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Design of a surface-immobilized 4-nitrophenol molecularly imprinted polymer via pre-grafting amino functional materials on magnetic nanoparticles

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ABSTRACT

In order to resolve the low adsorption capacity of the surface molecularly imprinting methods, an approach was developed for the preparation of magnetic imprinted polymers by pre-grafting the amino functional material, 3-aminopropyltriethoxysilane (APTES), on the surface of the silica coated magnetic substrate. APTES was used for amino functionalization of the silica coated Fe_3O_4 nanoparticles. Amino groups were used for immobilization of the template molecules on the magnetic surface and additionally to react with the terminal vinyl groups of cross-linker, ethylene glycol dimethacrylate (EGDMA), by the Michael addition reaction. In this way, the imprinting sites of the analytes formed on the substrate were increased. The sorbent was synthesized in the presence of 4-nitrophenol (4-NP) and EGDMA as the template and cross-linker, respectively. Different parameters affecting the adsorption, such as pH, desorption solvent type and adsorption time were evaluated and optimized. The prepared magnetic molecularly imprinted polymer (MMIP) showed high adsorption capacity and proper selectivity for the template molecule. The kinetic adsorption curve indicated that 90 min was sufficient to achieve the adsorption equilibrium for MMIP. The maximum adsorption capacity was 129.1 mg g^{-1}. The experiments exhibited a linear range of 10–3000 μg L^{-1} for 4-NP with the correlation coefficient (R^2) of 0.997. The results of the real sample analysis confirmed the applicability of the proposed MMIP for quantitative analysis of 4-NP in the aqueous samples.

1. Introduction

Molecularly imprinted polymers (MIPs) are common, robust and cost-efficient smart materials which are used to prepare a qualified substrate with selective recognition properties for the target molecules. The selective recognition sites are created by a process where the template molecules are imprinted into the polymeric matrices. During the recent decades, great attention was focused on improving synthesis conditions of MIPs. Surface imprinting is now among the most studied alternative methods to overcome the drawbacks related to the traditional MIPs such as bulk polymerization [1–3]. Surface graft imprinting improves the adsorption capacity, kinetic of binding and mass transfer in MIPs by controlling the position of the templates on the material's surfaces or in their vicinity. Several strategies have been proposed for the surface imprinting, such as the use of immobilized initiators on the supporting matrix [4], atom transfer radical polymerization (ATRP) [5,6], reversible addition fragmentation chain transfer (RAFT) polymerization [7] and grafting polymerization by modifying the surface [8].

Nanoparticles are promising support materials for the surface imprinting that expresses notable advantages owing to their large external surface area to volume ratio. Furthermore, the utilization of nanoparticles leads to enhancement of the physical and chemical properties of the sorbent, such as uniform spherical geometry, as well as stability and facile dispersion [9]. The perfect size of MIP nanoparticles can be achieved by the selection of proper nanostructured substrates and the control of imprinted layer thicknesses [3]. Different substrates were used as a support in the surface imprinting process, such as activated silica nanoparticles [2,10,11], Fe_3O_4 nanoparticles [12,13], gold nanoparticles [14], titanium dioxide [15], chitosan [16], activated polystyrene beads [4], quantum dots [17,18], alumina membranes [19], carbon nanotubes [20,21] and graphene [22].

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Recently, the frequently studied method for selective extraction of templates is based on the combination of magnetic nanoparticles and imprinting polymers. The encapsulation of magnetic components into the MIPs can create a selective composite polymer with magnetically susceptible characteristics [23].

In order to prepare the imprinted polymers, the functional groups undertake critical roles via binding to the target molecules before the actual imprinting [24]. An efficient procedure for creating the imprinted sites is based on an interaction between the pre-grafted functional material and template molecules rather than that between the template and functional monomers in the bulk solution. The pre-grafting of functional groups on the surface can also increase the imprinting sites formed for the target analytes. In the present technique, the templates were at first immobilized on the functionalized substrate through an effective non-covalent interaction [25–28]. Thereafter, the post-imprinting of the template molecules occurs in the grafted groups toward the reactive end groups of the special cross-linking agent. Therefore, the method demonstrates an effective approach to the surface imprinting methodology via immobilizing the template on the support material.

Nitrophenols are classified as priority and persistent contaminants due to their relatively high toxicity, even at trace level concentrations in the aqueous matrices [27]. Since these compounds are released into the aquatic environments through the effluents of various industries, the U.S. Environmental Protection Agency (U.S. EPA) has listed them as toxic pollutants. Among the mono nitrophenols, 4-nitrophenol (4-NP) is often considered owing to its high production in the world, toxicity and water solubility [28]. Because of the low concentration and high water solubility of 4-NP, and also the presence of much interferences in the water samples, the clean-up and pre-concentration steps are required. In this regard, different MIPs were developed for the selective and sensitive recognition of 4-NP [28–32].

In our previous work [31], we synthesized magnetic imprinted polymer via the “Grafting to” techniques for the selective recognition of 4-NP in the aqueous samples. The magnetic surface was at first modified via vinyl groups and then employed for the grafting polymerization of the functional monomer and cross-linker in the presence of target analytes. In the present work, an effective approach was developed for the preparation of magnetic MIP (MMIP) via pre-grafting of functional groups on the magnetic nanoparticles surface. Therefore, 4-NP was also used to evaluate the performance of the template immobilizing approach which are used here, than that the “Grafting to” method, used in our previous work. Template immobilizing was performed using 3-aminopropyltriethoxysilane (APTES) to associate the target analyte on the surface of the magnetic substrate. The post imprinting was also successfully performed by ethylene glycol dimethacrylate (EGDMA) in the presence of 2,2-azobisisobutyronitrile (AIBN). The results showed that the static adsorption capacity of the MMIP, prepared by the pre-grafting approach, was about two-folds as compared to that obtained in our previous work. It clearly confirmed the improvement of the adsorption capacity, number of sites and binding kinetic of the prepared MMIP.

2. Experimental

2.1. Materials

4-Nitrophenol (4-NP), 2-nitrophenol (2-NP), 2,4-dinitrophenol (2,4-DNP), phenol (Ph), 3-aminopropyltriethoxysilane (APTES) and 2,2-azobisisobutyronitrile (AIBN) were obtained from Merck (Darmstadt, Germany). Ethylene glycol dimethacrylate (EGDMA) and acetonitrile (HPLC grade) were purchased from Sigma–Aldrich (Beijing, China) and Caledon (Ontario, Canada) companies, respectively. Toluene, methanol (HPLC grade), iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), ammonium hydroxide and tetraethyl orthosilicate (TEOS) were also obtained from Merck (Darmstadt, Germany).

2.2. Instruments

The size, structure and morphology of the MMIPs were characterized by transmission electronic microscopy (Zeiss – EM10C – 80 kV TEM) and scanning electron microscopy (SEM Vega tescan), respectively. A Fourier transform infrared FT-IR (Bruker VERTEX 70 spectrometer) was utilized to investigate the infrared spectra of MMIPs using KBr pellets.

2.3. HPLC analysis

All chromatographic measurements were performed, using an Agilent 1100 high performance liquid chromatograph (Santa Clara, CA, USA) with a C_{18} column (250 mm × 4.6 mm i.d., 5 μm) and UV/vis detector. For quantitative analysis of 4-NP, a RP-HPLC method was used. The mobile phase for chromatographic analysis consisted of acetonitrile, containing 1% (v/v) acetic acid, as solvent A and Milli-Q water acidified to pH 2.5 with acetic acid, as solvent B. The gradient profile was 50–100% A from 0 to 10 min, and then isocratic elution for 2 min at a flow rate of 1 mL min^{-1}. All compounds were detected at 254 nm and the oven temperature was set at 25 °C.

2.4. Preparation of silica-based magnetic nanoparticles

The preparation of Fe_3O_4 nanoparticles was carried out by mixing $FeCl_3{\cdot}6H_2O$ (34.6 mmol) and $FeCl_2{\cdot}4H_2O$ (17.30 mmol) with 160 mL double distilled water, while being stirred under nitrogen gas atmosphere. Then, 20 mL of ammonium hydroxide (25%, v/v) was added drop wise to the solution while elevating the temperature of the solution up to 80 °C. The reaction was kept at the mentioned temperature for 30 min. The obtained Fe_3O_4 nanoparticles were dispersed in the mixture of ethanol (160 mL) and water (40 mL) by sonication for 15 min, then ammonium hydroxide (15 mL) and TEOS (2.1 mL) were added to the reaction mixture. The reaction was carried out for 12 h at 40 °C under continuous mechanical stirring. The final product was isolated by an external magnetic field, and then, thoroughly washed with ethanol and water, respectively.

2.5. Surface modification and pre-grafting functional material

$Fe_3O_4@SiO_2$ (400 mg), APTES (1 mL) and absolutely dry toluene (30 mL) were mixed in a flask under nitrogen atmosphere. The reaction was refluxed for 48 h under continuous mechanical stirring. The resulted pre-grafted amino-functionalized nanoparticles were washed with toluene and methanol thoroughly, and then dried at 55 °C for 3 h.

2.6. Preparation of the surface-immobilized 4-NP-MMIP

The template adsorption on the amino-functional nanoparticles was carried out in 20 mL acetonitrile, 0.4 mmol 4-NP and 200 mg modified magnetic silica at 0–2 °C for 12 h to obtain the modified magnetic silica self-assembled by 4-NP. Then, the cross-linker (EGDMA, 4 mmol) was added. The mixture was stirred for 30 min for the preparation of the preassembled solution. After sealing, shaking and purging the mixture with nitrogen, a 20 mL of acetonitrile solution containing 40 mg of AIBN was added to the reaction mixture while it was being sonicated and purged by the nitrogen gas in an ice bath for 15 min. The polymerization was performed