equilibrium time of 24 h was adopted for all the adsorption processes. All PCP solutions were obtained by dissolving PCP in deionized water with its pH adjusted to 3 by mixing predetermined volumes of 0.1 M HCl.

To evaluate the adsorption kinetic characteristics, 500 mg of PNIPAM-BA hydrogels or PNIPAM hydrogel were added into 300 mL 0.01 mmol/L PCP solution equipped with a mechanical stirrer. 1.0 mL sample was withdrawn at the regular time intervals and filtered immediately, then high performance liquid chromatography (HPLC) was employed to detect the concentration of PCP.

For the determination of the equilibrium adsorption isotherm, 100 mg PNIPAM-BA hydrogel or PNIPAM hydrogel were added into 50 mL simulated wastewater with different concentrations (0.01 to 0.1 mmol/L) of PCP for 24 h.

Desorption experiments

The regeneration of hydrogels was investigated with the adsorption-desorption process. The hydrogel saturated with PCP was placed into a batch containing 300 mL of deionized water at 323 K for 24 h. The regenerated hydrogels were used for another adsorption process, and the same adsorption procedure was performed in the succeeding cycles.

Analysis and characterization methods

The concentration of PCP was detected by high performance liquid chromatography (HPLC, Agilent 1260) using a chromatographic column (Eclipse SB-C18) with a UV determine wavelength 220 nm. The constituent of mobile phase was acetonitrile/water = 75/25. The groups of hydrogel were analyzed by the Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700) with a KBr tablet containing hydrogel powders. To observe the morphology of hydrogels, scanning electron microscope (SEM) observation was performed on the gold-sputtered specimens with an instrument (Hitachi SU-70) at 20 kV. The wettability of the PNIPAM-BA hydrogels was tested by measuring the contact angles of water. During these measurements, 2 μL water was dropped on the surface of PNIPAM-BA hydrogels, and the contact angles were obtained on Dataphysics OCA20.

The exploration of equilibrium swelling ratio (SR) was carried out in a thermostated water bath. The hydrogel samples were immersed in sufficient deionized water for a minimum of 48 h at different temperatures (283–323 K). The swelling ratio (SR) was calculated as SR = m_h/m_x, where m_h and m_x represented the weights of hydrogel and xerogel, respectively.

Results and discussion

Characterization

The FTIR spectra of PNIPAM and PNIPAM-11% BA hydrogels are shown in Fig. 1. The original PNIPAM hydrogel showed the characteristic of N–H stretching vibration at wavelength of 3300 cm^{-1} and C–H stretching vibration at 2970, 2934 and 2875 cm^{-1}. Meanwhile, the amide I band assigned to C═O stretching vibration at 1645 cm^{-1} and the amide II band assigned to N–H in-plane bending vibrations at 1540 cm^{-1} were also observed. In the case of PNIPAM-11% BA hydrogel, a typical carboxyl group (C═O) stretching peak appeared at 1720 cm^{-1}, indicating the existence of butyl acrylate (BA). SEM was used to observe the morphology of different hydrogels. As shown in Fig. 2A and B, SEM images of PNIPAM-11% BA and PNIPAM hydrogels both exhibited porous structures, and the cross-section of PNIPAM hydrogel was much more irregular. It should be noted that PNIPAM