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Enhanced adsorption of phthalic acid esters (PAEs) from aqueous solution by alkylbenzene-functionalized polypropylene nonwoven and its adsorption mechanism insight

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ABSTRACT

In this study, a novel adsorbent (PP-g-GMA-(n-OA)) was designed and synthesized via grafting polymerization of glycidyl methacrylate (GMA), and subsequent amination modification of 4-n-Octylaniline (n-OA) on the surface of polypropylene nonwoven. The morphological structure, composition and wettability of the PP-g-GMA-(n-OA) were thoroughly characterized by SEM, FT-IR, XPS, water contact angle. Results elucidated that the hydrophilic hydroxyl/amino groups and hydrophobic aromatic rings were successfully introduced onto the surface of PP-g-GMA-(n-OA), which could be selectively bind similar functional groups of phthalic acid esters (PAEs) by different adsorption interactions to achieve more satisfactory adsorption efficiently. Compared to unmodified PP nonwoven and several other reported adsorbents, PP-g-GMA-(n-OA) exhibited relatively high adsorption capacity for dioctyl phthalate (DOP) and dibutyl phthalate (DBP) (272.4 mg/g and 184.9 mg/g, respectively). The Freundlich isotherm model can be satisfactorily fitted the isotherm data, elucidating that it was a multilayer heterogeneous adsorption. The thermodynamic parameters confirmed the adsorption was spontaneous and exothermic process. In additional, the adsorbent still exhibited excellent adsorption capacity after multiple desorption/adsorption cycles. Adsorption mechanism was also investigated using the results of adsorption behavior and spectrum analyses after adsorption, which demonstrated that synergistic effect of π-π interaction, hydrophobic interaction and hydrogen bonds, especially π-π interaction played a dominated role in DOP and DBP adsorption. The current study provided a strategy for design and fabrication of high effective and low-cost adsorbents for remove of target contaminants from wastewater.

1. Introduction

Phthalic acid esters (PAEs) is an important group of plasticizers and softening agents that have been widely used in building materials, food packing, medical devices and cosmetics [1,2]. As endocrine-disrupting chemicals (EDCs), PAEs may cause the hormone system and the reproductive system. Even worse, PAEs is a persistent and easily bio-accumulated material, which can readily be transported over long distances; as a consequence, and it has been found in indoor dust [3], foods [4], air [5,6], water [7,8] and soil [9]. Besides, phthalate metabolites detected in urine in nearly 100% of individuals from various countries [10,11]. Therefore, the removal of PAEs from environmental is urgently needed.

Among numbers of well-developed methods for the removal of PAEs from water [12–15], adsorption is considered a simple and efficient method because of its comparatively low-cost, easy handing and fewer secondary products. In recently, a variety of adsorbents have been developed to remove PAEs that rely on van der Waals, hydrogen bonds, hydrophobic interaction and π-π interaction [16–19]. Polypropylene nonwoven material with network structure is widely utilized in adsorption and filtration process. The nonwoven with multiple connect macropores due to random overlapped fibers has the advantage of low resistance and rapid mass-transfer, as well as the low cost and good mechanical strength [20,21]. However, there are little available adsorption sites on the surface and the strong hydrophobic limits its further utilization. Hence, the surface modification of the polypropylene is

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needed for its further application.

In recent years, a strategy that design more specific interaction sites of adsorbents tailored to the features of targeted contaminants has been given much attention because of the high adsorption capacity and high selectivity [22–24]. A growing body of research has been focused on adsorbents surface modified by varies of functional groups [25,26]. These studies have shown that the structure of adsorbents can evidently influence the adsorption capacity of target contaminants, and a variety of functional groups on the surface of adsorbents could be selectively bind similar functional groups of target contaminants by different adsorption interactions to achieve more satisfactory adsorption efficiently. Recently, molecular imprinted polymers (MIPs) have been used as adsorbents for removing EDCs due to the special recognition ability for the given molecules. Regretfully, such MIPs suffered from the problem of time consuming and complex process for removing template, which is bound to affect the rebinding and selective recognition capacity to target molecules [27]. Surface modification is considered a simple and effective method to introduce specific functional groups onto the surface of the adsorbent [28,29]. Quan et al. investigated SBA-15 graft modified by two functional groups of cetyl and amino groups for removing 4-Nonyphenol. The results show that the adsorption capacity of bifunctionalized SBA-15 was significantly higher than that of monofunctionalized SBA-15 [30]. Similar results have been reported by Zhou et al. [31]. Besides, several studies proposed that hydrophilic adsorption materials would be beneficial to accelerate the diffusion or migration rate of target contaminant from bulk solution to adsorbents' surface [32,33]. If an adsorbent can combines the benefits of both special structure design and good hydrophilicity to synthesize dual-functional adsorbents, the adsorbents may have high efficiency for the removal of target contaminants and other contaminants with similar features. Nevertheless, to the author's knowledge, no works have studied the dual-functional adsorbents that are specially structure design to adapt the target contaminants DOP and DBP.

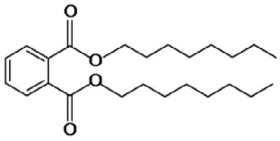
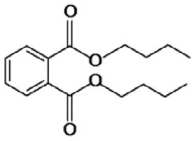
On the basis of the above ideas, according to the structural characteristics of DOP, the hydrophilic hydroxyl/amino and hydrophobic alkyl-chain/aromatic rings were introduced onto PP surface through electron beam induced graft polymerization and subsequent amination ring-opening reaction, and then used to removal of phthalic acid esters (PAEs) from aqueous solution. The novel adsorbent was systematically characterized by Scanning electron microscopy (SEM), Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), water contact angle and Raman spectra. Effects of contact time, initial concentration, and temperature on adsorption performance were investigated. In addition, five cycles of desorption/regeneration was discussed to assess the reusability and economical efficiency of PP-g-GMA-(n-OA). Finally, the adsorption mechanism was discussed on the basis of the adsorption behavior, adsorption kinetics, adsorption isotherm equilibrium and thermodynamics, and spectral analyses of adsorbents after adsorption.

2. Experimental

2.1. Materials and reagents

Dioctyl phthalate (DOP) and dibutyl phthalate (DBP) were purchased from Lianxing Biotechnology Company. Their chemical structures and basic physicochemical properties are shown in Table 1. Polypropylene (PP) nonwoven (70 g/m^2) used in this work was obtained from the Shijiazhuang Tobacco Center (Shijiazhuang, China). Glycidyl methacrylate (GMA), 1,4-dioxane, and anhydrous ethanol were purchased from Tianyi Chemical Factory (Tianjin, China). 4-n-Octylaniline (n-OA) and dodecylamine (DA) were purchased from J & K Scientific Ltd.

Table 1
Properties of DOP and DBP.

Chemicals	Abb	M	Structure	log K_{ow}
Dioctyl phthalate	DOP	390.56		8.06
Dibutyl phthalate	DBP	278.34		4.45

2.2. Preparation of PP-g-GMA-(n-OA)

Glycidyl methacrylate (GMA) grafted PP nonwoven (PP-g-GMA) was synthesized according to the published method [32], then the PP-g-GMA immersed in 1,4-dioxane solution containing excess 4-n-Octylaniline to convert epoxy group to hydroxyl and alkylbenzene. The reaction was performed at 353 K for a predetermined time (10 h). After the reaction, the modified PP nonwoven (PP-g-GMA-(n-OA)) was repeatedly washed with anhydrous ethanol and distilled water to remove unreacted solution, then dried at 333 K to constant weight. Besides, preparation of PP-g-GMA-DA as a contrast sample by the above method. The PP-g-GMA-(n-OA) was prepared according to the synthesis route in Fig. 1.

The degree of grafting (G, %) and amination ring-opening rate (AR, %) calculated from weight gain was determined as: [34,35]

$$G(\%) = \frac{(W_1 - W_0)}{W_0} \times 100\% \quad (1)$$

$$AR(\%) = \frac{(W_2 - W_1)M_{GMA}}{(W_1 - W_0)M_{n\text{-}OA}} \times 100\% \quad (2)$$

where W_0, W_1, W_2 are the weight of the original PP nonwoven, PP-g-GMA, and PP-g-GMA-(n-OA), respectively. M_{GMA} and $M_{n\text{-}OA}$ are molar mass of GMA (142.15 g/mol) and n-OA (205.34 g/mol), respectively.

2.3. Characterization

The surface functional groups were characterized by Fourier transform infrared (FT-IR) spectrometer (Necolet 6700, USA) over the wavelength range 4000–500 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition on the surface of PP samples via an AEM PHI 5300X spectrometer. The field emission scanning electron microscopy (FE-SEM) images were collected by Hitachi S-4800 microscope (Hitachi, Japan). The wettability was measured using a contact angle analyzer (KRUSS DSA100, Germany). A laser confocal Raman microscope (XploRA PLUS, Horiba, Japan) was used in this work.

2.4. Adsorption experiments

The adsorption experiments of DOP and DBP on modified PP nonwoven were carried out at pH 6.5 with batch techniques. The stock solution (10 g/L) of DOP and DBP were prepared using anhydrous ethanol by dissolved specific amounts of DOP and DBP into anhydrous ethanol, and then diluted sequentially to a series of concentrations (ranging from 10 to 110 mg/L) using distilled water. After that, the diluted solutions were under ultrasonic treatment for 1 h. The 25 mg adsorbent was added to 150 ml conical flasks with 100 ml of DOP and DBP aqueous solution. The flasks placed in an incubator shaker at 150 rpm for 20 h to ensure adsorption equilibrium. The initial (C_0) and