



Study on the nonylphenol removal from aqueous solution using magnetic molecularly imprinted polymers based on fly-ash-cenospheres



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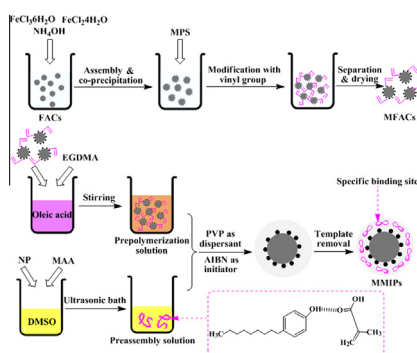
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HIGHLIGHTS

- ▶ MMIPs based on fly-ash-cenospheres behaved as an effective sorbent for NP.
- ▶ This work provide a novel method for making use of fly-ash-cenospheres resources.
- ▶ MMIPs were promising for selective adsorption and separation NP from aqueous solutions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 November 2012

Received in revised form 30 January 2013

Accepted 2 February 2013

Available online 13 March 2013

Keywords:

Magnetic molecularly imprinted polymers

Selective removal

Nonylphenol

Fly-ash-cenospheres

ABSTRACT

Fly-ash-cenospheres/Fe₃O₄ magnetic particles (MFACs) were firstly achieved by co-precipitation technique. After endowing with reactive vinyl groups onto the surface of MFACs, magnetic molecularly imprinted polymers (MMIPs) based on the modified MFACs were further prepared by suspension polymerization. The as-prepared MMIPs were characterized, and the results indicated that spherical MMIPs exhibited superparamagnetic property ($M_s = 20.99 \text{ emu g}^{-1}$), magnetic stability (at the pH = 6.0), thermal stability (<100 °C) and composed of imprinted layer. Batch mode adsorption experiments were carried out to investigate the specific adsorption equilibrium, kinetics and selective recognition. The initial pH = 6.0 was the optimal condition, and the hydrogen bond interaction may be the main recognition mechanism. The kinetic properties of MMIPs were well described by the pseudo-second-order equation, indicating chemical process could be the rate-limiting step in the adsorption process for NP. The adsorption equilibrium of NP using MMIPs was better modelled by the Langmuir isotherm equation, and the monolayer adsorption capacity of MMIPs at 298 K was 434.8 mg g⁻¹. The selectivity results showed that MMIPs had the specific adsorption for NP molecules, and the recognition process may be related to the size, structure and functional group of the template molecules.

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1. Introduction

Nowadays, most of the electricity in China is still generated from coal based thermal power plants. However, these power plants produce great amounts of by-products during the combustion of coal, such as Fly-ash (FA) [1]. In view of converting wastes

generated in some prime industries to a suitable material with practical utility, great efforts are being made to explore novel applications for fly-ash prior to disposal [2,3]. Possessing of enriched SiO₂ and a portion of unburned carbon, fly-ash could be the potential sorbent to remove various hazardous materials from wastewater. Although several investigations have been reported on fly ash for removal of textile dyes [4], phenolic compounds [5–7], phosphate [8], heavy metals [9], etc. more efforts are still needed for overcoming several disadvantageous limitations: (1)

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the lack of molecular selectivity; (2) low binding capacity and kinetics to target molecule.

Molecular imprinting is a well-established and simple technique to achieve molecular recognition in a material, namely molecularly imprinted polymers (MIPs). By assisted assembly and removal of the template, specific binding sites are well generated as cavities that fitting to the target molecules in shape, size, and main functional groups [10,11]. Thanks to the desired pre-determination, selectivity and practicability, MIPs are promising tools for specific separation, drug controlled release and reactive catalysis [12–14]. Traditionally, imprinting in a bulk polymer matrix with high cross-linking nature usually offers low binding kinetics and small binding capacity, due to deeply buried binding sites and long diffusion ways for the guest molecules [15]. Then, searching for the alternative imprinting methods facilitating guest molecule penetration is highly desired. This challenging task can be resolved by adopting a surface imprinting technique (SIT) which fabricated the MIPs layer on solid materials such as monodispersed polystyrene seeds and silica spheres [16]. SIT is receiving alarming attention owing to the advantages for improving mass transfer and reducing permanent entrapment of the template [17].

Magnetic nanoparticles (MNPs) have recently been considered as the ideal candidates of imprinting support for their superior characteristics such as the fast and controllable separation process [18]. When MNPs are encapsulated into MIPs, the resulting magnetic molecularly imprinted polymers (MMIPs) will not only have selectivity for the target molecules from complex matrix, but also be easily collected and separation by an external magnetic field without additional centrifugation, filtration and membrane separation, which greatly facilitate the lab work [19]. However, the pure MNPs such as Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ might have problem associated with forming of large aggregates, and MNPs leakage was also common in traditional MMIPs for the fragility of the MIPs film [20]. Accordingly, there is a considerable interest in combining conventional solid support with MNPs, and developing magnetic composites. In our recent studies, MNPs were firstly attached to silicon-based clays, especially the attapulgite and HNTs [21,22]. Then the MMIPs were further synthesized using magnetic composites as imprinting support. The results suggested that MMIPs based on magnetic composites could effectively prevent MNPs leakage.

With the wide range of applications of Alkylphenol polyethoxylates (APEOs) in pharmaceutical and personal care products and in other areas such as the textile, paper and leather industries, the nonylphenol (NP) as an endocrine disrupter occurs widespread in the environment [23]. Due to its aquatic toxicity and potential to disrupt the endocrine system, selective recognition and separation of target NP from water environment especially drinking water is frequently required [24]. Inspired by the above-mentioned work, herein we report an effective method to achieve fly-ash-cenospheres/ Fe_3O_4 magnetic particles (MFACs) by co-precipitation technique. Then the surface of MFACs was endowed with reactive vinyl groups through modification with 3-(methacryloyloxy)propyl trimethoxysilane (MPS). And then MFACs were further coated with a thin MIPs film. This film was obtained using NP as template, methacrylic acid (MAA) as functional monomer, 2,2'-Azobisisobutyronitrile (AIBN) as initiator, polyvinylpyrrolidone (PVP) as dispersant, and ethyl glycol dimethacrylate (EGDMA) as cross-linker. The characterization, adsorption equilibrium, kinetics, selectivity and reuse of MMIPs were investigated.

2. Experimental

2.1. Materials and apparatus

Fly-ash-cenospheres (FACs) were friendly supported by China Power Yaomeng Power Co. Ltd. (Henan, China). MAA, oleic acid,

AIBN, methyl sulfoxide (DMSO), and methanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). NP, 2,4-dichlorophenol (2,4-DCP), bisphenol A (BPA), 3,4-(methylenedioxy)phenol (MDP), p-(tert-octyl)phenol (PTOP), polyvinylpyrrolidone (PVP) and EGDMA were obtained from Aladdin reagent Co., Ltd. (Shanghai, China).

Infrared spectra ($4000\text{--}500\text{ cm}^{-1}$) were recorded on a Nicolet NEXUS-470 FT-IR apparatus (USA) using KBr disks. The morphologies of raw materials and as-prepared particles were observed by scanning electron microscope (SEM, S-4800). Magnetic measurements were carried out using a VSM (7300, Lakeshore) under a magnetic field up to 10 kOe. The identification of crystalline phase was performed using a Rigaku D/max- γ B X-ray diffract meter (XRD) with monochromatized with Cu K α radiation over the 2θ range of $20\text{--}80^\circ$ at a scanning rate of 0.02° s^{-1} . TGA of samples were performed for powder samples (about 10 mg) using a Diamond TG/DTA instruments (Perkin-Elmer, USA) under a nitrogen atmosphere up to 800°C with a heating rate of $5.0^\circ\text{C min}^{-1}$. 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 was used.

2.2. Synthesis of MFACs

The surface charges of the FACs became negative when the pH of the solution was above 3.0, because the pH of the zero point charge (pH_{ZPC}) of silico-aluminous fly ashes is 2.7 and that of sulfo-calcic fly ashes is 2.9 [25]. Then iron cations can be bonded onto the surface of FACs via electrostatic forces easily. The synthetic process of MFACs was followed a modified coprecipitation method [26]. The synthetic route of MFACs based on FACs was shown in Fig. 1a. As follows: $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (2.36 g) was added into 180 ml of deionized ultrapure water, and 1.5 g of FACs was dispersed into the mixture in ultrasonic bath for 30 min. Next, the mixture was stirred for 3.0 h, and a stable suspension was obtained. Then $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (0.86 g) was dissolved in the suspension with vigorous stirring (800 rpm) under nitrogen. When the solution temperature was increased to 80°C , 8.0 mL of NH_4OH (25%, w/w) added drop by drop under stirring, and the reaction was maintained for 30 min. The black precipitate was separated by putting the vessel on a Nd-Fe-B permanent magnet, and washed several times. Then vinyl groups were introduced onto the surface of MFACs through chemical modification with MPS for facilitating copolymerization with functional monomers. Briefly, 0.45 g of magnetic product was mixed with 5.0 mL of MPS and 75 mL of ethanol at 40°C for 12 h. The MFACs endowed with reactive vinyl groups were collected by Nd-Fe-B permanent magnet and washed with ethanol and water, and dried in vacuum at 50°C for 5.0 h.

2.3. Synthesis of MMIPs

The MMIPs were prepared followed our previous work with a few modification, and the synthetic route was shown in Fig. 1b. Firstly, 1.0 mmol of NP and 4.0 mmol of MAA were dispersed into the 10 mL of DMSO in ultrasonic bath for 1.0 h, and the preassembly solution was obtained. Then, MFACs particles (1.5 g) were mixed with 2.0 mL of oleic acid and stirred for 10 min. After that, 20 mmol of EGDMA was added into the mixture of MFACs and oleic acid, and this mixture was stirred (300 rpm) continually for 30 min to obtain the prepolymerization solution. Moreover, PVP (0.4 g) used as dispersant was dissolved into 120 mL of DMSO:water (9:1, v/v) in a three necked round-bottomed flask under stirring. Finally, the prepolymerization and preassembly solutions were added into the three-necked flask, and 0.3 g of AIBN used as initiator was also added into it. The mixture was stirred at 300 rpm and purged with nitrogen gas to displace oxygen while the tempera-

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