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Adsorption of Methyl Blue onto uniform carbonaceous spheres prepared via an anionic polyacrylamide-assisted hydrothermal route

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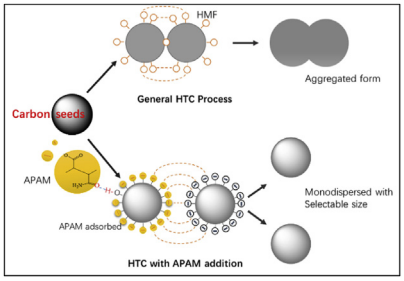
HIGHLIGHTS

- Anionic polyacrylamide-assisted hydrothermal route was used as novel surface inhibitor to produce carbon spheres.
- Monodispersed and uniform carbonaceous spheres with high starting glucose concentration were obtained.
- Surface modification with alkaline can enhance the adsorptive capability of spheres.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbonaceous microspheres (CAS) with tunable size, monodispersity and oxygenated functional groups have attracted intensive interest recently owning to potential use in various fields. A facile synthesis of glucose derived CAS is presented by hydrothermal treatment with the help of small amount of anion polyacrylamide (APAM). Different from most other CAS produced with high glucose concentration, the obtained spheres show regular shape and narrow sized distribution, which in turn exert great influence on their application as adsorbent. The results exhibit a substantial reduction in sphere size from 1.57 to 0.48 μm and 1.77 to 0.75 μm as the substrate glucose concentration was 0.5 M and 1 M, respectively. A degree of polymerization via intermolecular dehydration and aldol condensation is found reduced by the formation of hydrogen bond via the adsorption of APAM on carbonaceous seeds. The resulted increment in surface charge suppressed the crosslinking reaction thus promoted the monodispersity of CAS, which bestowed the CAS superior performance as an efficient adsorbent for a cationic dye Methyl Blue (MB). Experiments revealed that the CAS, which was further treated with alkaline, can have much higher MB adsorption capacity (348.1 mg/g) than most other reported materials due to the electrostatic interaction with those deprotonated hydrophilic functional groups on CAS surface.

1. Introduction

In recent years, carbon microspheres with controllable particle size, surface morphology and rich chemical composition are greatly appealing in the carbon community because of their superior performance applied in various fields, such as catalyst and catalyst

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supports [1], adsorbent [2], sacrificial template [3], electrode materials and so forth. Different synthetic route for carbonaceous spheres have been utilized such as chemical vapor deposition (CVD) [4], arc-discharge [5], high pressure carbonization [6] and template methods [7] on the basis of harsh conditions with high cost. Compared to the mentioned approaches, hydrothermal carbonization (HTC) process has established to be an applicable candidate for the synthesis of a whole range of biomass based carbonaceous spheres, such as glucose, xylose, maltose, starch and hemi cellulosic biomass for its mild operation conditions and environmental friendly renewable resource [8,9].

During a typical HTC process, the saccharides would primarily decompose into furfural or HMF and then proceed polymerization—condensation with the formation of small nuclei [10]. These nuclei grow according to the LaMer model until all the "monomers" have been exhausted and the final sphere size is attained. The aggregated morphology which is featured by interconnected or cross-linked carbon microspheres can easily be obtained by the cross-linking polymerization among different carbon nanoparticles [11,12] by using high concentrated substrate, though great efforts by HTC of saccharides has been made. Since the wide application (i.e., drug delivery, image agents, chromatograph) of CAS are partly depending on its controllable morphology, size distribution and monodispersity [13,14], thus it would be preferable if small size carbonaceous spheres with monodispersity could be produced in a facile and simple way.

Performing HTC at low temperature (<180 °C) or reaction time (<6 h) can improve this method, however the concentration of reactants in the hydrothermal environment are normally required at lower value (<0.4 M) to maintain monodispersity [15,16]. For example, Li et al. [17], prepared the monodispersed, uniform carbonaceous spheres with the size distribution ranging from 0.4 to 0.65 μm by controlling the glucose concentration below 0.3 M at 190 °C for 4 h. Other researchers programmed CAS with diameter between 0.16 and 0.20 μm with a two-step hydrothermal synthesis by applying the glucose concentration within 0.1 M [18]. The HTC with low concentration of curing agent apparently has several deficiencies, which cannot achieve the massive production thus leading to the decreased operational efficiency. Meanwhile a higher temperature than 180 °C is always needed for efficient saccharides dehydration thus limiting the condition regulation [12].

To address the problem, various additives were used as dispersant to tailor the morphology of as-prepared carbonaceous spheres. Zheng et al., found that alcohol in various saccharide solutions have positive effect on the symmetry of spheroid [19]. Xu et al., introduced KOH as inhibitor to prepare CAS with nanoporous structure and found that spheres with more uniform size distribution could be obtained with higher alkaline concentration [20]. Phenolic compounds [21], acrylic acids [22], and formic acids were also added in saccharide solutions to tailor the size of colloidal spheres. Although all the chemicals did work on regulating the size and morphology of CAS, unfortunately, they all induced the dramatic increase of the sphere diameter. Qi et al., found that levulinic acid as one of the by-products from rehydrated 5-hydroxymethylfurfural (HMF) acted as a building agent of carbonaceous spheres and would slow the growth of CAS [23]. However, the starting sucrose concentration was still lower (0.1 M) and the HTC time was required within 3.75 h. More recently, Gong et al. [24] introduced sodium polyacrylate (PAANa) as additive in HTC process for effective tuning the size and dispersity of carbonaceous spheres. The help of tiny amount of PAANa extended the reaction conditions of hydrothermal carbonization process (i.e., the reaction temperature and time could be extended to 200 °C and 24 h), and more importantly enabled sugar concentration exceeding 1.0 M.

In the light of the charge feature of PAANa, much cheaper and more abundant anion polyacrylamide (APAM) was therefore presented as a novel dispersant in the production of CAS via HTC in this work. The aim is to provide a simple, efficient and economic feasible route which offers CAS properties control in terms of microsphere size, dispersity and uniformity. APAM is a widely used chemical in wastewater treatment, which acts as flocculent due to the bridging between suspended solids and colloids via $CONH_2$ groups [25,26]. The anions on one side of APAM could interact with positively charged colloids and lead to electrostatic neutralization. However, the role of APAM in regulating the morphology and controlling the size of carbonaceous spheres has received little attention so far. Considering the fact that CAS prepared by this straightforward water based approach are basically nonporous and have unfavorable low surface areas, the CAS were further activated by alkaline to enhance its surface functionalities and then the practical application was conducted to compare the adsorptive behavior of carbonaceous spheres synthesized with or without APAM addition for a cationic dye methyl blue.

2. Materials and methods

2.1. Materials

D-(+)-glucose, anion polyacrylamide (APAM), NaOH (99%) were supplied by Sinopharm Chemical Reagent (Shanghai, China). Methylene blue (MB, $C_{16}H_{18}N_3SCl\cdot 3H_2O$, M.W. = 373.9) and ethanol were purchased from Sigma-Aldrich (Shanghai, China). All chemicals were analytical reagent and were used without further purification. The physicochemical properties of APAM are illustrated in Table 1 [27].

2.2. CAS synthesis

Carbonaceous spheres were synthesized by hydrothermal carbonization from glucose with small amount of APAM addition. Typically, 0.5 M and 1 M glucose were dissolved in 40 mL deionized water in a 100 mL glass beaker, then 10, 20 and 40 mg APAM, respectively, was added into the solution and was dissolved by magnetic stirrer for 0.5 h. The mixture was then transferred into Teflon-lined autoclave and heated at 200 °C for 8 h. The solid products were separated by centrifugation, washed with distilled water and alcohol for several times and finally dried at 60 °C for 12 h.

2.3. CAS activation

According to Song et al. [28], 0.5 g dried samples were added into 100 mL NaOH solution with concentration kept at 0.5 M. The mixture was stirred by magnetic stirrer for 1 h at room temperature and collected by centrifugation and washed with water until the pH of residual water reached near neutral. The activated carbonaceous spheres were dried in oven at 80 °C at night, noted as CAS/OH. Those carbonaceous spheres without activation are named as CAS.

Table 1
Physicochemical properties of APAM.

Parameters	Value
Chemical name	Anionic-polyacrylamide
Molecular formula	$(H_2CHCONH_2)_x(CH_2CHCOONa)_y$
Molecular weight (g/mol)	3 000 000
Log-Octanol-water coefficient	−0.67
Zeta potential (mV)	−27.4 (pH = 6.8)
pKa	6.87