High-efficient removal of phthalate esters from aqueous solution with an easily regenerative magnetic resin: Hydrolytic degradation and simultaneous adsorption

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ABSTRACT

Efficient removal of phthalate esters (PAEs) is of considerable concern since they pose serious ecological and human health risks. In this study, a magnetic strong base anion-exchange resin named MAER-OH was prepared and used as a solid basic catalyst and effective adsorbent. The MAER-OH was systematically characterized by scan electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, thermos-gravimetric analyses and vibrating sample magnetometer. Various factors influencing the removal of dimethyl phthalate (DMP) such as initial DMP concentration, resin dosage and temperature were investigated. The DMP can be completely converted to far less toxic phthalate at the final treatment stage, and more attractively, the potential hydrolysis intermediates were ion-exchanged by the resin simultaneously without obvious change of solution pH. The co-existing chloride was found to obviously enhance the DMP removal efficiency but result in an obvious increase of solution pH and formation of much more hydrolytic intermediates. The exhausted MAER-OH could be regenerated by 8.0% NaOH solution with negligible efficiency loss, and maintain its virgin removal efficiency for 20 successive cycles. Sequencing batch jar tests indicated that more than 5000 bed volumes of DMP solution (10 mg L^{-1}) were efficiently treated by the MAER-OH and the saturated capacity of MAER-OH for DMP removal was 134.9 mg g^{-1}. Taken together, this highly effective and reusable MAER-OH can be easily modularized and separated, promising its huge potential for industrial-scale PAEs wastewater treatment.

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1. Introduction

Water pollution by phthalic acid esters (PAEs) has become a serious environmental concern in recent decades as they can disturb the endocrine system of human and wildlife, even at trace concentration levels (Abdel daiem et al., 2012; Ayranci and Bayram, 2005). Because of the excessive use in manufacturing of plastics, PAEs are capable of migrating into the environment and have been frequently detected in environmental water streams (Bodzek et al., 2004; Gao and Wen, 2016; Zhang et al., 2016). Furthermore, PAEs are highly stable in natural environment (hydrolysis half-lives ranging from 3.2 to 2000 years), and have been listed as top priority pollutants in USA and China (Abdel daiem et al., 2012; Özer et al., 2012a; Gao and Wen, 2016). Therefore, it is highly desirable to get rid of PAEs from wastewater to meet regulatory requirement prior to discharge or for reuse purpose.

Many studies have reported different methods to remove PAEs from global waters, including biodegradation (Boonnorat et al., 2014; Reyes-Contreras et al., 2011), oxidation (Wen et al., 2011), adsorption (Li et al., 2015; Shi et al., 2014; Wu et al., 2013), and hydrolysis (Xu et al., 2014). Over the last decades, sorption-based water treatment techniques have been increasingly popular to remove and recover organic contaminants compared to other techniques due to their associated techno-economic and environmental advantages. Khan et al. (2015) investigated the adsorption of phthalic acid (PA) and diethyl phthalate (DEP) from aqueous solution with zeolitic imidazolate, which exhibited much higher removal efficiency than activated carbon. Huang et al. (2008)

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prepared the octadecyl-modified mesoporous SBA-15 silica molecular sieves for adsorption of dimethyl phthalate (DMP) and DEP. The results showed that alkyl SBA-15 particles could efficiently enrich the DMP and DEP from water samples. Zhang et al. (2007) used a hydrolytic hyper-crosslinked polymer resin NDA-702 for removal of DMP and found that the adsorption amount of DMP by using NDA-702 was much higher than that by using commercial XAD-4 resin and granular activated carbon AC-750. Recently, hydrolytic degradation and adsorption of esters by using strongly basic anion exchange resin has been reported. The hydrolytic role in degradation of targeted materials, such as ethyl acetate, ethyl phenylacetate, shikonin ester derivatives, and aziridines, has been well demonstrated (Abdel daiem et al., 2012; Miyazaki et al., 1996; Samelson and Hammett, 1956). Importantly, the resultant intermediates were preferably adsorbed by anion-exchange resin, suggesting that organic acids may form during the hydrolysis reaction and be simultaneously removed via electrostatic attraction (Elwakeel and Atia, 2014; Kanazawa et al., 2004; Xu et al., 2010). Due to the advantages of no chemical sludge, clean operation and high removal efficiency, the treatment of PAEs wastewater by anion-exchange resin may be a promising approach. According to the report by Xu et al. (2014, 2010), a macroporous strongly basic anion-exchange resin (OH-type) named D201-OH was used for efficiently catalytic degradation of DMP. The hydrolysis products were completely removed by the resin and the removal process exerted negligible adverse effects to the environment. However, this resin has a hydrophobic matrix and may cause serious resin fouling during hundreds to thousands of adsorption-regeneration cycles in real applications (Deng et al., 2010; Li et al., 2014; Mergen et al., 2008; Zaki et al., 2000; Zhu et al., 2013). The poly-acrylic resin has been reported to have much better anti-fouling performance for organic matters removal (Fu et al., 2015; Li et al., 2014; Ysla, 2012), but its reusability for degradation and adsorption of PAEs has rarely been reported.

On the other hand, the treated volume is considerably limited in the form of traditional fixed-bed resin column, along with the high capital cost (Cheng et al., 2014; Li et al., 2017a). The applications of magnetic adsorbents have received considerable attention in recent years for their advantage of easy separation (Boyer, 2015; Ma et al., 2014). MIEX resin, developed by Orica Co. Ltd., is currently the most widely applied magnetic adsorbent for multiple water treatment projects, which are mainly owing to its recognized advantages: good stability, high exchange capacity, improved kinetics and feasible regeneration (Arias-Paic et al., 2016; Boyer and Singer, 2008). Furthermore, due to its high density and excellent settling property, MIEX resin could be applied in the form of fluidized bed reactor in a continuous process, which could greatly improve the treatment flux and get a high recovery rate (>99.9%) (Indarawis and Boyer, 2012). As a result, the resin amount is reduced to only 2—12% of conventional fixed-bed column resin dosage (Boyer, 2015; Boyer and Singer, 2008). In this scenario, catalytic degradation of PAEs by using OH-type magnetic anion exchange resin seems more attractive. However, very limited studies are performed in this regard.

The main objective of this study was to effectively remove PAEs in aqueous phase by using the prepared magnetic strongly basic anion exchange resin (MAER-OH) act as a solid basic catalyst and adsorbent. The MAER-OH was systematically characterized before use. DMP was chosen as the representative PAE for it is one of the top-priority pollutants and has been widely detected in aqueous environment (Xu et al., 2010). The removal mechanism and effects of various factors for DMP removal, such as initial DMP concentration, resin dosage, and reaction temperature were systematically investigated. In addition, desorption and reusability performances of MAER-OH were evaluated.

2. Material and methods

2.1. Materials

Glycidyl methacrylate (GMA, > 99%), divinylbenzene (DVB, 63.3%), benzoyl peroxide (BPO), trimethylamine hydrochloride, toluene and polyvinyl alcohol (PVA, GH20) were all industrial products and supplied by J&K Chemical Co. Ltd., China. Commercial γ-Fe_2O_3 was obtained from Tangyin Zhongke magnetoelectric Co., Ltd. Tetraethoxysilane (TEOS) and dimethyldiethoxylsilane (DMDES) were purchased from Nanjing Capture Chemical Co., Ltd. The mono-methyl phthalate (MMP) and PA were obtained from Nanjing Chemical Reagent Company. DMP ($\geq$98.7%) was purchased from Sigma-Aldrich Chemical Company. All these chemicals were used as supplied.

The magnetic resin MAER was prepared by suspension poly-merization and subsequent amination reaction. The detailed preparation steps were shown in Supplementary Text S1. The resultant strongly basic anion resin MAER-Cl (in chloride form) was then converted to OH-form (denoted MAER-OH). About 50 mL MAER-Cl was rinsed with 500 mL of NaOH solution (2.0 M, 1 BV min^{-1}), and then washed by DI water to near neutral. Prior to use, the resins were purified with methanol and acetone for 12 h by Soxhlet extraction, and vacuum-dried at 323 K to constant weight.

2.2. Characterization

The morphologies of microbeads were characterized via scanning electron microscopy (SEM, S-3400, Hitachi). FTIR analysis was carried out by a FTIR spectrophotometer (Nexus 870, USA). The crystal structure of MAER-OH was assessed by X-ray diffraction (XRD) analysis with 2θ ranging from $10°$ to $70°$ (Shimadzu XRD-6000, Japan). Thermo-gravimetric analyses (TGA) were carried out on Pyris 1 DSC with the heating rate of 20 °C/min (PerkinElmer, USA). The magnetic characteristics of MAER were estimated by a vibrating sample magnetometer (VSM, LS 7307-9309). The specific surface area and pore distribution of the resins were measured by N_2 adsorption-desorption experiments at 77 K (ASAP, Micro-meritics, USA) based on the standard Brunauer—Emmett—Teller (BET) method.

2.3. Batch removal experiments

Batch DMP removal experiments were performed with a given amount of MAER-OH (0.10—0.90 g) and 500 mL DMP solution of known concentrations (10, 20, 40 and 50 mg L^{-1}) in 1000 mL conical flasks, and shaken in an incubator shaker at different temperatures (283, 293 and 318 K) and 150 rpm. At pre-settled time intervals, 1 mL of the solution was extracted and detected by HPLC (Agilent 1200, DAD detector, USA) with the mobile phase consisting of 55% methanol and 45% 0.2 M KH_2PO_4. The detective wavelength was 228 nm and column temperature was fixed at 303 K.

2.4. Desorption and reusability

The desorption and regeneration performance of MAER-OH could directly reflect its reusability. Batch parallel DMP removal experiments (0.10 g MAER-OH, 100 mL of 50 mg L^{-1} DMP solution) were conducted at 318 K for 12 h. The saturated resins were then regenerated by 20 mL of 8.0% NaOH solution at 150 rpm and 318 K for 1 h. Afterwards, the microbeads were rinsed by an excess amount of deionized water to neutral pH, and then used for next operation run. Successive cycles were undertaken for 20 times to verify the loss of virgin removal efficiency, and alternatively to know the extent of resin regeneration. The desorption efficiency