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Adsorption of bulky molecules of nonylphenol ethoxylate on ordered mesoporous carbons

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Abstract

Ordered mesoporous carbons (OMCs) with varying pore sizes were prepared using ordered mesoporous silica SBA-15 as hard templates. The OMCs possess abundant mesopores with narrow pore size distribution, on which the adsorption behavior of bulky molecules of nonylphenol ethoxylate (NPE) were investigated. The isotherms of NPE on OMCs can be fitted by Langmuir adsorption model, evidenced by the adsorption data. The surface area of the pores larger than 1.5 nm is a crucial factor to the adsorption capacity of NPE, whereas the most probable pore diameter of OMCs is crucial to the adsorption rate of NPE. The adsorption temperature has more significant effects on adsorption rate than the adsorption capacity. Theoretical studies show that the adsorption kinetics of NPE on OMCs can be depicted with the pseudo-second-order kinetic model. In addition, thermodynamic parameters of adsorption were evaluated based on the equilibrium constants related to the equilibrium of adsorption at different temperatures.

Keywords: Adsorption; Bulky molecule; Mesoporous carbon; Mesoporous silica; Adsorption isotherm; Adsorption kinetics

1. Introduction

Discharge of wastewater/effluent containing organic pollutants into natural surface waters poses serious risk to aquatic organisms and human beings besides imparting a carbolic odor to the receiving water. Phenolic compounds are frequent contaminants of ground water because of their wide use in industrial sectors [1]. These are widely present in the effluents such as those generated from coal tar, plastics, leather, paint, pharmaceutical, steel, textile, timber, paper pulp, insecticides, pesticides, and oil refineries [2]. Contamination of groundwater aquifers with phenolic compounds has been reported [3]. A series of diseases such as liver damage, diarrhea, mouth ulcers, dark urine and hemolytic anemia could be caused by repeated exposure to low levels of phenol in water. In animals, spilling of dilute phenol solution on the portion greater than 25% of the body surface may result in death [4]. Phenols have been registered as priority pollutants by the U.S. Environmental Protection Agency (USEPA) with a permissible limit of $0.1\ \text{mg}\,\text{L}^{-1}$ in wastewater [5].

The methods for the treatment of water containing phenolic wastes include microbial degradation [6], chemical oxidation [7], photocatalytic degradation using TiO_2 [8], sonophotochemical [9], ultrasonic degradation [10], enzymatic polymerization [11], adsorption [12], etc. Among these, adsorption offers an efficient and economically feasible technology for the removal of phenolic contaminants from wastewaters. Selective adsorption utilizing biological materials, mineral oxides, and activated carbon or polymer resins has developed great interest among the researchers and environmentalists. Activated carbon has been a dominant adsorbent in the liquid-phase adsorption, especially in wastewater treatment. In principle, the prominent adsorption performance of activated carbon for organic pollutants was attributed to its abundant pore structure and large specific surface area. However, the previous researches showed that micropores (<2 nm) were dominant in common activated car-

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bons, so that bulky molecules or macromolecules cannot easily penetrate into the micropores and adsorb onto them. Therefore, the performance of common activated carbon in bulky molecules adsorption is rather constrained due to the microporous nature of activated carbon [13–15].

Mesoporous (2–50 nm) carbon with open pore structure and large pore size have remarkable advantages in bulky molecular adsorption [16]. Kennedy et al. [17] studied the adsorption of bulky phenol onto the mesoporous carbon prepared from rice husks through two stages and displayed the superior adsorption capacities of mesoporous carbon for bulky phenol. Tanthapanichakoona et al. [18] studied the adsorption of phenol and dyes onto the mesoporous carbon prepared from waste tires using steam activation and found that the adsorption capacities of mesoporous carbon for phenol, Black 5 and Red 31 were higher than that of commercial activated carbon. It should be pointed out that the pore structures of these mesoporous carbons consist of both micropores and mesopores with a broad pore size distribution and disordered pore arrangement, which is an intrinsic trait of porous carbon prepared by steam activation. Therefore, this led to the difficulty in understanding the precise adsorption mechanism of bulky molecules over mesopores.

Compared with above-mentioned mesoporous carbon, ordered mesoporous carbons (OMCs) [19,20] have such advantages as periodic pore symmetry, large pore volume, high specific surface area, centralized mesopore distribution, and tunable pore diameter. So OMCs could be ideal model materials for studying the adsorption properties and mechanism of bulky phenolic compounds on mesopores. Although adsorption kinetic studies on common activated carbon have been well documented, very few study [21] on the adsorption of bulky molecules of phenolic compounds over OMCs has been reported in the literature. In this work, a series of OMCs with tuned pore sizes were prepared using a group of hard templates and tested as adsorbents for the bulky molecules of a phenolic compound, which revealed the adsorption behavior of the OMCs to the phenolic molecules. The effects of temperature and pore-structures such as pore size, pore volume and surface area were investigated.

2. Materials and methods

2.1. Preparation of OMCs

SBA-15 was prepared using Pluronic P123 (nonionic triblock copolymer, $EO_{20}PO_{70}EO_{20}$, BASF) as a surfactant and tetraethoxysilane (TEOS, 98%, Acros) as a silica source, according to Zhao et al [22,23]. Briefly, 32 g P123 was dissolved in 1000 g distilled water and 200 g HCl (35 wt%) solution at 35 °C and 68.8 g TEOS was then added. After the solution was magnetically stirred at 35 °C for 15 min, the mixture was retained at 35 °C for 24 h, and aged at 40 °C for another 24 h. The resulting deposit was recovered by filtration and washed with ethanol. Subsequently, the sample was calcined at 550 °C for 6 h in air to remove the surfactant completely. The product thus obtained was referred to as SBA-15-40. Keeping the preparation conditions unchanged except for the aging temperature, the samples aged at 70, 100, and 130 °C were referred to as SBA-15-70, SBA-15-100, and SBA-15-130, respectively.

Ordered mesoporous silica was employed as hard template for preparation of OMCs. Typically, 1 g of SBA-15-40 was mixed homogeneously with 5 ml of aqueous solution containing 0.68 g of sucrose and 0.07 g of H_2SO_4 (98 wt%). The amount of sucrose used is expected to just fill up the pores of SBA-15. The resulting sludge was dried at 100 °C for 6 h, and subsequently, 160 °C for another 6 h. Afterwards, the dried sucrose/silica composite was again impregnated with an aqueous solution consisting of 0.4 g sucrose, 0.05 g H_2SO_4 and 5.0 g H_2O. The resultant mixture was dried again at 100 and 160 °C. The second sucrose infiltration step aims at completely filling up the pores of SBA-15. The material thus obtained was heated to 900 °C in argon atmosphere. The sucrose was converted to carbon by such a process using sulfuric acid as catalyst. Finally, the silica framework was removed by dissolution in HF (10 wt%) aqueous solution. The resultant porous carbon material is referred to as OMC-40. Employing the same preparation strategy, OMCs derived from SBA-15-70, SBA-15-100, and SBA-15-130 were referred to as OMC-70, OMC-100, and OMC-130, respectively.

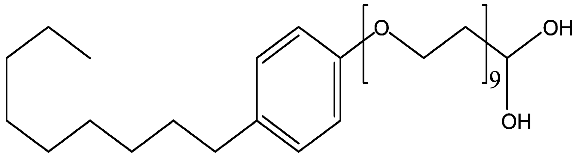
2.2. Material characterization

ASAP2010 (Micromeritics, USA) was used to characterize the surface area and pore-structure of the samples using N_2 sorption under −196 °C. The samples were degassed at 200 °C overnight before measurements. BET surface area was calculated by using the BET equation. The total pore volume (V_T) was obtained at $P/P_0 = 0.995$, and the pore size distribution was calculated by the BJH (Barrett, Joyner, Halender) method using the desorption branch of the isotherm.

2.3. Adsorption capacity of nonylphenol ethoxylate (NPE)

NPE is a bulky molecule with molecular weight of 646.8, of which the chemical structure is illustrated in Scheme 1. Since absorbency but not concentration is determined by spectrophotometer, establishment of a linear Beer-Lambert relationship is necessary. First, NPE solutions with different concentrations were prepared. Then the absorbency of NPE solutions was determined using a spectrophotometer (Model UV757CRT) at the wavelength of 223 nm.

The adsorption of NPE from aqueous solution onto carbon samples was performed by using batch equilibrium technique. Typically, 30 mg of OMC sample was introduced into glass tubes containing 30 ml of NPE solution with initial concentrations ranging from 1700 to 3100 mg L^{-1}. These tubes were transferred into a shaker and shaken for 24 h in order to reach



Scheme 1. Chemical structure of a NPE molecule.