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Synthesis and characterization of ion-imprinted chelating fibers based on PET for selective removal of Hg^{2+}

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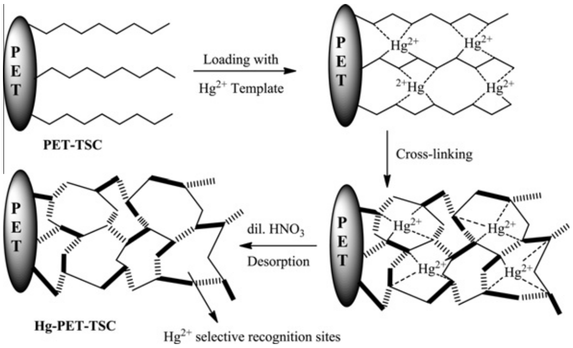
HIGHLIGHTS

- PET fibers were graft copolymerized with acrylonitrile.
- Further modification was carried out through the reaction with thiosemicarbazide.
- The resulted chelating fibers were imprinted in presence of Hg^{2+} as a template and formaldehyde as a cross-linker.
- The fibers were applied to selectively remove Hg^{2+} from aqueous solutions.

GRAPHICAL ABSTRACT



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ABSTRACT

The surface ion-imprinted poly(ethylene terephthalate)-thiosemicarbazide modified chelating fibers (Hg-PET-TSC) was prepared using Hg(II) as a template and formaldehyde as a cross-linker and showed higher adsorption capacity and selectivity for the Hg(II) ions compared with the non-imprinted fibers (NI-PET-TSC) without a template. The results showed that the adsorption of Hg(II) on the fibers was affected by the initial pH value, the initial Hg(II) concentration, as well as the temperature. Both kinetics and thermodynamic parameters of the removal process were evaluated and the obtained results indicated a spontaneous exothermic adsorption process that fit with the second-order kinetic model. Equilibrium experiments were fitted in both Langmuir and Freundlich adsorption isotherms and fits well with the Langmuir isotherm equation for the monolayer adsorption process. The maximum adsorption capacity values for Hg-PET-TSC and NI-PET-TSC were 137.13 mg/g and 77.51 mg/g, respectively. The selectivity coefficient of Hg(II) ions and other metal ions on Hg-PET-TSC indicated an overall preference for Hg(II) ions. Desorption studies revealed that HCl or EDTA solutions were the best eluents for the regeneration of the Hg-PET-TSC ion-imprinted chelating fibers.

1. Introduction

Molecular imprinting technique is a promising technique to prepare smart materials in which a plenty of specific cavities designed for a target template molecule is distributed and these cavities are in match with the target template molecules in shape, size and functional groups [1]. The comparative advantages of the molecular imprinted polymers (MIPs) such as chemical and mechanical stabilities, ease of preparation, low cost, and high selectivity allow them to be effectively utilized in a wide range of fields, such as chromatography, solid-phase extraction, and sensors [2–4]. MIPs were usually synthesized by bulk polymerization. However, this widely used technique could create some common disadvantages such as incomplete imprinted molecules removal, low rebinding capacity, low binding affinity to target molecule, irregular and heterogeneous binding site distribution [5]. Various

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preparation strategies have been proposed to minimize these problems, such as emulsion polymerization [6], suspension polymerization [7,8], multistep swelling polymerization [9], and precipitation polymerization [10–13]. But the disadvantages of bulk polymerization were only partially solved.

Another conventional way for preparation of MIPs through entrapment technique but also has some drawbacks, such as time-consuming, complicated synthesis process and less recognition sites within the matrices particles obtained via crushing and grinding the imprinted polymeric monolith [1]. There are many attempts to develop alternative and new routes in order to improve the recognition sites accessibility and better control the surface morphology of the MIP materials.

Surface imprinting is a desirable strategy in which the recognition sites are generated on the surface of suitable support material and the target molecules are permitted to elute and rebind more effectively. In this case the shape of the MIPs will be determined by the support. Various surface imprinting techniques are carried out on a variety of substrates, including films, membranes, silica particles, graphene, and inorganic materials [14–17]. Compared to granular and membrane adsorbents, fibers are promising materials with superior properties of large surface area and high mechanical and chemical stability. However, limited numbers of researches concerning the utility of fibers in surface imprinting [18].

Poly(ethylene terephthalate) (PET) is one of the most common synthetic polymers used to produce fibers, textile, beverage containers, package and engineering materials [19,20] and have high resistance toward weak mineral acids, even at high temperature, and to most strong acids at room temperature, oxidizing agents, sunlight and micro organisms.

In the present work, a surface imprinting technique was utilized to prepare an ion-imprinted fibers based on PET through graft copolymerization of acrylonitrile (AN) onto PET fibers followed by functionalization with thiosemicarbazide moieties and cross-linking of the grafted chains in presence of Hg^{2+} as a template imprinted ions using formaldehyde as a cross-linker (Hg-PET-TSC). The rebinding and selectivity performance of the ion-imprinted fibers was systematically evaluated by investigating the different factors affecting the uptake behavior such as pH, initial concentration of the Hg^{2+} ions, shaking time, and temperature. The adsorption kinetics and thermodynamic parameters of the uptake process were also calculated.

2. Materials and methods

2.1. Materials

The PET staple fibers (2D × 44 mm Semi Dull Raw White) used in these studies was provided by Jiangyin Hailun Chemical Fiber Co. (China). The fiber samples were Soxhlet-extracted until constant weight (for 6 h) with methanol and dried in a vacuum oven at 50 °C. Acrylonitrile (AN) (BDH-England) was treated with 3% (w/w) sodium hydroxide solution, washed with distilled water till neutralization and dried over calcium chloride followed by molecular sieves. $KMnO_4$ (BDH-England); oxalic acid (Adwic); Thiosemicarbazide (TSC), formaldehyde and $HgCl_2$ were purchased from Sigma Aldrich. All chemicals were used as received.

2.2. Synthesis of (Hg-PET-TSC) ion-imprinted fibers

The synthetic reaction was carried out according to the following steps. The first step involves the graft copolymerization of polyacrylonitrile (PAN) onto the PET backbone. The fiber sample (1 g) was dipped into dichloroethane (150 mL) for 2 h at 50 °C. After treatment, the solvent was removed using a filter paper and put into the polymerization medium. Polymerization was carried out in a 100 mL conical flask and the mixture containing the PET fibers sample (1 g) and the combined redox initiator system (10 mL of 2 mmol $KMnO_4$ and 10 mL 4 mmol oxalic acid) was vigorously shaken for 5 min then 0.12 mole of the monomer AN was added and the reaction was conducted for 3 h with stirring at 60 °C. Finally, Hydroquinone solution (10 mL, 3% (w/w)) was added to terminate the polymerization process. The products were filtered and washed with distilled water. The extraction of PAN homopolymer was achieved with DMSO. The grafted copolymer was dried at 40 °C till constant weight.

Grafting percentage (GP) was calculated as in the following expression (Eq. (1)):

$$\text{Grafting percentage (GP)} = (A - B/B) \times 100 \qquad (1)$$

where A and B are the weight of grafted product and native PET fibers, respectively.

These grafted PET fibers prepared with GP values 130% were named as PET-g-PAN.

In the next step, the modified PET-g-PAN was taken and to which alcoholic thiosemicarbazide solution (100 mL, 10% (v/v)) was added. The mixture was refluxed at about 80 °C for 6 h. The modified PET (PET-TSC) fibers were then filtered and washed with absolute ethanol then dried at 40 °C. Schematic presentation for the synthetic steps of the PET-TSC is shown in Scheme 1.

The Hg loaded PET-TSC fibers were prepared by placing 1 g of PET-TSC fibers in a flask containing 200 mL of Hg^{2+} solution at concentration of 100 mg/L and pH 5.0. The contents of the flask were equilibrated on the shaker at 150 rpm and 30 °C for 3 h. Then the Hg-PET-TSC fibers were removed and washed with distilled water. Then, the modified Hg-PET-TSC ion-imprinted fibers were prepared by soaking the Hg^{2+} loaded fibers in 200 mL 30% formaldehyde cross-linker solution. The pH value was adjusted to 5.0 with dilute hydrochloric acid and the cross-linking was performed via refluxing at 60 °C for 6 h. Finally, the template Hg^{2+} ions were removed from the polymeric fibers using 0.5 M HNO_3. The procedure was repeated several times until the template ions could not be detected in the filtrate. Then, the fibers were removed and washed with absolute ethanol and distilled water and dried at 40 °C. As a control, the non-imprinted PET-TSC fibers (NI-PET-TSC) were also prepared under identical conditions without adding Hg^{2+}. Schematic presentation for the imprinting process is shown in Scheme 2.

2.3. Charachterization of samples

The elemental analysis (E.A.) of PET, PET-g-PAN, PET-TSC and Hg-PET-TSC was obtained from a Perkin–Elmer 240 C Elemental Analytical Instrument (USA).

Infrared spectra (FTIR) were obtained with a Perkin–Elmer spectrum. The PET and modified PET fibers were dried overnight at 60 °C under reduced pressure and pressurized with a glass slide on top of the quartz window of the ATR instrument.

The surface morphologies of the native and modified fibers were visualized using a FEI Quanta-200 scanning electron microscope (FEI Company, The Netherlands), operating at a typical accelerating voltage of 20 kV. The samples were sputter-coated with gold for 40 s at 15 mA prior to the observation.

The specific surface area was measured by N_2 adsorption isotherm using an ASAP 2010 Micromeritics instrument and by Brunauer–Emmett–Teller (BET) method, using the software of Micromeritics.

To determine the crystallinity of the treated samples under different conditions, the sample was dispersed onto a stub and placed within the chamber of analytical X-ray powder diffractometer