



Self-flocculated powdered activated carbon with different oxidation methods and their influence on adsorption behavior



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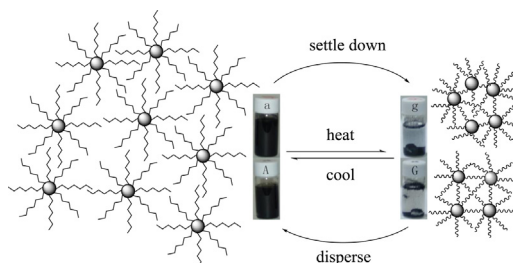
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HIGHLIGHTS

- Powdered activated carbon (PAC) is treated with two different oxidation methods.
- The oxidated PAC is grafted with poly (*N*-isopropylacrylamide).
- The grafted PAC via new oxidation method has good adsorption behavior of bisphenol A.
- The grafted PAC has excellent self-flocculation effect.
- The grafted PAC has high application in the water remediation required pre-heating.

GRAPHICAL ABSTRACT

Powdered activated carbon (PAC) has been treated with two different oxidation methods and grafted with poly (*N*-isopropylacrylamide) (PNIPAM). The new oxidation method of thermal treatment followed by acidification enables the carboxyl-rich PAC with large surface area. The PNIPAM graft PAC synthesized from the carboxyl-rich PAC will have good adsorption behavior of bisphenol A and self-flocculation effect with rapid response to temperature.



ARTICLE INFO

Article history:

Received 9 August 2015

Received in revised form 15 October 2015

Accepted 19 October 2015

Available online 26 October 2015

Keywords:

Powdered activated carbon

Oxidation

Adsorption

Poly(*N*-isopropylacrylamide)

Self-flocculation

ABSTRACT

The commercial powdered activated carbon (PAC) has been selectively oxidized by two methods. The two oxidized methods are wet oxidation with ammonium persulfate and thermal treatment after acidification with hydrochloric acid, respectively. The two oxidized PAC were then functionalized with thermoresponsive poly (*N*-isopropylacrylamide) (PNIPAM) in aqueous solution at ambient temperature. Comparing the two oxidized PAC products and their grafted derivatives, the oxidized PAC modified with thermal treatment after acidification shows larger surface area of 1184 m²/g and better adsorption of bisphenol A. Its derivative also exhibits relatively large surface area and adsorption capacity after grafted with PNIPAM. The maximum surface adsorption capacity simulated under Langmuir Models reached 156 mg/g. In addition, the grafted PAC products show self-flocculation behaviors with rapid response to temperature because of the thermal phase transition and entanglement behaviors of PNIPAM. The present study provides a new way to obtain carboxyl-rich activated carbon with large surface area and better adsorption capacity. The retrievable grafted PAC with good self-flocculation effect responsive to temperature will have high potential application in water remediation which requires pre-heating and emergency water treatment in the wild.

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1. Introduction

With the development of separation technology, there has been increasing number of water treatment methods required

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pre-heating, such as distillation, membrane distillation (MD) etc. Especially, MD is well known as the emerging thermally-driven separation process, which is based on the vapor transport across the hydrophobic microporous membrane driven by the vapor pressure gradient across the membrane and poses a lot of promise in desalination, water and wastewater treatment. [1] However, the loose pore structure of the microporous membrane results in the inefficient removing of organic pollutants from water during membrane distillation process, which also occurs during distillation process. Moreover, in the cases of drinking in the wild or purifying the water in swimming pool, a relatively high resultant temperature is needed, which also presents many difficulties in the removing of organic pollutants [2].

Activated carbon adsorption, which has a low capital cost and does not produce much toxic intermediates [3], seems to be a promising adsorbent for organic pollutants removal. Comparing the kinds of carbon adsorbent, powdered activated carbon (PAC) is much better than that of granular activated carbon (GAC) because of the larger surface areas [4–6]. However, the small particle size makes the retrieval of PAC from water difficult, and the residual PAC in the water will result in the secondary pollution. To recycle PAC, there are two obstacles need to be tackled, including the retrieve of PAC from the water and the regeneration of PAC. There have been a few studies on the regeneration of PAC [7], however, no research is on making the PAC retrievable. As the activated carbon could be functionalized [8], the retrieval limitation could be solved by modifying PAC, such as the PAC with reversible flocculation function upon the changing of temperature.

The reversible flocculation effect in response to temperature can be achieved by grafting thermoresponsive polymer on the PAC surface. As for surface modification, the carboxyl groups play a key role in providing anchoring sites for further surface modification by grafting or surface reaction [9,10]. There are many methods to create carboxyl group on carbon surface, and most of them are the wet oxidation in a solution of oxidant, such as H_2O_2 , HNO_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, NaOCl , KClO_3 , KIO_4 , KMnO_4 , AgNO_3 etc. at relatively lower temperature (20–120 °C) [11–14]. However, of all these wet oxidation reactions, the decrease of the surface areas and pore volumes of PAC is inevitable which will lower the adsorption performance for hydrophobic organics. Previous report [15] shows that carboxyl-rich carbon sphere can be obtained via a simple approach by the thermal treatment in air. In this report, we prepare the carboxyl-rich group functioned PAC by the thermal treatment based on the acidifying PAC firstly.

Surface-initiated atom transfer radical polymerization (Si-ATRP) is one of the most frequently used methods to covalently connect polymer chains to the solid surface [16–19], which can be employed in fabricating thermoresponsive PAC. We found that the modification of PAC surface by Si-ATRP has rarely been reported [9,19]. Furthermore, the carboxyl functionalized PAC in these articles is created by wet oxidation method which is known for the destruction of the pore structure of the PAC. Additionally, the influences of the oxidation and grafting reaction on surface areas and adsorption capacity of the PAC are also not discussed.

As one of the most widely studied thermoresponsive polymers, Poly (*N*-isopropylacrylamide) (PNIPAM) and modified PNIPAM are frequently used based on their potential applications in biological medicine field [20–22]. In recent years, using PNIPAM as flocculants has also been reported. [23] Compared with the conventional polymeric flocculants, the PNIPAM capped particles show hydrophobicity with the temperature higher than the LCST of 32 °C and thus will deposit in water; however, the hydrophilicity transition from hydrophobicity with the temperature lower than LCST provides the modified particles re-dispersing ability [24–26]. In this report, the PAC of thermoresponsive self-flocculation ability would be prepared by grafting PNIPAM on PAC surface via Si-ATRP.

Among all the organic pollutants, Bisphenol A, one kind of endocrine-disrupting chemicals (EDCs) [27,28], is widely used as an intermediate in the production of polycarbonates, epoxy resins, and other plastics. Bisphenol A has been detected in all kinds of environmental water. Moreover, many *in vitro* and *in vivo* assays have confirmed that bisphenol A increased the incidence of infertility, genital tract abnormalities and breast cancer [29,30]. Accordingly, there is an urgent need to develop effective technology to remove bisphenol A from aquatic environment.

In this paper, carboxyl functionalized powdered activated carbon (PAC) were obtained by two oxidation methods. After that, thermoresponsive PNIPAM graft PAC (PAC-PNIPAM) was synthesized in aqueous solution under ambient temperature by Si-ATRP. The surface and textual properties of the obtained carboxyl functionalized PAC and PNIPAM graft PAC were investigated. Furthermore, the influence of oxidation methods and the graft process was examined by studying the adsorption ability of bisphenol A on these obtained PAC. Additionally, the thermoresponsive self-flocculation effect of PAC-PNIPAM was investigated to estimate the retrievable performance.

2. Experimental

2.1. Materials

Bisphenol A (99% purity) [$\text{C}_{15}\text{H}_{16}\text{O}_2$] was purchased from Aladdin Chemical Company. The largest distance of bisphenol A molecule is 0.94 nm, and the first deprotonation of bisphenol A started at around pH 8.0 and the second one at around pH 9.0. In view of the high value of logKow (3.32), the stock solution of bisphenol A was prepared with methanol which was adsorbed slightly onto activated carbons in water [31]. Then the working solution of bisphenol A was obtained by diluting the stock solution with pure water. Monomer *N*-isopropylacrylamide (NIPAM, 98%, Aladdin) was used directly without further purification. In this paper, Copper (I) bromide (CuBr), 2-bromoisobutyryl bromide (BMPB, 98%), and *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA) were used as catalyst, initiator, and ligand, respectively, and all of them were obtained from Sigma–Aldrich and used without further purification. The 4-dimethylaminoipyridine (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. Ammonium persulfate and other reagents, organic solvents were purchased from Sinopharm.

2.2. Sample preparation

Carboxyl functioned PAC (PAC-COOH) was prepared by two methods, and Fig. 1 presents the preparation procedures of PAC-COOH and PNIPAM graft PAC.

2.2.1. Preparation of PAC-COOH via thermal treatment

The acidification of PAC was needed for low-temperature heat treatment in air, which was performed as follows. 3.0 g of PAC was added to a round-bottomed flask containing 50 mL of 12.0 mol L⁻¹ hydrochloric acid and dispersed by ultrasonic for 30 min (min). Subsequently, the mixture was transferred into an oil bath and heated 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. PAC-COOH was obtained by the thermal treatment of PAC-OH. The PAC-OH was heated to the desired temperature of 300 °C at a rate of 5 °C min⁻¹ under air atmosphere and kept for 5 h. The resultant product was washed with deionized water and subsequently with ethanol until neutral. Then, the product was dried at

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