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Synthesis of recyclable powdered activated carbon with temperature responsive polymer for bisphenol A removal

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ABSTRACT

Self-flocculated powdered activated carbon (PAC) with high recovery performance and unique adsorption performance of bisphenol A (BPA) has been synthesized. PAC was treated with acidification to increase its surface active points without influence on its surface area. The PAC after acidification was functionalized in the presence of macro-initiators and then grafted with *N*-isopropylacrylamide (NIPAM) in aqueous solution (PAC-PNIPAM). By controlling the grafting degrees of PNIPAM, the synthesized PAC-PNIPAM exhibited different removal efficiency of BPA, the maximum adsorption capacity simulated under Langmuir models reached 247.532 and 116.298 mg/g, respectively. Moreover, the desorption behaviors of BPA also changed significantly from two-stage desorption to minor desorption in water, suggesting the potential application of PAC-PNIPAM in removal of concerned pollutants. Additionally, PAC-PNIPAM showed a good self-flocculation effect, implying that PAC after adsorption could be easily retried and recovered to avoid the secondary pollution of the adsorbent. In all, our work demonstrated potential application of this newly synthesized PAC in water purification and micro-pollutant remediation.

1. Introduction

Activated carbon (AC) is widely used to adsorb organic contaminants in water purification [1,2]. With a larger surface area, powdered activated carbon exhibits better adsorption capacity than that of granular activated carbon (GAC) [3–6]. However, [5] the particle size (i.e., 1–150 μm) of PAC renders it a stable colloidal solution, which hinders efficient recovery of used PAC from the water. Thus, this limitation restricts the PAC only to be used in treating emergent pollution in water sources. Additionally, the residual PAC in the purified water will also be considered as a secondary pollutant. Moreover, although powdered activated carbon is a preferred adsorbent for contaminants removal, its widespread usage is also restricted due to the high cost [7].

Due the limitation of the PAC, there is a critical need in finding the low-cost adsorbents for the removal of hazardous compounds. Previous studies have investigated several low-cost adsorbents as substitutes to PAC, e.g., bark, chitosan, xanthate, zeolite, clay, peat moss, seaweed, dead biomass, and others [8–10]. Finding other methods to improve the aggregation and sedimentation properties of PAC is also a possible way to make PAC reusable. In summary, two obstacles need to be tackled: the retrieve of PAC from the water and the regeneration of PAC. There have been a few studies on the regeneration of PAC [11], but there has been no research on making the PAC retrievable. In this study, we will make the PAC retrievable by surface modification.

There have been some reports on the surface modification of AC. The modification of AC is usually crucial to its performance in various applications [12,13]. A variety of surface modification techniques based on chemical or physical processes have been developed in industry and academic field. Surface initiated atom transfer radical polymerization (Si-ATRP) is an effective method on surface modification. This method can covalently connect polymer chains to the surface of materials [14]. So far, the surfaces of carbon-based materials such as carbon nanotubes, carbon black, and carbon spheres have already been effectively adjusted in a controlled way using Si-ATRP [15–20]. Unexpectedly, modification of AC surface by Si-ATRP has rarely been reported. The only two examples we know are only focused on the polymerization behavior of the surface modified AC [21,22] after oxidation treatment. However, oxidation [22] will destruct the pore structure of the AC and result in the decrease of surface area and adsorption performance. In the previous report of our group [1], we have investigated the activated carbon with acidification and found that the

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acidification treatment did not have much influence on the surface area of PAC compared with the case of oxidation. Moreover, the acidification can also increase the content of phenolic hydroxyl and carboxyl functional groups.

Poly(*N*-isopropylacrylamide) (PNIPAM), one of the most widely studied thermoresponsive polymers, has a lower critical solution temperature (LCST) in aqueous solution at about 32 °C. When the temperature of the solution is below the LCST, the hydrophilic groups, i.e., hydroxyl group and amine group, will dangle out the polymer chain and render the PNIPAM a hydrophilic property. While the temperature rises above the LCST, the PNIPAM shows hydrophobic property with isopropyl groups dangling outsize the polymer chain. This change of phase behavior is ascribed to the detailed molecular structure of PNIPAM. There were extensive studies on PNIPAM and modified PNIPAM in the potential applications in biological medicine field [23–25].

However, the use of PNIPAM as a flocculant is rarely reported, compared with the conventional polymeric flocculants, in the flocculation process with PNIPAM, the temperature of the solution should be increased to above 32 °C to acquire the flocculation effect [26,27]. First, [28–30] the surface of the particles is covered with the adsorbed polymer molecules sufficiently by mixing the suspended particles with the thermoresponsive polymer below its LCST. Then heating the suspension above its LCST, the polymer chains that adsorbed on the particles become hydrophobic, so does the surface of the suspended particles. Thus the flocs are formed by these hydrophobic interactions. An adequate mechanical force to the flocs subsequently causes the rearrangement of the particles in the flocs, thereby discharging the water molecules and then leads to their compaction. However, there has been no research on making the PNIPAM as a flocculant with the PAC, not to say obtain the self-flocculated PAC which can get self-flocculation with change of the temperature.

The problem of water environment of endocrine disrupting chemicals (EDC) has attracted people's attention in recent years [31–34]. Among all of the endocrine disruptors, bisphenol A (BPA) [35] is widely used in the plastics industry as a monomer for production of epoxy resins and polycarbonate. So in this word, [36,37] bisphenol A can be used as a surrogate of phenolic pollutant to determine the adsorption performance of the grafted PAC.

In this paper, thermoresponsive powdered activated carbon (PAC) grafted with PNIPAM was synthesized in aqueous solution. The grafting reaction is conducted under ambient temperature using the surface-initiated ATRP of NIPAM from macroinitiators functionalized PAC after acidification treatment. By controlling the amount of surface grafting, the hybrid PAC-PNIPAM will have self-flocculation effect with rapid response to temperature, two-stage adsorption and corresponding desorption behavior of bisphenol A. These effects could provide a new way to re-use activated carbon in water purification and avoid secondary pollution due to its better self-flocculation property.

2. Experimental section

2.1. Materials

Monomer *N*-isopropylacrylamide (NIPAM, 98%, Aladdin) was used directly without further purification. In this report, the employed catalyst, initiator, and ligand were Copper (I) bromide (CuBr), 2-bromoisobutyryl bromide (BMPB, 98%), and *N*,*N*,*N*′,*N*″, *N*″-pentamethyldiethylenetriamine (PMDETA) respectively, and all of them were obtained from Sigma–Aldrich and used without further purification. The 4-dimethylamiopryidine (DMAP), triethylamine (TEA), and 3-aminopropyltriethoxysilane (APTES) were supplied by Aladdin. Powdered activated carbon (PAC) was purchased from Aladdin and dried at 120 °C in vacuum for at least 12 h (h) before use. Other reagents such as triethanolamine, hydrochloride acid and organic solvents were purchased from Sinopharm.

2.2. Characterization

FTIR was employed to verify the existence of NIPAM and conducted on an AVATER-360B FTIR spectrometer (Nicolet Co., USA) in the range from 400 to 4000 cm^{-1}. The grafting degree of NIPAM was quantitatively characterized with TGA [16], which was performed using a Pyris 6 thermogravimetric analyze (Perkin–Elmer, USA) at a heating rate of 10 °C min^{-1} from room temperature to 800 °C. X-ray photoelectron spectroscopy (XPS) technique was applied to detect the surface elemental compositions of the hybrids, which was carried out on a Thermo scientific esca lab 250Xi using a 200 W monochromated Al Kα radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. The surface morphologies of the composites were examined using a JEOL-6701F scanning electron microscope. The absorbance of bisphenol A was detected by UV–Vis spectrophotometer (Beijing Purkinje General Instrument Co., CN). The dispersion properties of the composites were observed by optical photographs and the turbidity was detected by a WGZ-2000 turbidity meter (Beijing Warwick Industrial Science and technology Co., CN). The experimental temperature were 25 ± 0.1 °C, 40 ± 0.1 °C and pH is 7.0 ± 0.1. Nitrogen adsorption–desorption isotherms were obtained with a Micromeritics ASAP 2010 instrument (USA) at −196 °C.

2.3. Sample preparation

The preparation of the grafted PAC is shown in Scheme 1, including the procedure as follows:

2.3.1. Acidification of PAC

PAC (3.0 g) was added to a round-bottomed flask containing 50 mL of 12.0 mol L^{-1} hydrochloride acid. The mixture was stirred in an ultrasonic bath for 30 min (min) and then transferred into an oil bath held at 60 °C for 3 h. The resulting mixture was filtered and thoroughly washed with deionized water until neutral. The resultant product was dried under vacuum at 110 °C and denoted as PAC-OH.

2.3.2. Synthesis of amino-functionalized PAC

The amino-functionalized PAC was prepared as follows. Firstly, 1.00 g of PAC-OH, 0.1 mL of triethanolamine was mixed with 50 mL of ethanol to produce a homogeneous suspension. The above ethanol suspension was transferred into a 150 mL flask equipped with a magnetic stir bar followed by heating to 60 °C. Then, 60 μL of ammonium hydroxide and 1.5 mL of deionized water were injected into the flask. Subsequently, 0.94 mL of APTES (4.0 mmol) was added dropwise. The resultant mixture was stirred at 50 °C for 12 h and then cooled to room temperature. The sediment was obtained by centrifuging the crude product at 8000 rpm and discarding the supernatant, and then was redispersed in ethanol and centrifuged once more. The above purification cycle was repeated three times to remove the excess APTES thoroughly. The resultant amino-functionalized PAC (PAC-NH_2) was finally redispersed in 50 mL of anhydrous tetrahydrofuran (THF) for storage.

2.3.3. Synthesis of 2-bromoisobutyrate-functionalized PAC

The above THF suspension of amino-functionalized PAC (50 mL) was mixed with DMAP (0.056 g, 0.47 mmol), TEA (1.4 mL, 10 mmol) in a flask. After cooling to 0 °C, 2-bromoisobutyryl