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Removal of perfluorooctanoic acid from water with economical mesoporous melamine-formaldehyde resin microsphere

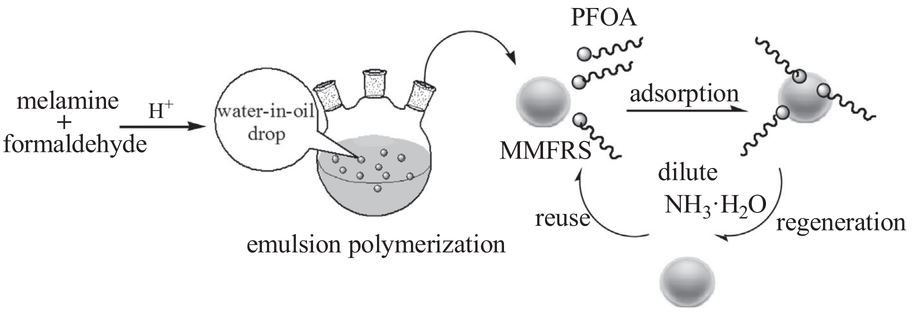
Jing Li, Qian Li, Lu-shuang Li, Li Xu *

Tongji School of Pharmacy, Huazhong University of Science and Technology, Wuhan 430030, China

HIGHLIGHTS

- Mesoporous melamine-formaldehyde resin microsphere was fabricated.
- It had high adsorption amount of perfluorooctanoic acid than activated carbon.
- The adsorption can be performed in a wide pH and temperature range.
- The material could be well regenerated by dilute ammonia solution.
- It was a potential adsorbent to remove perfluorooctanoic acid from water.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluoroalkyl and polyfluoroalkyl substances are priority contaminants of global concern. It is urgent to remove them from the environment. Adsorption is an efficient approach, but the adsorption capacity and regeneration of adsorbent were not satisfactory. In the present study, mesoporous melamine-formaldehyde resin microsphere (MMFRS) was fabricated through suspension polymerization. Owing to its mesoporous property and large anion-exchange capacity of 0.3 mmol/g, MMFRS was applied to the adsorption of perfluorooctanoic acid, a model target. The sorption kinetics obeyed pseudo-second-order equation and the sorption isotherms fitted both Freundlich and Langmuir models well. MMFRS exhibited a superiority over commercial powdered activated carbon on the adsorption amount. The sorption could reach equilibrium within 24 h. In addition, the material could be easily and economically regenerated by dilute $NH_3 \cdot H_2O$ (7.5 mM); a regeneration percentage (>85%) after 20 recycles was obtained. This study provides a facile, environmentally-friendly and low energy-consumption strategy for removal of perfluorooctanoic acid from aqueous solution in waste-water treatment.

1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are characteristic of C–F bond instead of C–H partially or completely in their structures. They are included in the Environmental Protection Agency's Contaminant Candidate List 3 of chemicals [1,2], which are related to low birth weight [3], thyroid disease [4], early menopause for women [5], children's attention deficit or hyperactivity disorder [6] and even kidney and testicular cancer [7]. They are ubiquitous in the environment [8,9], as they are widely applied in manufacturing industry including non-stick cookware, firefighting foams, photographic films and coating materials for food packing, etc [2,8]. Since these compounds are extremely persistent and bioaccumulative in organism through the contaminated environment [2], removal of PFASs from environment has recently been of global concern. However, owing to the stable C–F bond in the structure, PFASs were resistant to most frequently-used water

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* Corresponding author.
E-mail address: xulpharm@mails.tjmu.edu.cn (L. Xu).

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treatment techniques, such as coagulation, filtration, aeration, oxidation and disinfection. Hence, some neoteric treatments were explored for this purpose, such as plasma-based method [10], electrocoagulation [11], electron beam treatment [12] and photocatalytic decomposition [13]; while these technologies were complicated and/or high-capital required. Hence, adsorption is still the most popular method to remove PFASs [14–19]. The activated carbon which possesses considerable large surface area is the most preferred adsorbent, for its high adsorption capacity and low cost, but seldom for regeneration. Thus, various reusable materials were explored, including, but not limited to, surface-modified silica [20,21], multi-walled carbon nanotubes [22] and molecularly imprinted polymers [14]. Although these adsorbents had some superiority in terms of regeneration, they hardly had comparable or higher adsorption capacity over the activated carbons; in addition, the synthesis processes were not facile and economical. Hence, an adsorbent which simultaneously possesses large adsorption capacity and easy regeneration property is highly desired for the PFASs treatment.

Porous polymer, especially resin microsphere, has gained heightened attention for their porous networks and large surface areas in diverse applications. Particularly, as the adsorbent, resin microsphere has the characteristics of high dispersibility in solvents, large surface area and applicability to multiple operational formats. Melamine-formaldehyde (MF) resin was well known for its rich imino groups and triazine rings, which endowed the material electropositivity in acid, neutral and weak basic environment. The MF resin microsphere was fabricated through various approaches, including dilute solution precipitation polymerization [23], sol-gel method [24], hydrothermal method [25], template synthesis method [26] and dispersed polycondensation [27], etc. They found some applications as adsorbents for ionic dyes [28], CO_2 [29] and heavy metal ions [30]. Herein, taking advantages of both resin microsphere and MF resin, mesoporous melamine-formaldehyde resin microsphere (MMFRS) was deliberately fabricated through suspension polymerization. MMFRS was then applied to adsorb perfluorooctanoic acid (PFOA), one of the representative of PFASs. The regeneration ability of MMFRS was especially tested. The study would provide an alternative strategy to remove PFASs from the environment.

2. Experimental

2.1. Materials

Melamine, formaldehyde (37%, wt%), polyethylene glycol 20000 (PEG 20000), petrol ether (60 °C–90 °C), ammonium hydroxide ($NH_3{\cdot}H_2O$), ethanol (EtOH), phenol, CH_2Cl_2, NH_4AcO, HCl, NaOH, NaCl, KCl, $CaCl_2$, $MgSO_4$, $CuSO_4$, sodium dodecyl sulfonate (SDS), humic acid, Triton X-100 and lauryl dimethyl amine oxide (OB-2) of analytical reagent grade and powdered activated carbon (PAC, 5–10 μm) were all obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). PFOA (90%) and estradiol were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). High performance liquid chromatography (HPLC)-grade acetonitrile (ACN) was bought from Sigma-Aldrich Trading Co., Ltd. (Shanghai, China). Deionized water was produced with a Heal Fore NW system (Shanghai, China).

2.2. Preparation and characterization of MMFRS

MMFRS was fabricated by suspension polymerization, which is one of the popular heterogeneous polymerization method for the preparation of monodispersed polymer spheres. The detailed scheme was as follows. Melamine (12.5 g) and PEG 20,000 (6.0 g) were dissolved in formaldehyde solution (37%, 80 mL) at 50 °C under stirring till the solution became transparent, followed by filtration through polypropylene membrane to remove the insoluble particles, and the filtrate was the MF prepolymer solution. After the prepolymer solution was cooled down to room temperature, HCl solution (0.84 M, 4 mL) as a catalyst was added. Then, the oil phase, *i.e.* petrol ether (196 mL) containing Triton X-100 (1.4 g) and OB-2 (1.4 g), was poured into the prepolymer solution. With the agitation at 500 rpm and 50 °C, the water phase (the prepolymer solution) was mixed well with the oil phase for reaction. After 10 h, white suspension was formed, and the solid was collected by filtration and washed with petrol ether, ethanol and deionized water successively; thus-obtained material was MMFRS. To enhance the high three-dimensional cross-linking degree and thermostability, the material was hydrothermally treated at 140 °C for 10 h in a polytetrafluoroethylene pressure vessel. Afterwards, the material was centrifuged, dried at 80 °C and stored in a desiccator before use.

The obtained material was characterized as below. A JSM-35CF scanning electron microscopy (SEM) (JEOL, Japan) and a JEM-2100 HR transmission electron microscope (TEM) (JEOL, Japan) were used for morphology and porosity observation. An AVATAR 360 transform infrared spectrometer (FT-IR) (Thermo, USA) was used to characterize the functional groups. To analyze the thermal behavior of the material, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted on a TG 209 F1 Libra thermogravimetric analyzer (NETZSCH, Germany) and a Q2000 DSC differential scanning calorimeter (TA instruments, USA), respectively. The nitrogen adsorption isotherms for porous characterization were obtained on a TriStar II surface area analyzer (Micromeritics, USA). The zeta potential of MMFRS was measured by a ZetaPALS Zeta Potential Analyzer (Brookhaven, USA).

The anion-exchange capacity of MMFRS was determined by conductometric titration with a DDS-307 conductivity meter (Leici, Shanghai, China), referred as previous literature [31]. Typically, MMFRS (50 mg) was dispersed in 5 mL NaOH (0.1 M), and titrated by HCl (20 mM). Accordingly, the conductivity of the system was recorded to calculate the anion-exchange capacity of MMFRS (mmol/g resin). The p*K*a value of MMFRS was determined by the potentiometric titration method with a Delta 320 pH meter (Mettler Toledo, Shanghai, China).

2.3. Batch adsorption experiments

The general adsorption experiment was carried out as below. MMFRS (10 mg) was added to the PFOA aqueous solution (700 ppm, 4 mL), adjusted with HCl or NaOH to the desired pH. The adsorption was assisted by a SPX-250B-D constant shaking incubator (Boxun, Shanghai, China) at 50 rpm and 25 °C for 24 h. After adsorption, the solution was filtrated and the filtrate was injected to a HPLC-evaporative light scattering detector (HPLC-ELSD) system to determine the residual concentration of PFOA. The HPLC-ELSD system consisted of a Shimadzu (Tokyo, Japan) LC-20AD pump, a Dionex C18 column (4.6 × 150 mm, 5 μm, USA), and an Alltech 2000ES ELSD (Grace, USA). The mobile phase was 55% NH_4AcO (20 mM)–45% ACN at a flow rate of 0.5 mL/min and a column oven of 40 °C. The temperature of drift tube was 100 °C, and the flow rate of carrier gas (N_2), which was produced from a WSK-A auto air generator (Tianjin, China), was set at 2.8 mL/min.

The effects of sample pH, temperature and the coexisting pollutants on the adsorption and adsorption process were studied. (1) To investigate the effect of pH on adsorption, the pH of PFOA solution (700 ppm) was adjusted with HCl or NaOH to the desired pH as specified and the adsorption was conducted at room temperature. The following experiments were conducted without pH adjust-