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Research Paper

Polyimide-based carbon nanofibers: A versatile adsorbent for highly efficient removals of chlorophenols, dyes and antibiotics

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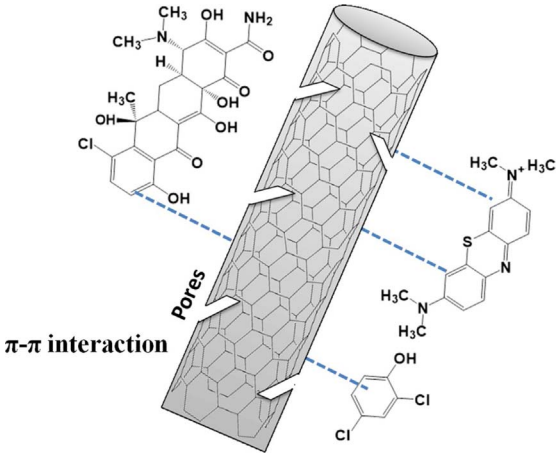
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, polyimide (PI)-based carbon nanofibers (CNFs) were prepared via electrospining polyamic acid solutions followed by thermal imidization and carbonization. And its versatile adsorption performance for removal of 2,4-dichlorophenol (2,4-DCP), methylene blue (MB) and tetracycline (TC) was evaluated. PI-based CNFs with a high specific surface area of 715.89 $m^2 g^{-1}$ exhibited a maximum adsorption of 483.09 mg g^{-1}, 272.48 mg g^{-1} and 146.63 mg g^{-1} for 2,4-DCP, MB and TC, respectively. The MB adsorption efficiency was highly pH-dependent with an optimal pH 11, while the CNFs performed well towards TC and 2,4-DCP adsorption in the wide pH range of 4–7 and 3–7. Kinetics and isotherm experiments were fitted well with pseudo-second-order kinetics model and Langmuir model, respectively. Thermodynamic parameters showed that adsorption was spontaneous and endothermic. Moreover, the reusability of PI-based CNFs was evaluated, and the result showed that the removal of 2,4-DCP, TC and MB was kept its high efficiency after 5 consecutive cycles. This

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study demonstrated that the CNFs should be a powerful adsorbent for the removal of a great number of organic pollutants from aqueous environments.

1. Introduction

The harmful emerging organic contaminants (EOCs) in water resources, such as antibiotics, chlorophenls and dyes are considered as one of the pivotal environmental problems and pose a great threat to environment and human health [1–3]. Various antibiotics are widely used in human therapy and livestock industry. The longterm, widespread or improper use has resulted in excessive accumulation in aquatic environment, which cause adverse impacts to many organisms, including aquatic photosynthetic organisms, antibiotic-resistant genes, indigenous microbial populations [4–6]. Chlorophenols represent an important class of environmental water pollutants, which have been widely used as intermediates in the production of dyes, papers, pesticides, herbicides and phenolic resins. The structural stability, persistence, toxicity, carcinogenicity and difficult degradation make them become one of the most dangerous pollutants. Besides antibiotics and chlorophenols, synthetic dyes have received increased concerns because of the fast development of industry, such as textile, paper, food processing, plastics, printing and dye manufacturing industries. Most of these dyes resist aerobic digestion and are stable to heat, light, and oxidizing agents due to their complex structures and low biodegradability [7,8]. It is well known that the discharge of these antibiotics, chlorophenols or dyes into the aqueous environment can cause severe health and ecological problems to human beings [9]. Therefore, the rational and efficient treatment of these discharged pollutants has been regarded as an urgent and important issue in the field of environmental engineering.

In general, water treament methods include adsorption processes, oxidation processes, photocatalytic degradation, biological degradation and hybrid technologies [10–12]. Among these methods, adsorption is a kind of benign process to remove contaminants because of environmental friendliness, low cost and simplicity of operation. Some traditional carbon adsorbents were widely used to remove micropollutants from aqueous solutions. For example, the mesoporous activated carbon has been known as the most popularly used adsorbent for pollutants removal. Noorimotlagh et al. used the mesoporous activated carbon with specific area of 565 m^2/g to adsorb Acid orange 7, and the result showed that the adsorption capability was 99 mg/g [13]. The carbon nanotube has been intensively reported as an adsorbent to eliminate micropollutants. Gong's group comprehensively explored methylene blue adsorbed onto magnetic multi-wall carbon nanotube, and the maximum adsoption capacity was 16 mg/g [14]. These adsorbents are subjected to low adsorption capacity or slow adsorption rate since their relatively low surface area and weaker electronic attraction. Therefore, it is urgently need to produce novel adsorbent with high specific surface area and abundant pore structure.

Recently, the electrospun porous carbon nanofibers (CNFs) have been intensively developed, and CNFs are considered as a promising adsorbent to remove pollutants due to their high porosity and large specific surface area [15,16]. Polyacrylonitrile (PAN) has been widely used as precursor for electrospun-derived carbon fiber, Singh et al. used PAN as electrospun solution and combined carbonization to prepare PAN-based CNFs, which is applied in removal of disinfetion byproducts [17]. Lee's group prepared electrospun carbon fibers with the surface area of 375 m^2/g using PAN as the carbon precursor, showing a good performance in formaldehyde adsorption [18]. Compared with PAN, the polyimide (PI) has attracted more interest and been investigated in more extensive practical application fields due to its superior properties, such as outstanding mechanical properties, excellent thermal stability, chemical resistance and high carbon yield. Till now, the electrochemical performance of PI-based CNFs has been widely reported in previous studies [19–22]. Kim et al. create a highly porous material using polyimides as carbon precursor for electrical double layer capacitors [21]. Dong et al. prepared the PI-based nitrogen-doped CNFs for high performance flexible supercapacitors [22]. However, the study on PI-based carbon nanofibers as adsorbent for the removal of organic pollutants has been rarely reported.

Herein, the main objective of this study is to explore the synthesized porous PI-based CNFs as adsorbent for the adsorptive removal of various organic contaminants. The PI-based CNFs were prepared by polymerization from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) in DMF and followed by electrospinning and simple thermal treatment. In order to examine adsorptive ability of the CNFs towards organic pollutants, 2,4-dichlorophenol (2,4-DCP), tetracycline (TC) and methylene blue (MB) were selected as model pollutants. MB and 2,4-DCP are the typical dye and chlorophenols contaminant, respectively, and TC is one of the most important broad spectrum antibiotic. To examine the adsorption performance, batch adsorption experiments including impact of solution pH, ion intensity, adsorption kinetics, equilibrium isotherms and thermodynamics were conducted, and reusability of PI-based CNFs were also evaluated.

2. Materials and methods

2.1. Materials

Tetracycline hydrochloride (USP grade) was purchased from Aladdin. Methylene blue and 2,4-dichlorophenol was obtained from Aldrich. Their typical physicochemical properties were listed in Table 1. PMDA and ODA were dried under vacuum at 80 °C. DMF purchased from Sinopharm Chemical Reage Co., Ltd was dried with molecular sieve. Ultra-pure water was employed throughout the experiments for solution preparation.

2.2. Preparation of PI -based CNFs

Polyamic acid (PAA) was synthesized by low-temperature solution polycondensation in the DMF, and the molar ratio of PMDA and ODA was 1.02. PMDA, ODA and DMF were added to flask with three necks, and the mixture was stirred for 6 h at 0 °C to form a homogeneous PAA solution. Then the PAA polymer solution was added into a 3 ml plastic syringe with a stainless steel spinneret. During the electrospinning, the PAA solution was driven by pump and the rate of fedding was 0.25 ml/h. The PAA nanofibers were collected on a piece of aluminum foil placed 15 cm away from the spinneret. The foil and the spinneret were connected to a high votage supply set at 18 kV. The obtained fibers were dried under room temperature overnight.

The imidization of PAA fibers were carried out by stepwise heated at 70 °C for 1 h, 100 °C for 30 min, 150 °C for 30 min, 200 °C for 30 min, 250 °C for 30 min, 300 °C for 30 min, 350 °C for 1 h. Then the imidized fibers were carbonized by stepwise heat treatments under nitrogen atmosphere at 350 °C for 1 h, 400 °C for 30 min, 500 °C for 30 min, 600 °C for 30 min, 700 °C for 30 min, 800 °C for 30 min, 900 °C for 1 h. The obtained material was PI-based CNFs.

2.3. Characterization of PI -based CNFs

The surface morphologies and structures of the PI-based CNFs were characterized by field emission scanning electron microscope (FE-SEM, FEI Sirion 200) and X-ray diffraction (XRD, Bruker F8 Focus Powder