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Hollow poly(cyclotriphosphazene-co-phloroglucinol) microspheres: An effective and selective adsorbent for the removal of cationic dyes from aqueous solution

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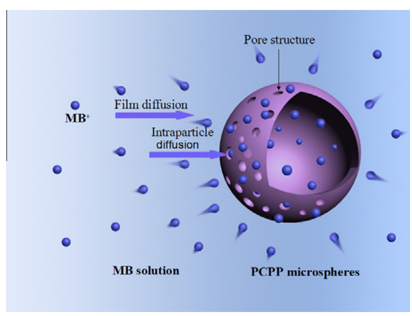
HIGHLIGHTS

- Hollow PCPP microspheres as an adsorbent could be facilely synthesized.
- The adsorbent owns numerous electron-rich N and P atoms and hydroxyl groups.
- The adsorbent exhibited an effective and selective adsorption behavior.
- The pseudo-second-order model could be better to describe the adsorption of MB.
- The MB adsorption onto Hollow PCPP microspheres was endothermic and spontaneous.

GRAPHICAL ABSTRACT



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ABSTRACT

Hollow poly(cyclotriphosphazene-co-phloroglucinol) (PCPP) microspheres, synthesized by a facile precipitation polymerization method and then a simple solvent-treatment procedure, were evaluated as a potential adsorbent for the removal of cationic dyes from aqueous solution. The adsorbent was characterized by SEM, TEM, FTIR, N_2 adsorption/desorption isotherms, zeta potential and particle size analysis. The adsorption process with respect to operating parameters was investigated to evaluate the adsorption characteristics of the hollow PCCP microspheres for methylene blue (MB). Systematic research including equilibrium, kinetics and thermodynamic studies were performed. The results showed the hollow PCCP microsphere was a potential adsorbent with an adsorption capacity of 50.7 mg/g at 298 K. The adsorption behavior followed the pseudo-second-order kinetic model and the adsorption equilibrium data obeyed the Langmuir isotherm well. Thermodynamic analyses confirmed that the adsorption was a physisorption process with endothermic, spontaneous and random characteristics. In addition, the possible adsorption mechanism was also proposed based on the experimental results. The study of selective adsorption further indicated the hollow PCCP microspheres could also remove other cationic dyes efficiently and be used a selective adsorbent.

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1. Introduction

Nowadays, environment pollution caused by dye industries has been attracting huge attention due to its serious harm to aqueous flora, microorganisms and human beings [1–4]. Since dyes existed in industrial effluents are toxic to microorganisms and can impede the photosynthesis of aqueous flora, the ecological balance may be destroyed ultimately [5,6]. What is worse, dyes can also threaten human health by polluting river and groundwater [7]. As a result, it is necessary to treat these industrial effluents before discharge. Among numerous technologies used to remove dyes from wastewater, adsorption has distinct advantages due to its efficiency, low cost and ease of operation [8–11]. To date, a large number of adsorbents have been proposed and studied [12,13]. However, these conventional adsorbents have many disadvantages such as low adsorption efficiency, long adsorption time, and separation inconvenience [14]. Therefore, it is necessary to develop novel and high-efficiency adsorbents.

To date, many efforts have been focused on micro-/nanostructured materials including spheres, sheets, wires, rods, tubes and leaves due to their specific morphologies, fascinating properties and potential applications [15–21]. Among them, micro-/nanospheres with a hollow structure have gained more and more attention because of their unique interior cavity which can bring them broad applications in the fields of pollutant disposal, microreactors, Li-ion batteries, biomedicines, sensors, catalysis, and many others. For example, V_2O_5 hollow microspheres were applied as a high-capacity cathode material for lithium-ion batteries [22]. BiOI hollow microspheres exhibited the enhanced photocatalytic activity [23]. New mesoscopic hollow spheres composed of $CaO/Ca_{12}Al_{14}O_{33}$ were proved to own high adsorption capacities and rapid adsorption kinetics for high temperature CO_2 capture [24]. Hollow mesoporous carbon spheres showed excellent adsorption ability for bilirubin [25]. Thus, hollow microspheres might be an excellent adsorbent due to their interior cavity and high specific surface area, which can provide abundant adsorption active sites. To our knowledge, suitable surface groups on adsorbents can also benefit dye adsorption largely. For instance, some negatively charged groups such as carboxyl, sulfonic and hydroxyl groups have been demonstrated to promote the efficient adsorption of cationic dyes [26–28]. Besides, adsorbent materials with a spherical morphology are usually the first choice because they can be easily operated in practical processes as reactor fillers [29]. As a result, mciro-/nanomaterials owning hollow structures, spherical morphology and numerous surface groups would be a high-efficiency adsorbent.

In this study, we have successfully prepared hollow poly(cyclotriphosphazene-co-phloroglucinol) (PCPP) microspheres by a facile precipitation polymerization, which were evaluated as a possible adsorbent for the removal of a cationic dye (methylene blue, MB). We have systematically and thoroughly investigated the adsorption process including various influencing factors, equilibrium, kinetics and thermodynamics. Results showed that the hollow PCPP microspheres had a larger adsorption capacity compared with solid PCPP microspheres which were the precursor of hollow PCPP microspheres without taking solvent-treatment procedure. Besides, the adsorption capacity of hollow PCPP microspheres at 25 °C was larger than that of most reported adsorbents such as rice husk [30], jute processing waste [31], zeolite [32], polyurethane foam [33], poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol) nanospheres [28], polyaniline nanotubes [34], carbon nanotubes [35], etc. We also studied the adsorption ability of hollow PCPP microspheres for other dyes (anionic dyes: methyl orange (MO), acid chrome blue K (ACBK), eosin-Y (EY), eosin-B (EB), cationic dyes: safranine T (ST), malachite green (MG), and neutral dye: neutral red (NR)). And the hollow PCPP microspheres could remove cationic dyes from mixed dye solutions preferentially and thoroughly. As a result, the hollow PCPP microspheres might be an efficient and selective adsorbent for the removal of cationic dyes

2. Materials and methods

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP), phloroglucinol, triethylamine (TEA) were purchased from Sinopharm Chemical Reagent Co., Ltd. HCCP was recrystallized from dry hexane followed by sublimation (60 °C, 0.05 mmHg) twice before use (mp = 112.5–113 °C). Acetonitrile, acetone, ethanol, methylene blue (MB), methyl orange (MO), acid chrome blue K (ACBK), eosin-Y (EY), eosin-B (EB), safranine T (ST), malachite green (MG) and neutral red (NR) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. and used without further purification. The chemical formula of MB was $C_{16}H_{18}ClN_3S{\cdot}3H_2O$. And different concentrations of MB solutions were prepared by dissolving the required amounts of MB in deionized water.

2.2. Preparation of hollow PCPP microspheres

The solid PCCP microspheres were prepared by typical precipitation polymerization. In a typical experiment, 0.5 g HCCP (0.9 mmol) and 0.467 g phloroglucinol (1.8 mmol) were added into a flask with 400 mL acetonitrile. After ultrasonic dispersion for 10 min at room temperature, 16 mL TEA (acid-acceptor) was injected into the above solution by a syringe. Then, the mixed solution was kept at 40 °C under ultrasonic irradiation (150 W, 40 kHz) for 2 h. After reaction, the solution was centrifuged with rotation rate of 2000 r/min and then the precipitates were washed three times with ethanol and deionized water, respectively. Ultimately, the products were dried in a vacuum oven to yield solid PCPP microspheres.

A facile solvent-treatment procedure to prepare hollow PCPP microspheres is as follows: 0.2 g solid PCPP microspheres and 280 mL acetone were added into a 500 mL flask and kept for 30 min at room temperature under ultrasonic irradiation (150 W, 40 kHz). Then the products were centrifuged, washed with ethanol and dried to yield hollow PCPP microspheres.

2.3. Adsorption experiments

To study the adsorption process of the hollow PCPP microspheres as the adsorbent to remove MB dye, batch adsorption experiments were performed on a constant shaking incubator at a shaking speed of 150 rpm in triplicate. Kinetic experiments were performed by mixing 50 mg hollow PCPP microspheres into 100 mL MB solution (50 mg/L) at 25 °C at appropriate time intervals. The concentrations of MB left in supernatant solutions were determined using a UV–vis spectrophotometer. The amount of MB adsorbed per unit mass of hollow PCPP microspheres (q) and the dye removal efficiency (R) could be calculated by applying the Eqs. (1) and (2), respectively:

$$q = V(C_0 - C_t)/m; \quad (1)$$

$$R = 100(C_0 - C_t)/C_0 \quad (2)$$

where C_0 and C_t (mg/L) are the initial and final (after adsorption) concentration of MB solution, respectively; m (g) represents the mass of the adsorbent and V (L) is the volume of MB solution.