C8-modified magnetic graphene oxide applied to adsorption of DEHP from aqueous solution

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Abstract. C8-modified magnetic graphene oxide (C8-MGO) was synthesized and characterized using Fourier transform infrared spectroscopy and transmission electronic microscopy. The C8-MGO was applied to the adsorption of di-(2-ethylhexyl) phthalate (DEHP) from aqueous solution, and the adsorption performance was examined. The experimental results indicated that the sorption equilibrium was achieved within 2.5 h, the adsorption capacity was 2.5 mg/g, and the adsorption process could be well described by Freundlich isotherm model and pseudo-second-order kinetic model. There are π–π interaction, hydrogen-bond interaction and hydrophobic interaction of C8-MGO with DEHP. The prepared C8-MGO can be a potential sorbent for removal of DEHP at low levels from aqueous solution.

1. Introduction

Di-(2-ethylhexyl) phthalate (DEHP) is the main plasticizer to make polyvinyl chloride more flexible and processable, and has been extensively spread in environment and among people. DEHP is now considered as a suspected endocrine modulator for humans. The Environmental Protection Agency (EPA) of the U.S.A has listed DEHP as one of the environmental priority pollutants [1]. Therefore, it is necessary to develop methods for DEHP removal from water. Adsorption is one of the most important methods for separation of metal ion and organic pollutants from aqueous solutions [2-7], because of its high efficiency and easy operation. Obviously, sorbent plays the key role in this technique.

Graphene oxide (GO) is the oxidized derivative of graphene with a high surface area, superior chemical property and excellent thermal stability. Nowadays, GO has been used as a sorbent material [8, 9]. If GO is modified with an alkyl chain, the adsorption of non-polar compounds such as DEHP onto GO will be improved.

Magnetically separation technology provides an easy and rapid way for removal of magnetic particles from solution by applying an appropriate magnetic field [10-14]. Thus, magnetic adsorbent can be easily isolated from matrix solutions after adsorption of target compounds.

In this study, C8 modified magnetic GO (C8-MGO) was prepared and characterized, and was utilized in the removal of DEHP from aqueous solution. The adsorption behaviors of DEHP on the C8-MGO were tested and evaluated.

2. Materials and methods

2.1 Reagents
DEHP was purchased from Aladdin Reagent (Shanghai) Co., Ltd (Shanghai, China). Nature graphite powder (99.95%) was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other chemicals and materials were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

2.2 Instruments
A 7890A-5975C GC–MS system (Agilent, USA) using a HP-5MS capillary column was utilized for separation. Mass spectrometry detection of DEHP was carried out on a quadrupole mass spectrometer using electron ionization mode.

2.3 Preparation of C8-MGO
Graphite oxide (GO) was prepared from nature graphite powders by a modified Hummers method [15]. Magnetic graphite oxide (MGO) was synthesized by a one-pot solvothermal reaction [16]. C8-MGO was obtained by maxing MGO with octyl-trimethoxysilane in toluene and reaction at 60 °C for 20 h.

3. Results and discussion
3.1. Characterization of C8-MGO
The FT-IR spectrum of the prepared C8-MGO was measured. In the spectrum, the peak at 579 cm⁻¹ was related to Fe–O stretching vibrations, the peak at 1402 cm⁻¹ was assigned to C=C from unoxidized sp² CC bonds, the peak at 1584 cm⁻¹ was corresponded to ν(C=O) of –COOH on the GO after coating with Fe₃O₄, the peak at 2958 cm⁻¹ was from the C–H stretching, and the peak at 3432 cm⁻¹ was attributed to O–H stretching vibrations. These results indicated the successful synthesis of C8-MGO.

From the TEM observation (Fig.1), it was found that Fe₃O₄ particles were loaded on GO with an average diameter of around 20 nm.

![Fig.1 TEM image of C8-MGO.](image)

The magnetic property of the C8-MGO was measured with a vibrating sample magnetometer. It was found that the greatest saturation magnetization was 36.7emu/g, and both the remanence and coercivity were near zero, suggesting that the C8-MGO was superparamagnetic and could be used for rapid solid-liquid phase separation.

3.2. Adsorption properties of DEHP on C8-MGO
The sorption of DEHP on C8-MGO was performed using batch experiments and conducted in duplicate. The sorption capacities varied with initial DEHP concentrations. Langmuir and Freundlich isotherms were applied to describe the sorption behaviors (Fig.2 and Fig.3). It was found that Freundlich isotherm mode fitted the experimental data better (R²=0.9852) than the Langmuir model (R²=0.7422), suggesting that the sorption of DEHP onto the C8-MGO followed the Freundlich isotherm.

The effect of contact time on DEHP adsorption with the C8-MGO was investigated using an initial concentration of 1.0 mg/ L. The results showed that the sorption occurred fast within the first 1 h and...
then gradually dropped down until reaching equilibrium (2.5 h). The kinetics of DEHP sorption on the C8-MGO was studied by using pseudo-first-order and pseudo-second-order kinetic models (Fig. 4 and Fig. 5). The correlation coefficient ($R^2$) of C8-MGO for the pseudo-second-order adsorption model had a higher value (0.991) than pseudo-first-order adsorption mode (0.912). Therefore, the pseudo-second order kinetic equation could describe the adsorption better.

![Fig.2 Langmuir isotherm model for DEHP adsorption on C8-MGO.](image)

![Fig.3 Freundlich isotherm model for DEHP adsorption on C8-MGO.](image)
4. Conclusions
C8 modified magnetic graphene oxide was successfully synthesized and applied to adsorption of DEHP from aqueous solutions. C8-MGO has hexatomic ring as well as alkyl, carboxyl, carbonyl, epoxy and hydroxy groups, which resulted in π–π interaction, hydrophobic interaction and hydrogen-bond interaction of C8-MGO with DEHP. The sorption results obtained from this work suggest that the prepared C8-MGO can be a potential sorbent for removal of low concentration of DEHP from water and waste water.

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