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Adsorption of dibutyl phthalate in aqueous solution by mesoporous calcium silicate grafted non-woven polypropylene

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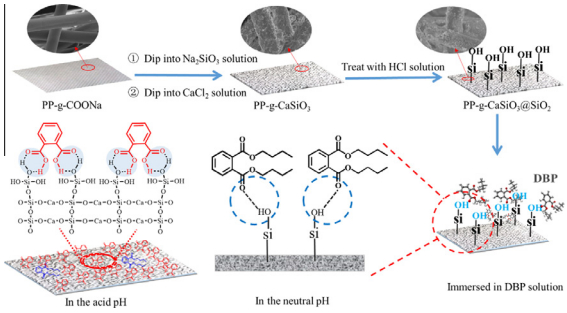
HIGHLIGHTS

- PP-g-$CaSiO_3$@SiO_2 was synthesized and used to absorb DBP in aqueous solution.
- Large surface area and Si—OH on PP-g-$CaSiO_3$@SiO_2 improved the adsorption of DBP.
- Six-caned hydrogen bond was formed between Si—OH of PP-g-$CaSiO_3$@SiO_2 and DBP hydrolysate.
- A low temperature and low pH is beneficial for the adsorption of DBP.
- PP-g-$CaSiO_3$@SiO_2 costs low, can be easily prepared without any pollutants, and reused.

GRAPHICAL ABSTRACT

The schematic of hydrogen bonding for DBP binding to PP-g-$CaSiO_3$@SiO_2.



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ABSTRACT

The purpose of this research is to synthesize mesoporous calcium silicate grafted non-woven polypropylene (PP-g-$CaSiO_3$@SiO_2) and to evaluate its adsorption performance for dibutyl phthalate (DBP). The results indicated that the adsorption capacity of PP-g-$CaSiO_3$@SiO_2 was superior to non-woven polypropylene fabric (PP) and $CaSiO_3$ grafted PP non-woven (PP-g-$CaSiO_3$). The adsorption mechanism of DBP by PP-g-$CaSiO_3$@SiO_2 at different pH values was investigated. When the initial concentration of DBP was 130 mg/L (pH = 3.0, 298 K) the adsorption capacity of DBP by PP-g-$CaSiO_3$@SiO_2 reached 54.8 mg/g, and the adsorption equilibrium time was two hours. The large surface area and Si—OH groups on PP-g-$CaSiO_3$@SiO_2 could improve the adsorption capacity and affinity for DBP. Isothermal titration calorimetry (ITC) was used to illustrate the driving force for the adsorption of DBP to $CaSiO_3$@SiO_2. The binding constant K, binding enthalpy (ΔH) and binding entropy (ΔS) between DBP and $CaSiO_3$@SiO_2 were obtained to be 3.54×10^3 L/mol, −66.2 kJ/mol and 0.154 kJ/(K*mol), respectively. The Gibbs' energy change during the binding process was −20.24 kJ/mol, indicating that the adsorption process was thermodynamically favorable. Freundlich model was more suitable to describe the adsorption of DBP onto PP-g-$CaSiO_3$@SiO_2. Lower temperature and lower pH can promote the adsorption of DBP. PP-g-$CaSiO_3$@SiO_2 can be recycled for reuse. It is promising to be used as a good adsorption material to remove DBP or other contaminants from aqueous solutions.

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1. Introduction

Dibutyl phthalate (DBP) has received considerable social attention because of its widespread occurrence as an endocrine disrupting compound (EDC). The adverse effects of DBP are well known as reducing the reproductive ability, decreasing sperm count, raising the incidence of prostate cancer, and causing other reproductive disorders via interaction with the endocrine system [1,2]. Over past decades, trace-level DBP have been detected in surface water, soil, groundwater, plastic products, and landfill leachates [3–6]. Consequently, effective treatments are required to eliminate DBP from water [7].

Several separation processes have been used to remove DBP from water, such as biodegradation [8], coagulation [9], enzymatic polymerization [10] and adsorption [11]. Among these techniques, adsorption received most researchers' attention because there is no phase change during the removal process [12,13]. Additionally, the simple fabrication methods and consequent low costs of the adsorbents extend their application range in water treatment.

Many conventional adsorbents [14–17] showed limited efficiency and capacity when they were used to remove DBP, for example, the activated carbons. The activated carbons are not as effective in polar pollutant removal as in non-polar compounds removal because of their natural properties and non-polar surface [18,19]. Additionally, the re-collection and regeneration of the activated carbons in the continuous water treatment process are still difficult [20]. Consequently, it is necessary to find more suitable adsorbents [21].

Mesoporous silica has attracted great attention due to its high specific surface area, low manufacturing cost, prominent adsorption capacity, and without any secondary pollution. Yu et al. [22] synthesized ordered mesoporous silica materials by a novel route using diatomite as the silica source. The prepared materials possessed regular hexagonal mesoporous structure and high surface area. Regli et al. [23] prepared mesoporous silica encapsulated Si-NCs by dispersing encapsulated Si-NCs within silica shell in aqueous media. The mesoporous silica encapsulated Si-NCs with high surface area mesoporous is potential to be used as drug delivery agent. The nanoparticles are difficult to be recycled, though they have high adsorption capacity for pollutants. They are commonly mixed with polymers to obtain composite materials. However, the resulting adsorption efficiency will be much compromised because many nanoparticles are agglomerated and entrapped in the polymer matrix [24–26].

Recently, polypropylene (PP) non-woven fabric was utilized in adsorption and filtration process because of its good flexibility, high thermal and chemical stability [27]. Liu et al. [12] constructed amphiphilic segments on the surface of polypropylene (PP) nonwoven by grafting polymerization using ultraviolet (UV) irradiation. The prepared materials were used to remove endocrine disrupting compounds from aqueous solutions. In our previous research, calcium silicate particles containing mesoporous SiO_2 on the surface ($CaSiO_3$@SiO_2) were grafted onto polypropylene non-woven fabric [28]. Its adsorption performance for bisphenol A (BPA) was preliminarily investigated. However, the interaction of the endocrine disrupting compounds and PP-g-$CaSiO_3$@SiO_2 was not clearly explained.

In this research, the PP-g-$CaSiO_3$@SiO_2 was synthesized for the adsorption of DBP. The adsorption behaviors of DBP were investigated, and the results indicated that the adsorption capacity and adsorption rate were superior to PP and PP-g-$CaSiO_3$. Its larger specific surface area and the interactions between DBP and Si—OH on PP-g-$CaSiO_3$@SiO_2 can promote the adsorption. Isothermal titration calorimetry (ITC) was used to illustrate the driving force for the adsorption of DBP to $CaSiO_3$@SiO_2. The equilibrium adsorption capacity of PP-g-$CaSiO_3$@SiO_2 can be reached within 2 h. The PP-g-$CaSiO_3$@SiO_2 has been proved to be an excellent candidate material to remove DBP from aqueous solutions considering its low cost, fast adsorption rate, and reusability performance.

2. Experimental

2.1. Materials

Sodium silicate was purchased from Tianjin Jiangtian Chemical Co. Ltd. Calcium chloride was purchased from Tianjin Huazhen Special Chemical Reagent Factory. Acrylic acid (AA), sodium hydroxide (NaOH) and anhydrous ethanol were purchased from Tianjin Second Chemical Reagent Factory. Polypropylene (PP) non-woven was purchased from China Non-woven Co. Ltd. in Xianghe County of Hebei Province. Hydrochloric acid (HCl) was purchased from Tianjin Jiangtian Chemical Co. Ltd. Dibutyl phthalate (DBP) was purchased from Lianxing Biotechnology Company.

2.2. Preparation of PP-g-$CaSiO_3$@SiO_3

Polyacrylic acid grafted PP non-woven (PP-g-PAA) was synthesized using reported method [28]. Sodium polyacrylate grafted PP non-woven (PP-g-COONa) was prepared by neutralizating PP-g-PAA with NaOH. The PP-g-COONa was dipped into 15 wt.% Na_2SiO_3 solution for 0.5 h, followed by dipping the PP-g-COONa with Na_2SiO_3 solution into 5 wt.% $CaCl_2$ solution for 3 h to synthesize $CaSiO_3$ grafted PP non-woven (PP-g-$CaSiO_3$). Then the PP-g-$CaSiO_3$@SiO_2 was produced by acid treatment the PP-g-$CaSiO_3$ using HCl solution (pH = 3) [29]. Finally, the resulted PP-g-$CaSiO_3$@SiO_2 was washed repeatedly with deionized water and dried at 60 °C in vacuum for 24 h to obtain dried samples. The grafting rate (G) of PP non-woven fabric was calculated using the equation below:

$$G\ (\%) = (W_1 - W_0)/W_0 \times 100\%, \quad (1)$$

where W_0 and W_1 are the weight of the PP non-woven fabric and PP-g-$CaSiO_3$@SiO_2 or PP-g-$CaSiO_3$, respectively.

The PP-g-$CaSiO_3$@SiO_2 and PP-g-$CaSiO_3$ with the grafting ratio of 31.5 ± 3.5% were selected for characterizations and adsorption tests.

2.3. Preparation of $CaSiO_3$@SiO_3

It is difficult to study the interaction between PP-g-$CaSiO_3$ and DBP directly. So the $CaSiO_3$ containing mesoporous SiO_2 ($CaSiO_3$@SiO_2) was prepared. Firstly, the $CaSiO_3$ suspension was synthesized by a chemical precipitation method using the mixed solution of $NaSiO_3$ and $CaCl_2$ with uniform molar concentration at room temperature [29]. Then the $CaSiO_3$@SiO_2 suspension was produced by acid treatment using HCl aqueous solution with the pH value of 3.0. The $CaSiO_3$@SiO_2 was washed 5 times with deionized water to remove the Na^+ and Cl^- ions.

2.4. Adsorption of DBP

Batch adsorption experiments of dibutyl phthalate (DBP) were conducted. DBP was dissolved in ethanol/deionized water solution (the volume ratio of anhydrous ethanol and deionized water was 1:5) to get a 50 mg/L DBP solution. The pH value of DBP solution was set at 3.0 using hydrochloric acid. Then, 0.10 g of PP, PP-g-$CaSiO_3$ or PP-g-$CaSiO_3$@SiO_2 was put into 100 mL of above DBP solution in a conical flask. The concentration of DBP was determined by a UV spectrophotometer after sufficient stirring at 298 K in a shaking incubator. The adsorption capacity (Q_t) of DBP was calculated by the equation below: