Journal of Colloid and Interface Science 452 (2015) 134–140

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

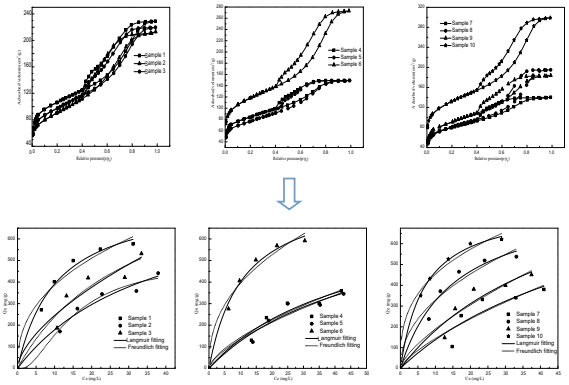
www.elsevier.com/locate/jcis

# Enhancing adsorption efficiency of dichloroacetic acid onto mesoporous carbons: Procedure optimization, mechanism and characterization

Ying Ding, Jianzhong Zhu *, Dongliang Ji, Yang Cao, Xiaojia Ling, Wei Chen

*Key Laboratory for Integrated Regulation and Resource Development on Shallow Lake of Ministry of Education, College of Environment, Hohai University, Nanjing 210098, China*

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 27 January 2015
Accepted 19 April 2015
Available online 25 April 2015

*Keywords:*
Mesoporous carbon
Thermal reaction optimization
Dichloroacetic acid
Adsorption

## ABSTRACT

Highly ordered mesoporous carbon may be directly synthesized via supramolecular self-assembly with in situ evaporation-induced crystallization process by controlling thermal reaction temperatures and carbon mass loading. In the present study, the effects of thermal reaction temperatures on the structural characterization and adsorption capacity of mesoporous carbon have been investigated and analyzed with orthogonal test experiments. The results show the carbonization temperature ($R = 32.1$) plays a more important role than the self-assembly temperature ($R = 8.5$) and thermal polymerization temperature ($R = 10.1$) in manipulating the pore texture structures. The optimization grouping temperature was 40–110–500 °C. The optimum mesoporous carbon sample had the highest BET specific surface area (474 $m^2/g$), the largest pore volume (0.46 $cm^3/g$), and with reasonable uniform pore size distribution. The adsorption evaluation also shows the adsorption capacity is strongly correlated with the pore structure of mesoporous carbon, the optimized mesoporous carbon sample displayed the largest adsorption capacity (350 mg/g) at an initial concentration of 20.0 mg/L of dichloroacetic acid. The study results indicate optimization of thermal reaction parameters is an effective approach for synthesis of ordered mesoporous carbons.



## 1. Introduction

As one of the most important public health advances of the last century, application of water disinfection reduced cholera incidence by 90%, typhoid by 80% and amoebic dysentery by 50% in the U.S. [1]. The chlorination of drinking water has for several decades been playing a leading role in reducing mortality and morbidity rates associated with waterborne pathogens [2]. Disinfection by-products (DBPs) are mainly formed when disinfectants react with naturally-occurring organic matter and anthropogenic contaminants, such as bromide and iodide, during the production of

* Corresponding author.
*E-mail address:* zhuhhai2010@hhu.edu.cn (J. Zhu).

http://dx.doi.org/10.1016/j.jcis.2015.04.040
0021-9797/

drinking water [3]. Recently much research has found out that some diseases have close relationship with $DBP_S$ which are believed to be harmful to human health. The control of haloacetic acids (HAAs) such as dichloroacetic acid [4–6] is a challenge and a necessity because of the uncertainty of their generation mechanisms upon halogenations of natural organic matter (NOM) in drinking water, the high hydrophilicity, high yield at pH < 7 and the health effects that are putatively associated with them [7].

Adsorption process for separation and purification of disinfection by-products like dichloroacetic acid from drinking water is believed to be widely used, effective and simple to operate. Some commercial adsorbents including silica gel ($SiO_2$), alumina ($Al_2O_3$), activated carbon, polymer resins and minerals such as bentonites and zeolites have been used for purifying disinfection by-products [8–10]. However, high adsorption capacity, high selectivity and efficient regeneration are difficult to achieve on these conventional adsorbents. It is an exhilarating task to make development in effective adsorbents with high adsorption capacity, high selectivity and efficient regeneration. In this work, synthetic material achieved a good pore structure through the optimization of synthetic temperature.

The properties of mesoporous carbons such as high specific surface areas, large pore volume, regular and tunable pore structures, along with good mechanical stability [11,12], make these materials be an attractive adsorbent. Mesoporous carbon materials have been proven to be very efficient in application of removing environmental pollutants such as organic compounds from wastewater [13–17] and adsorptive purification of biomolecules from aqueous solutions [18,19]. Normally, mesoporous carbons can be produced through the hard template [20] or the soft template approaches [21,22]. Process optimization is effective to adjust the mesoporous structure to material synthesis such as thermal reaction parameters. Triblock copolymers Pluronic F-127 and P-123 are two commonly used soft templates [23–25] for adjusting the pore size of mesoporous carbons. Other previous studies of adsorption of disinfection by-products on mesoporous carbons have suggested that mesoporous carbon is a promising adsorbent for effective adsorption and purification of dichloroacetic acid from the drinking water. However, available experimental data are currently limited about the adsorption of disinfection by-products such as dichloroacetic acid on mesoporous carbons, and no literature is available about the relationship between pore textural properties of mesoporous carbons and their adsorption properties for dichloroacetic acid, which is essential for identifying suitable mesoporous carbon adsorbents.

The main objective of this work was to explore the effects of the thermal reaction parameters on the pore textures of mesoporous carbon adsorbents, to establish the relationship between the pore textural properties of mesoporous carbons and adsorption properties for dichloroacetic acid, to identify suitable mesoporous carbon adsorbents for this application, and to provide a process optimization method for preparing best structure of mesoporous carbon material. Ten mesoporous carbon adsorbents were synthesized, characterized, and evaluated for adsorption of dichloroacetic acid from aqueous solutions by batch adsorption equilibrium experiments. The optimized adsorption results obtained were compared with those on other mesoporous carbons.

**Table 1**
The main properties and the thermal reaction parameters of the mesoporous carbons.

| Sample | Thermal reaction parameters (self-assembly temperature; thermal polymerization temperature; carbonization temperature) °C | BET specific surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Average pore diameter (nm) |
|---|---|---|---|---|
| Sample 1 | 40; 90; 500 | 383 | 0.35 | 3.698 |
| Sample 2 | 40; 100; 700 | 327 | 0.33 | 4.079 |
| Sample 3 | 40; 110; 900 | 349 | 0.34 | 3.898 |
| Sample 4 | 50; 90; 700 | 307 | 0.23 | 3.041 |
| Sample 5 | 50; 100; 900 | 275 | 0.23 | 3.352 |
| Sample 6 | 50; 110; 500 | 425 | 0.42 | 3.979 |
| Sample 7 | 60; 90; 900 | 292 | 0.22 | 2.977 |
| Sample 8 | 60; 100; 500 | 292 | 0.30 | 4.133 |
| Sample 9 | 60; 110; 700 | 326 | 0.28 | 3.493 |
| Sample 10 | 40; 110; 500 | 474 | 0.46 | 3.901 |

## 2. Experimental

### 2.1. Materials

The triblock copolymer Pluronic F127 and formaldehyde solution (36.5–38 wt.%) were obtained from Sigma–Aldrich. Phenol and dichloroacetic acid (>98% purity) were purchased from Nanjing chemical reagent Co., Ltd. (Nanjing, China), AR grade ethanol, phenol, HF, HCl, NaOH were from Nanjing the preferred chemical Co., Ltd. (Nanjing, China). All these materials were used without further purification.

### 2.2. Synthesis of resol precursors

A soluble phenolic resin resol was synthesized from phenol and formaldehyde solution in a base-catalyzed process. 6.1 g of phenol was melted at about 40 °C in a flask, 1.3 g of 20 wt.% NaOH aqueous solution was then added into the melted phenol and the solution was mixed with 10.5 g of formaldehyde solution under stirring. After being stirred for 1 h at 70 °C, the mixture was then cooled to room temperature. The pH of the mixture was adjusted with a 0.6 mol/L HCl solution to about 7, and water was removed at 50 °C in a vacuum oven. The final product was dissolved in ethanol to obtain a 20 wt.% phenolic resin resol ethanolic solution.

### 2.3. Synthesis of mesoporous carbons

The mesoporous carbon samples were synthesized with the preformed phenolic resin resol solution as a carbon resource, and triblock copolymer F127 as templates in an ethanol solution. The synthesis compositions were phenol resin/F127 (mass ratio) = 1:1 [26]. In a typical preparation, 5.0 g of 20 wt.% preformed phenolic resin resol solution, 1.0 g of F127 and 19.0 g of ethanol were then added into the mixture under stirring for about 10 min until F127 was completely dissolved, and a homogeneous solution was obtained [27,28]. After that, the solution was poured into an uncovered petri dish to evaporate ethanol at 40–60 °C for about 12 h, then held at 90–110 °C in a muffle furnace for 24 h and the detailed thermal reaction parameters is listed in Table 1. Synthesis temperature of the sample 10 depends on the orthogonal analysis of experimental results of samples 1–9 adsorption removal rate of dichloroacetic acid. The orthogonal analysis of experimental conditions and results can be seen in Tables 2 and 3. The transparent film obtained after those steps was loaded in a quartz boat for calcination in a nitrogen atmosphere with a flow rate of 70–100 $cm^3$/min. Calcination was carried out in a tubular furnace at 400 °C for 6 h first to remove the triblock copolymer template, followed with a carbonization step at 500–900 °C for 3 h, and the heating rate was set to be 0.5–3.0 °C/min throughout