Novel hydrophobic cotton fibers adsorbent for the removal of nitrobenzene in aqueous solution

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ABSTRACT

In order to improve the superhydrophobic and oil-wet properties of raw cotton fibers come from Jiangsu province, China. A novel adsorbent, hydrophobic cotton fibers (HCF) with an excellent superhydrophobic and larger length was synthesized via modified sol–gel method and examined for the removal of nitrobenzene in aqueous solution. Results show that the treated raw cotton fibers exhibited outstanding non-wettability with the WCA of 152° and the larger length of 0.2–0.4 cm, which offers an opportunity to separation in for the removal of nitrobenzene. It was found that adsorption isotherm and kinetics of nitrobenzene onto HCF were well described by the Freundlich and pseudo-second-order kinetic models, respectively. The thermodynamic data showed that the nitrobenzene adsorption onto HCF was a spontaneous, endothermic and physisorption reaction. The monolayer adsorption capacity of nitrobenzene was found to be 16.85 mg/g at 30 °C.

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1. Introduction

Nitrobenzene is listed as a priority pollutant because it is a carcinogen and mutagen (Guo et al., 2012). Nitrobenzene has been widely used in the manufacture of dyes, plastics, pesticides, explosives, pharmaceuticals, and as an intermediate in the synthesis of chemicals. Aqueous solutions containing nitrobenzene are typically discharged into wastewater treatment plants that are not completely effective in treating/removing all existing pollutants in solution. Consequently, nitrobenzene is discharged into the water environment. It also has been threatened the ecosystem's stabilization and human health. Hence, the removal of nitrobenzene from aqueous solution is essential. Various technologies, such as adsorption, ozonation, and advanced oxidation processes, have been considered for the purification of nitrobenzene-contaminated water (Liu & Wang, 2011). Among these treatment processes, adsorption is the most versatile and effective method (Jin, He, & Wei, 2011). Moreover, various adsorbents, such as activated carbon, organoclays, biological wastes, molecular sieves, high silica zeolites, resins, activated sludge, and lipoids have been used for the removal of nitrobenzene in aqueous solutions (Wei, Sun, Jin, Cui, & Wei, 2014). Some conventional adsorbents, such as

synthetic cation exchange resins, are often non-recyclable and non-biodegradable. In contrast, natural materials, such as cellulose and chitosan, are recyclable, biodegradable, cheap, and abundant. Furthermore, these materials can be chemically modified to enhance their interaction with nitrobenzene in solution or to reduce their water/ethanol adsorption capability by introducing some new functional groups (Wojnarovits, Foldvary, & Takacs, 2010).

In previous studies, various approaches have been considered to improve the removal efficiency of nitrobenzene. For example, our group examined activated carbon treated with HNO_3 for the removal of nitrobenzene in aqueous solution (Liu & Wang, 2011). However, there exist the competing adsorption phenomena between the solvent molecules and nitrobenzene. And nitrobenzene is insoluble in water. In most cases, the solvent nitrobenzene was ethanol. Hence, designing adsorbents with resistance to ethanol/water adsorption is required. Hydrophobic coating is an attractive strategy to achieve selective adsorption of nitrobenzene onto adsorbents because of the decreased water affinity of the adsorbent (Kim et al., 2012).

In recent years, some materials possessing superhydrophobicity have attracted great interest for fundamental research and potential application in water–oil separation. Biomass materials, such as cotton fibers, wood fibers, leaves, cellulose and kapok fibers are more abundant, low costs and recyclable than petroleum-based material. However, cotton fibers, wood fibers, cellulose, and kapok fibers have good hydrophilicity, relatively low oil adsorption capacity, and low hydrophobicity. These biomass materials may

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be changing its wettability to obtain superhydrophobic oil adsorbent. Herein, cotton fibers had received increasing attention as an oil-absorbing material (Singh, Kendall, Hake, & Ramkumar, 2013; Wang et al., 2015). With the increase demand of superhydrophobicity material in environmental protection, researchers have paying attention to how to fabricate superhydrophobic coatings onto the surface of biomass materials with a simple technique. At present, there are some methods including sol–gel method (Wang et al., 2008), polymer-phase separation (Wei, Liu, Tian, Xiao, & Wang, 2010), etching technique (Baldacchini, Carey, Zhou, & Mazur, 2006), chemical vapor deposition (Li, Xie, Zhang, & Wang, 2007) and solvothermal technique (Wu, Xia, Lei, & Wang, 2011) have been used to prepare superhydrophobic coatings onto the surface of materials (Huang, Song, Xing, & Dai, 2010). Among these methods, sol–gel method is a simple and effective technique for fabricating superhydrophobic surface. However, the length of the obtained superhydrophobic fiber materials via sol–gel method was short and unfavorable to separation in application. Also, most superhydrophobic fiber materials only have been applied in the field of oil spill cleanup. So far there has yet to be any report on the use of superhydrophobic cotton fibers for the removal of nitrobenzene.

The raw cotton fibers had a lower content of pectin and wax, come from Jiangsu province, China. It has stronger hydrophilicity and weaker hydrophobic, so the application as a kind of oil adsorption materials was limited. Therefore, the aim of this study was to explore the efficiency of modified hydrophobic cotton fibers for the removal of nitrobenzene in aqueous solution. The raw cotton fibers were used as raw material because of its extensive, low costs and biodegradable. However, it was very difficult to keep a longer size of modified hydrophobic cotton fibers in modified reaction, which offers an advantage to separation in the process of adsorption. In this study, not only the modified hydrophobic cotton fibers had an excellent superhydrophobic property but had a larger length via modified sol–gel method. To evaluate the potential use of modified cotton fibers, its nitrobenzene adsorption capacity, and adsorption parameters on the adsorption performance was investigated. Accordingly, the adsorption isotherms, thermodynamics, and kinetics of the adsorption of nitrobenzene onto the modified cotton fibers were determined.

2. Materials and methods

2.1. Materials

Raw cotton fibers were obtained from Xuzhou Tianxin Medical Materials Co. (Jiangsu Province, China). Tetraethyl orthosilicate (TEOS), absolute ethanol, and NaOH were obtained from Tianjin Wing Tai Chemical Co., Ltd. (China). Trichloro(octadecyl)silane (OTS) was obtained from TCI Chemical Co. (China). Ammonia solution (25%), Toluene and Nitrobenzene (98%) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (China). All the chemicals used were of analytical grade.

2.2. Preparation of hydrophobic cotton fibers (HCF) adsorbent

Raw cotton fibers were sectioned into lengths of 1 cm and immersed in 100 mL ethanol/NaOH solution (mass fraction of NaOH was 8%) at a lower temperature (20 °C) for 12 h to keep cotton fibers has a larger length. TEOS-derived silica colloids were prepared by hydrolysis of TEOS (32 g) in 75 mL ethanol upon dropwise addition of ammonia (25 wt%). Then, the contaminant-free cotton sample was added to the solution. Finally, the modified cotton fibers sample was immersed in a fresh OTS-toluene solution under specific conditions (Fig. 1). The hydrophobic silylated cotton surface was

washed with toluene and ethanol several times, and then blow-dried with pure nitrogen gas for storage.

2.3. Characterization

FT-IR spectra were recorded on a Nicolet 6700 spectrophotometer with 128 scans per sample. The XRD patterns of the samples were performed on a Philips PW 1840 diffractometer equipped with a Cu K radiation source (40 kV, 40 mA), in the 2θ range of 10–50°. The morphology of the sample was characterized by an FEI QUANTA200 scanning electron microscope. Contact angles were obtained by a Krüss CCA200 contact angle analyzer at room temperature, and the values were averages from measurements on at least three different positions for each sample.

2.4. Adsorption experiments

A nitrobenzene standard solution (1 g/L) was prepared by dissolving 0.83 mL nitrobenzene in 100 mL ethanol and 900 mL Milli-Q water. 0.1 g HCF was dispersed in 1000 mL 1.0 g/L nitrobenzene solution to investigate the effect of temperature on the removal of nitrobenzene from aqueous solution. The absorption mixtures were shook for 2 h to ensure equilibrium. After equilibrium was reached, the amounts of nitrobenzene adsorbed by the HCF were evaluated by the residual concentrations of it in the nitrobenzene solutions, which were determined by a UV spectroscopy (Beijing Puxi, China) at 267 nm. To investigate the effects of adsorbent dosage, adsorption experiments were conducted by a batch method.

The amount of nitrobenzene adsorbed was expressed as percentage of the removal R (%) (Eq. (1)), while the amount of nitrobenzene uptake at equilibrium q_e (mg/g) was calculated using the mass balance equation (Eq. (2)):

$$\%Removal = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0, C_e (mg L^{-1}) are the initial and equilibrium concentrations of nitrobenzene in the aqueous solution, respectively; m (g) is the mass of adsorbent; and V (L) is the volume of solution containing nitrobenzene.

2.5. Adsorption models

2.5.1. Adsorption isotherms

Analysis of adsorption isotherm data is important for predicting the adsorption parameters (Peng, Hidajat, & Uddin, 2005). To describe the adsorption isotherm, three widely used models (i.e., the linear forms of the Langmuir, Freundlich, and Redlich–Peterson (Eqs. (3), (4), and (5), respectively)) were fitted to the experimental data as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

$$\log\left(\frac{K_{RP}}{q_e} - 1\right) = \beta \log C_e + \log\alpha \tag{5}$$

where q_e (mg g^{-1}) is the amount of solute adsorbed at equilibrium per unit weight of adsorbent; C_e (mg L^{-1}) is the equilibrium concentration of solute in the bulk solution; K_L (L mg^{-1}), K_F [(mg g^{-1})(L mg^{-1})$^{1/n}$], and K_{RP} (L g^{-1}) are the constants related to the Langmuir, Freundlich, and Redlich–Peterson isotherms, respectively; Q_0 (mg g^{-1}) is the saturated adsorption capacity; $1/n$ is the