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Magnetic imprinted nanomicrosphere attached to the surface of bacillus using miniemulsion polymerization for selective recognition of 2,4,6-trichlorophenol from aqueous solutions

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ABSTRACT

In the work, we reported an effective method for the preparation of surface molecularly imprinted polymers based on bacillus as substrate material with superparamagnetic property through miniemulsion polymerization. Then, the obtained magnetic surface molecularly imprinted polymers (MMIPs) were evaluated as adsorbents for selective recognition 2,4,6-trichlorophenol (2,4,6-TCP) from aqueous medium. The resulting MMIPs were characterized by several techniques including FT-IR, SEM, TEM, Raman, XRD, VSM and TGA. The results demonstrated rod-shaped MMIPs was covered with imprinted layer, and exhibited chemical stability and good magnetic sensitivity. Batch mode of binding studies were carried out to determine the equilibrium isotherm, kinetics, selectivity adsorption and regeneration of MMIPs toward 2,4,6-TCP. The results indicated that the selective adsorption behaviors of MMIPs were well described by the Langmuir isotherm model and the pseudo-second-order kinetics model. The specific adsorption capacity of MMIPs was 45.16 mg g^{-1} at 298 K, which was 2.15 times higher than that of magnetic non-imprinted polymers (MNIPs). The selective recognition studies demonstrated the outstanding affinity and selectivity toward 2,4,6-TCP in the presence of competitive phenols. The regeneration study showed excellent adsorption capacity even after five regeneration cycles. In addition, MMIPs were successfully applied to the extraction of 2,4,6-TCP from milk sample.

Introduction

Molecular imprinted technique (MIT) is a commonly used technique for preparing molecularly imprinted polymers (MIPs) with predetermined molecular recognition properties [1]. In order to fabricate the specific binding sites, the cross-linking monomers and co-polymerization functional monomers are first incorporated with template molecule to create polymeric matrix. Then the target molecule is removed from the polymeric matrix, which resulted in leaving three-dimensional specific binding sites in MIPs that are complementary in geometry, size and spatial distribution to the target molecule [2]. Due to the remarkable advantages of MIPs, such as preparation simplicity, low-cost and mechanical/chemical stability, MIPs have been applied in a wide range of fields, including antibody mimics, bioassay, separation, chemical sensing [3]. Panahi et al. prepared MIPs for selective sorption cefuroxime [4]. Singabraya et al. prepared MIPs for specific recognition of heparin sulfate [5]. However, the full advantage of MIPs will not be achieved until some of their inherent limitations are solved, such as incomplete template removal, small binding capacity, poor accessibility of the binding sites and heterogeneous binding site distribution [6]. One of main reason is that the template molecule extracted from interior of polymer materials is quite difficult. Moreover, target molecules can't access the interior binding sites even if a large number of cavities existed in the MIPs. As a result, MIPs prepared by traditional techniques exhibited high selectivity

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but low binding capacity and poor site accessibility to template molecule [7]. In recent years, surface molecular imprinting techniques (SMIPs) solved the limitation by taken certain measures to fabricate the specific binding sites on the surface of substrate material. After the imprinting polymerization and the removal of template molecule, the binding sites obtained are situated on the surface are all valid for the target [8]. Lv et al. prepared SMIPs for selective recognition biomacromolecules [9]. Gao et al. prepared SMIPs for selective separation glycoprotein [10].

Generally, the substrate materials used in the SMIPs are magnetic nanoparticles [11], carbon nanotubes [12] and silica beads [13]. Compared with traditional substrate material, microbial biological materials have incomparable advantages of more available resource, lower price and higher compatibility with organic polymer, which have become a promising substrate material in preparing SMIPs [14]. Bacillus is a kind of rod-shaped gram positive bacteria, which has a wide distribution and strong resistance to the harmful external factors [15,16]. At present, the study of microorganisms as adsorbent materials are mainly concentrated in the adsorption of heavy metal ions, dye and pesticide residues. But its use for substrate materials to prepare surface molecularly imprinted adsorbent is rarely reported.

In recent years, magnetic separation technology has been widely studied and used for many applications in biomedical, biotechnological, cell biology and environmental technology [17]. When magnetic susceptible materials are introduced into MIPs, magnetic imprinted polymers not only have the advantage of highly recognition characteristics to the template molecule, but also the magnetic response characters. Wang et al. prepared magnetic imprinted polymers for estrone recognition [18]. Jing et al. prepared magnetic imprinted polymers for recognition lysozyme [19]. magnetic imprinted polymers can be easily isolated from aqueous solution by an external magnetic field instead of tedious filtration or centrifugation, which makes separation more efficient and faster. Magnetic imprinted polymers will significantly broadening the application field of imprinted technology.

Chlorophenols (CPs) and its derivatives are extensively used as chemical raw materials, such as petroleum refineries, chemicals, plastic, rubber, tanning, steel plants, pharmaceuticals, disinfectant, wood, paper photographic and dye [20]. Due to their widespread use, CPs is widely distributed in the surface and groundwater. However, because of high toxicity, CPs has been listed as priority pollutants by both European Union Priority Substances (EUPS) and Environmental Protection Agency (EPA). As refractory organic pollutants, CPs persisted in the environment and long-term damage to biology and environment. The wastewater containing CPs compounds were suspected to be the cause of cancer [21]. Therefore, it is crucial to develop more feasible and efficient method to remove CPs from aqueous environment. Nowadays, MIPs used as adsorbent has been proved to be a very promising strategy to selective removal CPs from aqueous solutions. Pan's team prepared a variety of molecularly imprinted adsorbents [23,26]. Miniemulsion polymerization is a convenient one-step method to synthesize MIPs. The principle of this technique is that the polymerization carried out in stable oil droplets in an aqueous dispersion with an emulsifier. Miniemulsion are dispersed into a relative stable droplets under high shear device, which the size in the range of 50–500 nm. The droplet could indeed be treated as a small nanoreactor [22].

In this work, magnetic surface molecularly imprinted polymers (MMIPs) were prepared based on bacillus as substrate material via miniemulsion polymerization. The MMIPs were synthesized by using styrene and methacrylic acid as monomer, potassium persulfate as initiator, sodium dodecyl sulfate as emulsifier, divinyl benzene as crosslinking agent, 2,4,6-trichlorophenol (2,4,6-TCP) as template molecule. Then, MMIPs were used as adsorbents for selective recognition 2,4,6-TCP from wastewater, Preparation scheme was illustrated in Fig. 1. The obtained MMIPs were characterized by FT-IR, SEM, TEM, Raman, XRD, VSM and TGA. The adsorption properties, such as equilibrium isotherm, kinetics, regeneration and selectivity of MMIPs were investigated through the batch mode adsorption experiments. Furthermore, the MMIPs were also used as adsorbents for the extraction of 2,4,6-TCP from the milk samples.

Experimental

Materials

Ferric trichloride ($FeCl_3·6H_2O$), ferrous chloride ($FeCl_2·4H_2O$), oleic acid, styrene (St), sodium dodecyl sulfate (SDS), potassium persulfate (KPS), ethanol and HPLC-grade methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ammonia (25%, w/w) ($NH_4·OH$), divinyl benzene (DVB) and methacrylic acid were obtained from Aladdin reagent Co., Ltd. (Shanghai, China). 2,4,6-TCP, thymol, 3-chlorophenols (3-CP) and 2,6-dichlorophenol (2,6-DCP) were purchased from Tianda Chemical Reagent Factory (Tianjin, China). Bacillus was friendly supported by Ruigu biotechnology co., LTD. (Baoding, China). Deionized ultrapure water used throughout the experiments was purified with a Purelab ultra (Organno, Tokyo, Japan). All solvents used in this work were of analytical or HPLC grade.

Characterization

Infrared spectra (3500–500 cm^{-1}) were recorded on a Nicolet NEXUS-470 FT-IR apparatus (USA). The morphologies of MMIPs were observed by transmission electron microscope scanning electron microscope (TEM, JEOL, JEM-200CX) and field-emission scanning electron microscope (SEM, JEOL, JSM-7001F). Thermo gravimetric analysis (TGA) of samples were carried out using a Diamond TG/DTA instruments (STA 449C Jupiter, Netzsch, Germany) under a nitrogen atmosphere up to 800.0 °C with a heating rate of 5.0 °C min^{-1}. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM, 7300, Lakeshore) under a magnetic field up to 10 kOe. The identification of crystalline phase was performed using a Rigaku D/max-γB X-ray diffractometer (XRD) with monochromatized Cu $K\alpha$ radiation over the 2θ range of 30–70° at a scanning rate of 0.02̊ s^{-1}. Raman spectra were utilized to analyze the chemical composition and crystallographic structure of the nanoparticles in the range of 200–700 cm^{-1} at room temperature using a WITEC Spectra Pro 2300I spectrometer. Ion measurements were carried out using a TBS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., Beijing, China) with a deuterium background correction and a GF990 graphite furnace atomizer system. Ultrasonic cell disruption was performed by ultrasonic cell crusher JYD-900 (Shanghai, China). HPLC analysis was performed on a Shimadzu LC-20A system (Shimadzu, Kyoto, Japan) equipped with a UV–vis detector. PHS-2 acidimeter (The Second Analytical Instrument Factory of Shanghai, China) was used to measure pH value.

Preparation of oleic acid-modified Fe_3O_4 magnetic nanoparticles

The synthetic process of Fe_3O_4 nanoparticles was followed by coprecipitation method [17]. As follows: $FeCl_3·6H_2O$ (4.72 g) was dispersed into 180 mL of deionized ultrapure water under ultrasonic stirring. Then, $FeCl_2·4H_2O$ (1.72 g) was added into the mixture with vigorous stirring (800 rpm) under nitrogen, and a stable suspension was obtained. Next, the reaction temperature