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Synthesis and properties of core-shell magnetic molecular imprinted polymers

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ABSTRACT

A general fabricating protocol for the preparation of core-shell magnetic molecularly imprinted polymers (MIPs) for chlorinated phenols recognition is described. In this protocol, Fe_3O_4 magnetic nanoparticles were first prepared using the chemical co-precipitation method. Then, the obtained magnetic nanoparticles were coated with a silica shell through modified Stöber method. Finally, MIP films were coated onto the surface of silica-modified magnetic nanoparticles by surface molecular imprinting technique. The resultant polymers showed a high saturation magnetization value (31.350 emu g^{-1}), and short response time (30 s). Meanwhile, the as-synthesized magnetic MIPs showed an excellent recognition and selection properties toward imprinted molecule over structurally related compounds.

1. Introduction

During the last decade, molecularly imprinted polymers (MIPs), as synthetic antibody mimics [1], have attracted much attention due to their outstanding advantages, such as high selectivity and affinity to the target molecule, high mechanical strength, chemical stability, and reusability. These properties open up wide opportunities for the use of MIPs in many fields [2]. Particularly selective recognition and separation of organic pollutants from aqueous solution using MIPs as a tool have been recently demonstrated [3–11]. However, MIPs suffer from some nature drawbacks in their practical applications. For example, the small particle sizes bring difficulties when trying to separate them from aqueous sample, which eventually lead them far from real application.

Recently, magnetic nanoparticles (MNPs) have been considered ideal candidates for biological and environmental applications, because they have unique magnetic properties that enable them to be handled by magnetic field, and allow the separation of target from the samples [12]. It is expected that the marriage of the MNPs and MIPs will provide a new approach toward separation application and broaden the use of MIPs. Meanwhile, the combination of magnetically susceptible characteristic of MNPs and the merit of MIP not only provide the selectivity for the target molecule but also have the ability of one-step separation. Li et al. [13] synthesized magnetic MIPs nanowires within the nanoporous of alumina membrane for theophylline recognition. Tan et al. [14] reported the preparation of bovine serum albumin surface-imprinted submicrometer particles with magnetic susceptibility. Jin et al. [15] detailed a synthetic route to generate superparamagnetic core-shell molecular imprinting microspheres. Wang et al. [16] reported the synthesis of Fe_3O_4 magnetic nanoparticles coated estrone-imprinted polymer using a semi-covalent imprinting strategy. Lu et al. [17] prepared bifunctional superparamagnetic surface molecularly imprinted polymer *via* surface atom transfer radical polymerization. Chen et al. [18] demonstrated a selective method for the determination of sulfonamides in honey based on magnetic molecularly imprinted polymer. Zhang et al. [19] have introduced a microwave heating technique for the preparation of magnetically imprinted polymer beads. In the recent works of Li et al. [20], core-shell bovine hemoglobin imprinted magnetic nanoparticles with a mean diameter of 210 nm were synthesized. Jing et al. [21] synthesized the magnetic molecularly imprinted nanoparticles for recognition of lysozyme. Kan et al. [22] reported the synthesis of core-shell micro-nanostructured magnetic MIPs for protein recognition. Gai et al. [23] described a novel fabricating protocol of surface-imprinted polymer grafting on Fe_3O_4 magnetic particles through atomic transfer radical polymerization in aqueous media. Gu et al. [24] reported the preparation of chlorogenic acid surface-imprinted magnetic polymer nanoparticles through water-in-oil-in-water multiple emulsions suspension polymerization. More recently, our group presented a general protocol for the making of surface-imprinted core-shell magnetic beads *via*

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reversible addition-fragmentation chain transfer polymerization [25].

Nowadays, despite these recent achievements, the drawbacks of these methods lie in the tedious and complicated operations, and show poor responsivity to an external magnetic field. Therefore, it is still desirable to develop a simple and general method for preparing magnetic MIPs and expanding their scope of application. In this study, we report a simple approach for synthesizing core-shell MIPs beads with iron oxide core and their potential application in binding studies with 4-chlorophenol. 4-Chlorophenol was selected as the template molecule since it is harmful to organisms even at ppb levels and for being frequently detected in the environment [26]. The as-synthesized magnetic MIPs showed a high affinity and easy separation behavior.

2. Experimental

2.1. Preparation of Fe_3O_4@SiO_2 beads

Fe_3O_4 magnetic nanoparticles were prepared using the chemical co-precipitation method [27]. Fe_3O_4@SiO_2 microspheres were prepared according to the method reported with some modifications [28]. Typically, the previous synthesized Fe_3O_4 ferrofluid (4 mL) were diluted with 200 mL water-ethanol (1:4, v/v) solution, followed by the addition of 5 mL ammonia solution (25 wt%) and 2.0 mL TEOS sequentially. The mixture was reacted for 24 h at the room temperature under continuous stirring.

Afterwards, 3-(trimethoxysilyl)propylmethacrylate (MPS) is used to modify the silica-coated magnetic nanoparticles. In the procedure, the resulting silica-coated magnetic nanoparticles (500 mg) were dispersed in 55 mL of methylbenzene. A solution of 4.0 mL MPS was then added. After ultrasonic treatment for 40 min, a solution of triethylamine (2.0 mL) in methylbenzene (5.0 mL) was slowly added and mixed. When the solution was dissolved completely in this solution, the mixture solution was heated at reflux for 24 h under nitrogen protection.

After the surface modification step, the samples (Fe_3O_4@SiO_2-MPS) were washed with methylbenzene and methanol, alternately. Then the particles were dried under vacuum.

2.2. Preparation of MIP nano-film

MIP nano-film on the surface of Fe_3O_4@SiO_2 (Fe_3O_4@SiO_2-MIP) was prepared using our previously reported method [29].

2.3. Characterization

The samples were characterized by scanning electron microscopy (SEM, Hitachi S-4800, 15 kV), X-ray diffractometer (XRD, D/max-3C), and Fourier transform infrared spectrometer (FT-IR, Avatar 360, with a resolution of 2 cm^{-1}).

Magnetic properties were measured with a LakeShore 7307 (Lakeshore Cryotronic) vibration sample magnetometer (VSM) at 300 K.

2.4. Adsorption measurement

To investigate the adsorption thermodynamic of the MIPs, 20.0 mg polymer was equilibrated with varied initial concentrations (0.06–1.50 mmol L^{-1}) of adsorbate in each centrifuge tube. After 12 h, the saturated polymer was separated by centrifugation, and the residual concentration of 4-chlorophenol was determined using HP1100 (Agilent) high performance liquid chromatograph (HPLC) with a UV–vis detector.

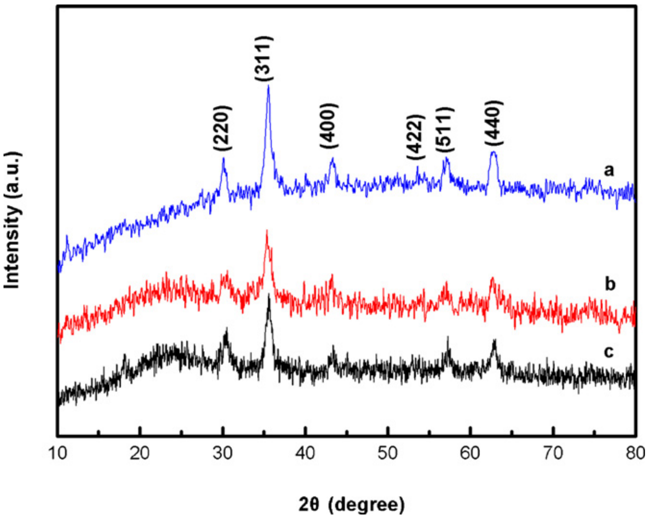

Fig. 1. XRD patterns of Fe_3O_4 (a), Fe_3O_4@SiO_2 (b), and Fe_3O_4@SiO_2-MIP(c).

3. Results and discussion

Fig. 1 compares the XRD patterns of Fe_3O_4, Fe_3O_4@SiO_2, and Fe_3O_4@SiO_2-MIP. In the 2θ range of 10–80°, six characteristic peaks for magnetite were observed for the three samples. According to the JCPDS file no. 19-0629 for the magnetite, the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) planes of Fe_3O_4 are observed at $2\theta = 30.19°$, 35.58°, 43.35°, 53.57°, 56.95°, and 62.70°, respectively, suggesting the presence of magnetic phase in the composites. The peak positions of three samples remain unchanged, indicating that a step-by-step coating procedure did not cause any crystalline structure change of the Fe_3O_4. In addition, there were slightly differences in peak width for the as-synthesized samples, reflecting the differences of size [20].

Fig. 2 depicts the SEM images of Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2-MIP microspheres. The size of the Fe_3O_4/SiO_2 microspheres is around 242 nm, and the Fe_3O_4@SiO_2-MIP microsphere is about 254 nm in diameter and roughly spherical shape, which is suitable for rebinding of template molecules. The silica shell of Fe_3O_4@SiO_2 provided biocompatibility and stability, and prevented magnetic nanoparticles oxidation and aggregation. Furthermore, some silanol groups were attached to the surface of the Fe_3O_4@SiO_2 by introduction of MPS, which could offer possibilities for further grafting with MIP. It is well-known that molecularly imprinted technique offers rapid kinetics and site accessibility. In our strategy, the as-prepared polymer layer had a thickness of about 12 nm, revealing the binding sites almost existed at the surface of Fe3O4@SiO2-MIPs. The imprinted cavities can improve the mass transfer rate for rebinding and releasing the template molecules.

FT-IR spectra of Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-MPS, and Fe_3O_4@SiO_2-MIPs were compared in Fig. 3. As illustrated, the absorption band at 571.9 cm^{-1} corresponded to the Fe—O stretching bond for Fe_3O_4 nanoparticles. In curve b, the absorption bands at 1096 cm^{-1} and 952.9 cm^{-1} are attributed to Si—O—Si and Si—O—H stretching vibrations, respectively, indicating the formation of silicon shell. Then, the vibration of the C═O bond of MPS at 1710 cm^{-1} verified the successful modification of MPS. Meanwhile, the characteristic peak of C–Cl band at 626 cm^{-1}verified the successful grafting of polymer shell from Fe3O4@SiO2-MPS.

The magnetic properties of the synthesized Fe_3O_4@SiO_2-MIPs were studied by a VSM at 300 K. It can be seen from Fig. 4, the magnetic hysteresis loops of two samples are similar general shape and symmetrical about the origin, and both coercivity and resonance are zero, suggesting superparamagnetic behavior of the