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Thermosensitive molecularly imprinted polymers on porous carriers: Preparation, characterization and properties as novel adsorbents for bisphenol A

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ABSTRACT

Thermosensitive molecularly imprinted polymers (T-MIPs) on porous carriers were prepared *via* the synergy of dual functional monomers of 4-vinylpyridine (VP) and N-isopropylacrylamide (NIPAM), for selective recognition and controlled adsorption and release of bisphenol A (BPA) by the temperature regulation. The porous polymer supporter was synthesized by multistep swelling of polystyrene and then both the NIPAM with temperature responsiveness and the basic monomers of VP were grafted on them in a simple way. The resultant T-MIPs showed high binding capacity, fast kinetics, and the adsorption processes were found to follow Langmuir–Freundlich isotherm and pseudo-second-order kinetic models. The adsorption capacity increased slightly along with the rise of temperature (such as 20 °C) under lower critical solution temperature (LCST, 33 °C) and decreased fast above LCST (such as 50 °C). Subsequently, the T-MIPs were employed as novel adsorbents for selective solid-phase extraction (SPE) of BPA from seawater and yogurt samples. Satisfying recoveries in the range of 94.83–98.47% were obtained with the precision of 3.21% at ambient temperature (20 °C). Through 6 adsorption–desorption cycles, the reusable T-MIPs exhibited a good recoverability with the relative standard error within 9.8%. The smart T-MIPs provided great potentials for selective identification, adsorption/release and removal of BPA by simple stimuli responsive regulation.

1. Introduction

Phenolic environmental estrogens (PEEs) have received considerable concerns in the field of pollution monitoring and remediation, which may change the function of the endocrine systems and consequently elicit negative health effects [1,2]. Bisphenol A (BPA), one of PEEs, has been widely used as raw material of plastics and resins, antioxidants and polymerization inhibitors [3,4]. However, prolonged utilization and abuse of BPA leads to its accumulation in environment and thereafter causes environmental and health threats [3–5]. Some hazards and adverse influences have been identified in model animals exposed to low doses of BPA even much lower than the regulated safe dose levels [5]. Meanwhile, complicated matrix effects make the residue analysis of BPA face crucial challenges [6]. So, it is urgently required to develop simple, fast and high sensitive methods for identifying the presence and determining the levels of BPA.

The most frequently used methods for separation and determination of BPA mainly include high performance liquid chromatography (HPLC), HPLC–mass spectrometry (MS), and gas chromatography–MS (GC–MS), generally following suitable sample pretreatment processes such as the widely used liquid–liquid extraction (LLE) and solid-phase extraction (SPE) [7–11]. The main problem associated with traditional sorbents of SPE is the low selectivity and thereby low adsorption capacity and enrichment efficiency. Therefore, developing specific materials with high selectivity is necessary. Molecularly imprinted polymers (MIPs) are gaining popularity [12]. For example, Wang et al. synthesized MIPs *via* ring-opening metathesis polymerization [13] and Li et al. prepared hollow porous MIPs using tetrabromobisphenol A as dummy template [14], which were both used as SPE sorbents to enrich BPA combining with HPLC–UV determination.

Besides, another promising material, stimuli-responsive polymers (SRPs), also known as environmental responsive polymers or smart polymers, has also attracted widespread interest [15,16]. SRPs are able to respond to specific external stimuli with considerable

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changes in their physicochemical properties, including molecular chain structure, solubility, surface structure, swelling or dissociation behavior, *etc*., and various stimuli signals are available such as temperature, pH, magnetism and light [17]. By combining MIPs with SRPs, the resultant seductive functional materials, stimuli responsive MIPs (SR-MIPs) have been developed, occupying the advantages of molecular recognition ability for template/target species and responsive ability to external stimuli [17–19]. That is, the release and adsorption of template/target molecules can be achieved through external stimuli regulation. Excitedly, a number of SR-MIPs have been designed and synthesized for recognition and detection of BPA [17,20–23]. For instance, Griffete et al. presented inverse opals of imprinted hydrogels for the detection of BPA and displayed large responses to external pH stimuli related to the thickness of hydrogel film [20]. Liu et al. described a novel core-shell BPA imprinted nanoparticle by polychloromethylstyrene coated superparamagnetic material *via* surface initiated atom transfer radical polymerization [21]. Lin et al. adopted bisphenol F as a dummy template to prepare MIPs for BPA with a magnetic supporter which could increase the extraction efficiency [22]. Lu et al. fabricated a photoelectrochemical (PEC) sensor to detect BPA based on vertically aligned TiO_2 nanotubes with surface molecularly imprinted polypyrrole, and a highly sensitive PEC response for BPA was obtained [23]. It is found that magnetic SR-MIPs are mostly discussed; other type ones are rarely mentioned. Meanwhile, to the best of our knowledge, temperature responsive SR-MIPs have never been reported for BPA till now.

N-Isopropylacrylamide (NIPAM) is a well-known intelligent material that is responsive to the temperature, which has the property of a soluble (hydrophilic)–insoluble (hydrophobic) transition at a lower critical solution temperature (LCST) of about 33 °C [24]. It displays a coil (soluble) state when the solution temperature is below the LCST, as well as a collapsed (insoluble) state at above the LCST [24]. The thermally responsive behavior of NIPAM can be used to design smart MIPs; this may be the ideal way to controlled adsorption and release of template molecules according to temperature changes.

In this work, we firstly synthesized the smart material of thermosensitive MIPs (T-MIPs) by using NIPAM as temperature responsive functional monomer, for selective recognition and extraction of BPA from real water and food samples. A simple synthesis protocol was used by grafting two types of functional monomers on porous polymers carrier, and plenty of hollow pores were beneficial for mass transfer. The synergy effect of dual monomers of NIPAM and 4-vinylpyridine (VP) would contribute greatly to the performances of T-MIPs. Binding property, imprinting ability and temperature-regulated behavior were systematically investigated. Accordingly, the obtained smart T-MIPs were successfully applied to SPE for BPA in seawater and yogurt samples, indicating great potential for the analysis/removal of the PEEs in complicated matrices.

2. Experimental

2.1. Materials and instruments

Poly-vinylpyrrolidone (PVP), poly-vinylalcohol (PVA), N-isopropylacrylamide (NIPAM, 98%) and N,N′-methylenebis(acrylamide) (MBAA, 99%) were purchased from Aladdin (Shanghai, China). Ethylene glycol dimethacrylate (EGDMA, 98%), divinylbenzene (DVB, 80%), styrene (99%), thioglycolic acid, 2,2-bis(4-hydroxyphenyl) (BPA), 17β-estradiol (β-E2, 99%), phenol (PE, 99.6%) and cholesterol (CE) were obtained from Aladdin (Shanghai, China). Estriol (E3, 99.5%), estrone (ET, 99%), 4-vinylpyridine (VP, 95%) and methacrylic acid (MAA, 99%) were provided by Sigma-Aldrich (Shanghai, China). Acetonitrile (ACN, 99.9%) was purchased from J&K Scientific Ltd. (Beijing, China). Dibutyl phthalate (DBP), benzoyl peroxide (BPO, CP), toluene and dichloromethane were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Dimethylbenzene, absolute ethanol, methanol and sodium dodecyl sulfate (SDS) were attained from Tianjin Reagent Plant (Tianjin, China). Potassium persulfate (KPS) and 2,2-azobisisobutyronitrile (AIBN) were purchased from Shanghai Chemical Plant (Shanghai, China). DVB and MAA were distilled in vacuum to remove stabilizers and AIBN was refluxed over sodium and then distilled. All reagents were of analytical grade and used directly without further purification unless otherwise specified. Aqueous solutions throughout the work were prepared using doubly purified deionized water, which was produced by a Cascada TM LS Ultrapure water system with the water outlet operating at 18.2 MΩ cm (Pall Corp., USA).

The microstructure and elaborated morphology evaluation were examined by an inverted microscope (XDS-1B), a scanning electron microscope (SEM, Hitachi S-4800FE-SEM, 3 kV; samples dispersed in ethanol and adding a drop on an aluminum sheet followed by sputter-coated with gold for 85 s under high vacuum) and a transmission electron microscope (TEM, JEOL, JEM-1400, samples dispersed in ethanol and adding a drop on a copper grid). The particle sizes were measured by Malvern Zetasizer (Nano ZS90, dispersed in absolute ethanol). The chemical component and characteristic functional groups were measured with a thermal gravimetric analyzer (TGA, Mettler 5 MP, 800 °C, 10 °C/min, nitrogen 50.0 mL/min) and a Fourier transform infrared spectrometer (FT-IR, Nicolet iS10, deduct air background), respectively. The information of specific surface area and pore size was detected by a specific surface and pore size analysis instrument (3H-2000PS4, Beijing). UV–vis spectra were recorded using a Thermo Scientific spectrophotometer (NanoDrop 2000/2000c, USA). Analytes were determined by high performance liquid chromatography (HPLC, Skyray LC-310, China). And HPLC conditions were employed for BPA: mobile phase, ACN/H_2O (90:10, v/v); flow rate, 1.0 mL/min; column temperature, 20 °C; UV detection, at 226 nm; injection volume, 20 μL; analytical column, C_{18} column with 250 mm × 4.6 mm (5 μm particle, Waters, USA).

2.2. Synthesis of polystyrene (PS) seed particles

PS was synthesized according to the classical dispersion polymerization method [25] with a little modification. Briefly, anhydrous ethanol (100 mL), deionized water (20 mL) and PVP (0.7 g) were added to a 250 mL three-necked flask and then dispersed evenly by ultrasound and vigorous stirring. Then 5 mL styrene was added to the above solution. After pouring with nitrogen for 30 min, AIBN (40 mg) was added to the mixture and then heated to 60 °C and polymerized for 24 h under nitrogen atmosphere. The obtained PS seed particles were washed five times with ethanol and dried to constant weight under vacuum at 40 °C.

2.3. Synthesis of hollow porous polystyrene particles (HPS)

HPS was prepared by a three-step swelling polymerization method [26] with necessary modification. Typically, SDS (0.125 g) and deionized water (50 mL) were added to a 100 mL two-necked flask. Then PS (0.2 g) was added to the above solutions and formed a homogenous emulsion by ultrasound and stirring. Firstly, DBP (0.7 mL) was added to the emulsion and was stirred for 24 h at room temperature; secondly, toluene (10 mL) and MAA (4 mmol) were added to the solutions and kept for swelling for 24 h; thirdly, DVB (4.0 mL) and BPO (60 mg) were added to the emulsion, stirring for 24 h, and the temperature of the emulsion was raised to 70 °C and the reaction was performed for another 24 h under nitrogen atmosphere. Finally, the HPS particles were obtained by