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Magnetic Molecularly Imprinted Polymer Nanoparticles for Selective Separation of di- (2- ethylhexyl) Phthalate from Aqueous Solution

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ABSTRACT

Magnetic molecularly imprinted polymer nanoparticles (MMIPs) for di(2-ethylhexyl)phthalate (DEHP) were synthesized by surface imprinting technology, and used for selective separation of DEHP from aqueous solution. The prepared MIIPs were characterized using Fourier transform infrared spectroscopy, scanning electronic microscopy, thermogravimetric analysis and vibrating sample magnetometer. It was found that the MMIPs had an average diameter of around 33 nm and a saturation magnetization of 15 emu g^{-1}. The adsorption behavior studies showed that the adsorption of DEHP onto the MMIPs was spontaneous and exothermic, the adsorption equilibrium was achieved within 1 h, the maximum adsorption capacity was 30.7 mg g^{-1}, and the adsorption process could be described by Langmuir isotherm model and pseudo-second-order kinetic model. The MMIPs had good adsorption selectivity for DEHP, the imprinting factor of DEHP was 3.6, and the selectivity coefficient of DEHP with respect to structural analogues, di-n-octyl phthalate (DNOP) and dibutyl phthalate (DBP), were 5.2 and 4.8, respectively. The reusability of MMIPs was demonstrated for at least 8 repeated cycles without significant loss in adsorption capacity.

1. INTRODUCTION

Di-(2-ethylhexyl) phthalate (DEHP) is widely present in products like building materials, clothing, cosmetics, pharmaceuticals, electric cables, packaging materials, etc. Studies have shown that phthalates such as DEHP may act as endocrine disruptors (Svechnikova 2007). Because DEHP is non–covalently bound to polymers, it can easily leach from various plastic materials into the environment. DEHP is now listed as a priority toxic pollutant by the United States Environmental Protection Agency (EPA 1984). Therefore, it is necessary to develop effective methods to reduce DEHP concentrations to environmentally acceptable level. Among various approaches for pollutant removal, adsorption is one of the most important one, due to its high efficiency

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and easy operation, especially when the pollutant exists at low concentration in a wastewater stream.

Magnetically separation technology provides an easy and rapid way for removal of magnetic particles from solution by applying an appropriate magnetic field (Ziaei, 2014). Thus, magnetic adsorbent can be easily isolated from matrix solutions after adsorption of target compounds.

In order to improve adsorption selectivity, molecularly imprinted polymers have been used, due to their binding groups in porous polymeric structure that are adapted to the shape and functionalities of the templates (Dolak 2015). Therefore, MIPs can selectively recognize target molecules in complex systems.

In this work, a novel sorbent, magnetic DEHP-imprinted polymer nanoparticles (MMIPs) were prepared and characterized, and were applied to the selective removal of DEHP from aqueous solution. The adsorption behaviors of DEHP on the MMIPs were investigated, and the effects of temperature, contact time and solution pH on the adsorption were evaluated. The selectivity and reusability of the sorbent were also examined.

2. RESULTS AND DISCUSSION

The SEM photo and XRD pattern of the MMIPs are shown in Fig.1 and Fig.2, respectively. From the SEM observation, it was found that these particles were almost regular in shape with an average diameter of around 33 nm.

The XRD pattern was in agreement with the standard spectra of magnetite (Fe_3O_4) with inverse spinel structure, which has six characteristic diffraction peaks, revealing that the crystalline form of Fe_3O_4 retained during the imprinting process.

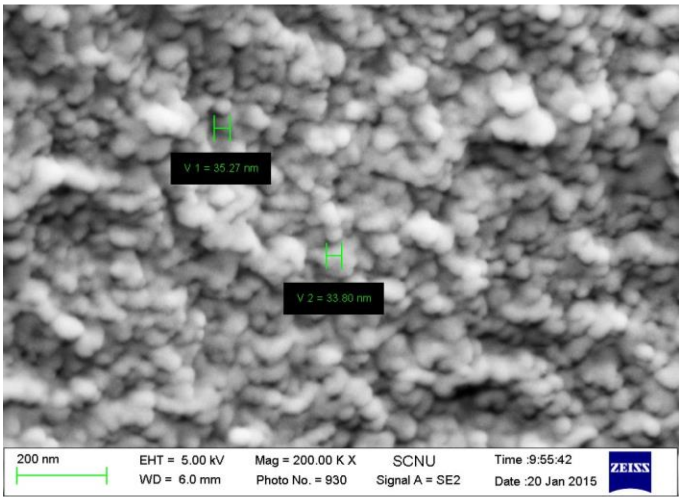

Fig. 1 SEM photo of MMIPs

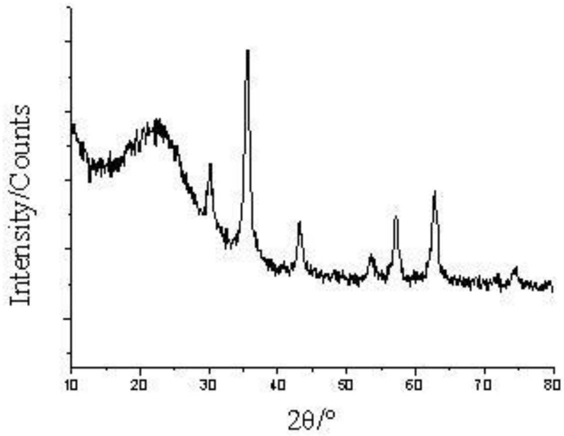

Fig. 2 XRD pattern of MMIPs

The magnetic property of the MMIPs was tested with a vibrating sample magnetometer. The greatest saturation magnetization was 15.0 emu g^{-1}, and both the remanence and coercivity were near zero, suggesting that the MMIPs were superparamagnetic.

The adsorption of DEHP on the MMIPs was examined using batch experiments and conducted in duplicate. Langmuir and Freundlich isotherms were used to describe the adsorption behaviors. Langmuir isotherm mode fitted the experimental data better than the Freundlich model, suggesting that the adsorption of DEHP onto the MMIIPs followed the Langmuir-type isotherm. The maximum adsorption capacity was 30.7 mg g^{-1}. Some important thermodynamic parameters variations including standard Gibbs free energy ($\triangle G^0$), enthalpy ($\triangle H^0$) and entropy change ($\triangle S^0$) for the adsorption process were obtained. $\triangle G^0$ has negative value (-12.5 KJ mol^{-1}), indicating that the adsorption was spontaneous. On the other hand, the positive value of $\triangle H^0$ (50.9 KJ mol^{-1}) suggested an endothermic nature of DEHP adsorption.

The effect of contact time on DEHP adsorption with the MNIPs was investigated using an initial concentration of 50 mg L^{-1}. The results showed that the adsorption occurred rapidly within the first 30 min and then gradually slowed down until reaching equilibrium (1h). The kinetics of DEHP adsorption at different temperatures was studied by using pseudo-first-order and pseudo-second-order kinetic models. It was found that the pseudo-second order kinetic equation could preferably describe the adsorption.

In order to verify the selectivity of the MMIPs and MNIPs (magnetic non-molecularly imprinted polymers) to DEHP, di-n-octyl phthalate (DNOP) and dibutyl phthalate (DBP) were selected as the analogs. The selectivity coefficient (α) and imprinting coefficient (β) were used to estimate the selectivity properties of MMIPs and MNIPs toward DEHP and structurally related phthalates DBP and DNOP.

$$\alpha = K_d\,(\mathrm{DEHP}) / K_d\,(\mathrm{M}) \quad (1)$$

where K_d is the distribution coefficient (mL g^{-1}) and M represents DNOP or DBP.

$$\beta = \alpha_{\text{imprinted}} / \alpha_{\text{non-imprinted}} \quad (2)$$

where $\alpha_{\text{imprinted}}$ and $\alpha_{\text{non-imprinted}}$ are the selectivity coefficients of the MMIPs and MNIPs for DEHP, respectively.

The $\alpha_{\text{imprinted}}$ of DEHP with respect to DBP and DNOP were 5.2 and 4.8, respectively, and the β value was 3.6. These results indicate that the MMIPs exhibited high selectivity for DEHP, suggesting the template DEHP had a relatively higher affinity for the imprinted material than its competitive compounds.

To assess the practical utility of the MMIPs sorbent, adsorption–desorption experiments were conducted. Desorption of DEHP from the sorbent was performed with chloroform. It was found that the adsorption capacity of the recycled sorbent decreased only about 10% after 8 cycles of adsorption–desorption.

3. CONCLUSIONS

A novel magnetic molecular polymer nanocomposite sorbent (MMIPs), was prepared and characterized. Thermodynamic studies indicated that adsorption of DEHP onto the MMIPs was a feasible, spontaneous and endothermic process. The sorbent showed good selectivity for DEHP, as well as excellent stability during adsorption–desorption cycles. These results obtained suggest the prepared MMIPs can act as a suitable adsorbent for selective, fast and efficient removal of low concentration of DEHP from aqueous solutions.

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