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Regular Article

A facile approach towards amino-coated polyethersulfone particles for the removal of toxins

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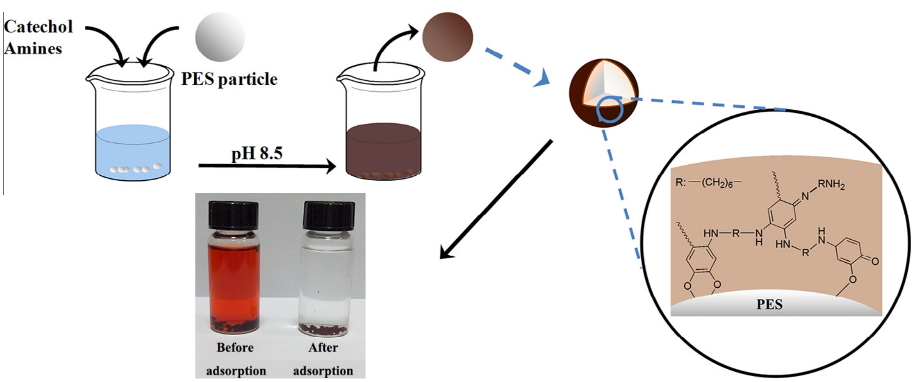
GRAPHICAL ABSTRACT



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ABSTRACT

The removal of toxins is important due to the damage to aquatic environment. In this work, a facile and green approach based on mussel-inspired coatings was used to fabricate amino-coated particles via the reaction between amine and catechol, using hexanediamine as the representative amine. The particles were characterized by Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), thermo gravimetric analysis (TGA), and scanning electron microscopy (SEM). The particles showed selective adsorption capability to Congo red (CR) and the adsorption process fitted the pseudo-second-order model, the intraparticle diffusion model, the Langmuir isotherm, the Freundlich isotherm and the Sips isotherm well. Furthermore, this approach was verified to have applicability to various amines such as diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA), and the amino-coated particles exhibited diverse adsorption capacities to CR, Cu^{2+} and bilirubin. Considering that the approach is easy to operate and the whole preparation process is in an aqueous solution, it is believed that the facile, green and economical approach has great potential to prepare particles for wastewater treatment.

1. Introduction

Nowadays, the removal of environmental toxins from industrial wastewater has aroused extensive attentions, since serious environmental problems have been caused by the discharge of

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industrial wastewater. Environmental toxins, like organic dyes, could cause considerable pollution to aquatic environment and had serious health risks for human beings and aquatic organisms due to their potential toxicity [1–6]. Till now, researchers have explored various approaches for the removal of toxins from wastewater [7–11] and adsorption has been extensively studied owing to its ease of operation, low cost, and high-efficiency.

As one of the most important adsorbents, polymeric adsorbent has been studied by numerous researchers, since polymeric adsorbent could adsorb toxins via physical adsorptions and chemical adsorptions, and could be easily processed into different shapes [12,13] to meet different requirements. However, the applications of the adsorbent were sometimes limited by low mechanical strength, low oxidation and heat resistance. Since polyethersulfone (PES) shows outstanding oxidative, thermal and hydrolytic stabilities as well as good mechanical strength and chemical resistance [14], we have prepared various modified PES particles for versatile adsorptions such as the removal of organic dyes, heavy metal ions, bilirubin and creatinine [15–18]. Since the adsorption process usually occurred on the external surface and pore surface of particle and the impact on the inherent properties of the substrates could be minimized by surface modification, we attempt to use aqueous surface modification to fabricate adsorbents directly by mussel-inspired method [19].

It has been reported that dopamine could form multifunctional polydopamine coatings onto materials via Schiff's base reaction or Michael addition reaction in alkaline solution. Inspired by the mechanism, we used hexanediamine (HDA) and catechol to prepare amino coatings on the surface of PES particle via the direct reaction between amino groups and phenol groups [20–22] in aqueous solution. Then the adsorption of organic dyes, the adsorption kinetics and isotherms were systematically studied. Furthermore, diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA) were also introduced to prepare coatings with more amino groups on the surfaces of PES particles to confirm the applicability of the approach to various amines and the adsorptions of Cu^{2+} and bilirubin were also investigated to show the versatile adsorption abilities of the amino-coated particles.

2. Materials and methods

2.1. Materials

Commercial polyethersulfone (PES, Ultrason E6020P) was purchased from BASF. N,N-Dimethylacetamide (DMAc), diethylenetriamine (DETA, 99%), copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, 99%), sodium dodecyl sulfate (SDS, 99%), methylene blue (MB, 99%), and Congo red (CR, 99%) were obtained from Chengdu Kelong Chemical Reagent Co. Ltd. (China). Catechol (99%), bilirubin (98%), polyethylene glycol (PEG, average M_n 600), 1,6-hexanediamine (HDA, 99%), triethylenetetramine (TETA, 99%), and tetraethylenepentamine (TEPA, 99%) were purchased from Aladdin Industrial Corporation. All the reagents above were used as received. De-ionized (DI) water was used throughout this study.

2.2. Preparation of PES particles

A phase inversion technique was used to prepare PES particles as reported in our previous studies [14,23]. Briefly, polyethersulfone (PES) was dissolved in N,N-dimethylacetamide (DMAc), and polyethylene glycol (PEG-600) was added as pore forming agent. The mass ratio of PES to PEG was controlled at 1:1 with the total concentration of 16 wt.%. The PES solution was injected into DI water, in which sodium dodecyl sulfate (SDS, 0.5 wt.%) was added, with a 0.6 mm-diameter syringe needle to prepare particles. Then the particles were washed in DI water to elute the residual solvent thoroughly.

2.3. Preparation and characterization of amino-coated particles

Amino-coated particles were prepared by a facile approach. Firstly, the as-prepared PES particles were dipped into a solution of amine in phosphate buffered saline (PBS, pH 8.5). Hexanediamine (HDA) was chosen as a representative diamine and then catechol (1 mg/mL) was added into the solution. The mole ratios of catechol to hexanediamine were controlled at 1:1, 1:2, 1:4 and 1:8 to investigate the effect of mole ratios on the adsorption capability. The reaction was carried out for desired time (0.5 h, 1 h, 2 h, 3 h, 4 h, 8 h, 24 h) at room temperature with stirring. Subsequently, the particles were washed with DI water and ethanol to remove the unreacted molecules and termed as PES-HDA.

Furthermore, different amines, including diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA) were used to fabricate amino-coated particles through the same procedures.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet 560, USA) and X-ray photoelectron spectroscopy (XPS, KRA- TOS XSAM800, Britain) were used to characterize the chemical structures and surface compositions of the coated particles.

The thermo gravimetric analysis (TGA) and differential thermal gravity (DTG) curves of the pristine and amino-coated particles were obtained using TG 209 FI NETZSCH from 30 to 800 °C at the speed of 10 °C/min under nitrogen atmosphere. The coating amounts onto the particles were verified by calculating the mass loss between the TGA curves of pristine PES particles and coated particles.

Scanning electron microscope (SEM, JSM-7500F, JEOL, Japan) was employed to characterize the morphologies of the pristine and amino-coated particles. To prepare the samples for the SEM observation, the particles were quenched by liquid nitrogen, and then cut with a single-edged razor blade. After freeze drying for 12 h, the particles were attached to the sample supports and coated with a gold layer.

2.4. Determination of ion exchange capacity (IEC)

In order to determine the ion exchange capacity, the coated particles were firstly incubated with 0.01 mol/L HCl and 0.01 mol/L NaOH solution in turns for several times. DI water was used in between to remove the residual HCl or NaOH solution. Then, the particles were put into 0.01 mol/L HCl solution for 24 h. The volume of HCl was adjusted to twice theoretically required volume, which could be calculated by assuming that all the amino groups on the particles could be protonated. Then the HCl solution was titrated with a standard NaOH solution (0.001 mol/L). In order to reduce errors, the operation was repeated at least three times and the results were averaged. The titrated IEC was calculated as follows [24]:

$$IEC\ (mequiv./g) = \frac{V_{HCl}N_{HCl} - V_{NaOH}N_{NaOH}}{m_c} \times 1000 \quad (1)$$

where V_{HCl} and N_{HCl} are the volume and normality of the HCl solution, V_{NaOH} and N_{NaOH} are the volume and normality of the NaOH solution, and m_c is the weight of the dried particles.

2.5. Adsorption experiments

In order to investigate the adsorption of Congo red (CR) and methylene blue (MB), 30 particles (about 0.021 g) were put into