



A novel hybrid of β -cyclodextrin grafted onto activated carbon for rapid adsorption of naphthalene from aqueous solution

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ABSTRACT

A novel hybrid material was prepared by grafting β -cyclodextrin (β -CD) onto the surface of oxidized AC for the rapid adsorption of naphthalene. AC and CDACs were characterized using the N_2 adsorption–desorption method, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and solid state CP MAS ^{13}C NMR. All the results demonstrate that β -CD grafted successfully onto AC. Batch experimental adsorption data had a higher correlation to Freundlich isotherm model and the pseudo-second-order model. The adsorption equilibrium capacity of $178.73 \text{ mg} \cdot \text{g}^{-1}$ was reached in just 10 s at an AC/ β -CD grafting ratio value of 1:1. It had a faster adsorption rate than many reported adsorbents. Additionally, the positive free energy change (ΔG°), and the positive enthalpy change (ΔH°) suggest that it is a viable, spontaneous and endothermic process, which will provided a new path to a highly-efficient and fast-adsorption-rate adsorbent for naphthalene or its analogues discharged into the environment.

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1. Introduction

With the rapid development of oil refining, surface petroleum operations and coke-making industries, more and more chemical wastewater is continuously discharged into the environment [1]. Polycyclic aromatic hydrocarbons (PAHs) are the most widespread contaminant groups, generally produced by engine exhaust, industrial outlet, crude oil and incomplete fuel combustion [2]. Naphthalene is the simplest, hydrophobic PAH and can be easily found in the environment because of its high boiling and melting points and electrochemical stability, meaning that it can accumulate in soils and water for a long time, and some of its properties was listed in Table 1 [3]. Once naphthalene enters the water system, it will present a great threat to the local ecosystem and public health, provoking such issues as water contamination, severe oxidative DNA damage and even cancer [4]. Many researchers have been attracted to the development of efficient methods to remove naphthalene from aquatic environments. A number of methodologies, including electrolysis, biodegradation, photodegradation, UV irradiation, ozonation, membrane filtration, coagulation and adsorption have been investigated [5,6]. Adsorption is the most effective and appropriate method

to use to reduce pollutants in wastewaters. Activated carbon (AC) is the most widespread adsorbent material thanks to its large specific surface area and porous structure. However, some inherent drawbacks, such as slow pollutant uptake and lower polar organic compound adsorption, still limit its use. A new path to modifying active carbon has been reported recently to solve these problems, and polyethylenimine [7], NaOCl solution [8], metallic oxide [9], Nickel hydroxide nanoplates [34] have all been used. Despite some shortcomings still existing, such as poor availability, environmental issues and expense, this new pathway can play a vital role in seeking a new eco-friendly agent for modified active carbon.


β -Cyclodextrin (β -CD) is a common inexpensive cyclic oligosaccharide easily produced from the enzymatic degradation of corn starch by bacteria [10,11]. It is characterized by a hydrophilic periphery face and a hydrophobic interior cavity, which can display an exceptional ability to selectively bind nonpolar and suitably sized aliphatic and aromatic molecules to form inclusion complexes [12]. β -CD may therefore have the potential application of removing naphthalene from wastewater. However, its solubility in water impedes its practical application in aqueous systems and a hybrid of β -CD grafted onto activated carbon could be a promising approach. β -CD has been grafted onto the surface of various materials, such as silica nanoparticles [13], magnetic graphene [Duan et al., 2016], multiwall carbon nanotubes [14], as functional molecules to remove contaminants in aqueous solution. Meanwhile, AC possesses various functional groups and can be easily obtained [15]. Nevertheless, only few researchers have used β -CD to graft AC in recent years. Fuhrer et al. have developed a path to

Abbreviations: β -CD, β -cyclodextrin; AC, activated carbon; HMDI, hexamethylene diisocyanate; DMF, N, N-dimethylformamide; CDACs, The novel hybrid of graft β -cyclodextrin on the surface of activated carbon; BET, Brunauer–Emmett–Teller; FTIR, Fourier transform infrared spectroscopy; TGA, Thermogravimetric analysis.

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Table 1
Representative properties of naphthalene.

PAHs	Structure	Molecular	Size(Å × Å × Å)	Molar volume (cm ³ /mol)	Solubility (ng/g)	logKow
Naphthalene		C ₁₀ H ₈	9.1 × 7.3 × 3.8	148	30,800	3.30

immobilize β -CD on surface-modified carbon-coated cobalt nanomagnets and investigated the adsorption of organic contaminant, meanwhile, Kwon et al. researched the synthesis, characterization and adsorption process of modified AC with β -CD [16,17]. So, this could be provided us with an opportunity to develop a novel, efficient and green hybrid for the rapid removal of naphthalene.

β -CD has been grafted onto the surface of AC, using hexamethylene diisocyanate as the cross-linking agent in *N,N*-dimethylformamide, in order to improve its adsorption rate and naphthalene eliminating efficacy in the case of a large amount of pollutants in an aqueous system [18]. The obtained hybrids have been characterized using the N₂ adsorption–desorption method, Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and solid state CP MAS ¹³C NMR. In this work, adsorption kinetics were used to study the relationship between contact time and adsorption capacity in order to determine equilibrium time and equilibrium capacity, while pseudo-first-order and pseudo-second-order models were used to fit the experimental data and illustrate the adsorption mechanism. Furthermore, Langmuir, Freundlich and Temkin models were used to fit the adsorption isotherm and identify the adsorption process and practical applications. This paper provides a new pathway to the development of a promising and appropriate adsorbent for the quick adsorption of naphthalene and its analogues in case of emergency.

2. Materials and experimental methods

2.1. Materials and chemicals

AC was purchased from Farmlabor, Italy. Biological reagent (>99.0%) β -Cyclodextrin was purchased from Sichuan Kelong chemical reagent, China. Nitric acid and ethyl alcohol were used analytically pure and were purchased from Tianjin Fengchuan chemical reagent and Tianjin Fuyu fine chemical reagent, China, respectively. *N,N*-dimethylformamide (DMF) 99.8% was obtained from Adams reagent co. LTD and (HMDI) 98% was obtained from Tokyothe Chemical Industry. Naphthalene 98% was purchased from Aladdin reagent Co. LTD.

2.2. Grafting β -CD onto the AC surface

Firstly, AC (2.00 g) was mixed with 10% nitric acid (100 mL) in a 250 mL conical flask and shaken in a thermostatic shaker water bath at ambient temperature at 150 rpm for 3 h. The treated AC was then separated from the liquid by filtration and the solid phase was washed in distilled water repeatedly until the pH value of the last residual solution drop was near 7.0. The treated AC was then dried in an air oven at 80 °C for 4 h. 1.0 g of the obtained AC was dispersed in 5 mL of *N,N*-dimethylformamide (DMF) by sonication and this solution mixture was then added to round bottom flasks containing various quantities of β -CD (0.25 g, 0.5 g, 1.0 g, 1.25 g, 1.5 g) and 40 mL DMF. A bifunctional linker, HMDI (1 mL) was added to this mixture drop-wise. The resulting mixtures were stirred at 1000 rpm and heated in an oil bath at 70 °C for 7 h under inert conditions, under N₂. These composites were washed in alcohol and distilled water repeatedly, then centrifuged and the obtained composite polymers were dried in an air oven at 80 °C for 4 h. The composite hybrids were marked as CDAC0.25, CDAC0.5, CDAC1.0 and CDAC1.5.

2.3. Characterization methods

2.3.1. Brunauer-Emmett-Teller (BET) surface area and pore size

The physical surface properties of AC and CDACs were determined using the nitrogen adsorption–desorption method (Micrometrics Instrument 3Flex). The samples were degassed under N₂ flow at 350 °C for 6 h before an adsorption isotherm was generated by N₂ at 77 K. The surface area (S_{BET} , m²·g⁻¹) was calculated using the BET equation. The total pore volume (V_{T} , cm³·g⁻¹) was obtained from the adsorption isotherm at $P/P_0 = 0.1516$, while the microspore area (S_{mic} , m²·g⁻¹), microspore volume (V_{mic} , cm³·g⁻¹) and external surface area (S_{e} , m²·g⁻¹) were analysed using the t-plot method. The average pore size was calculated using Eq. (1).

$$r = \frac{4V_{\text{T}}}{S_{\text{BET}}} \quad (1)$$

2.3.2. Fourier transform infrared (FTIR) spectrometer

Samples were dried at 80 °C for 24 h before analysis. The FT-IR spectra of AC, β -CD and CDAC1.0 were recorded on a Nicolet Magna-IR 750 spectrometer, which used KBr as the background over the frequency range of 4000–400 cm⁻¹.

2.3.3. Thermogravimetric analysis (TGA)

A TAQ600 was used to determine the weight loss of AC, β -CD and CDAC1.0, while thermal analysis was carried out at a heating speed of 10 °C/min from room temperature to 800 °C.

2.3.4. Solid state CP MAS ¹³C NMR

The solid state NMR (¹³C CP MAS) data of CDAC1.0 and β -CD was measured under an 11.74 T magnetic field for <10 μ s in a Bruker ER200-SRC to identify the chemical structures.

2.4. Adsorption experiments with naphthalene

The use of ethanol (4% v/v) as a co-solvent improved the solubility of naphthalene in aqueous solution. Batch adsorption kinetics, adsorption isothermal and adsorption thermodynamics were studied. The initial concentration of naphthalene was 30 mg·L⁻¹ during adsorption kinetic studies and adsorbents (15 mg) were added to the naphthalene solution (100 mL), then shaken in a thermostatic shaker water bath at 25 °C at a speed of 150 rpm for a given time. The adsorption times were set at 2 s, 5 s, 10 s, 30 s, 2 min, 5 min, 10 min and 20 min and every adsorption time was repeated twice. The liquid phases were separated by filtration. Naphthalene concentrations were measured using a UV-75 N spectrophotometer at 219 nm. The adsorption amount of naphthalene q_t (mg·g⁻¹) at time t (s) can be calculated according to Eq. (2):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0 and C_t (mg/L) are the liquid phase concentration of naphthalene at the initial concentration and at any time t (s), respectively. m (g) is the adsorbent dose and V (L) is the volume of naphthalene solution.

Batch adsorption was conducted in 150 mL conical flasks at three different temperatures (297, 313 and 321 K) during adsorption

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