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Adsorption dynamics of methyl violet onto granulated mesoporous carbon: Facile synthesis and adsorption kinetics

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ABSTRACT

A new and facile one-step synthesis method for preparing granulated mesoporous carbon (GMC) with three-dimensional spherical mesoporous symmetry is prepared to remove large molecular weight organic compounds in aqueous phase. GMC is synthesized in a single step using as-synthesized mesoporous carbon particles and organic binders through a simple and economical synthesis approach involving a simultaneous calcination and carbonization process. Characterization results obtained from SEM, XRD, as well as surface and porosity analysis indicate that the synthesized GMC has similar physical properties to those of the powdered mesoporous carbon and maintains the Brunauer-Emmett-Teller (BET) surface area and pore volume because the new synthesis method prevents the collapse of the pores during the granulation process. Batch adsorption experiments revealed GMC showed a substantial adsorption capacity (202.8 mg/g) for the removal of methyl violet as a target large molecular contaminant in aqueous phase. The mechanisms and dynamics modeling of GMC adsorption were also fully examined, which revealed that surface diffusion was rate limiting step on adsorption process of GMC. Adsorption kinetics of GMC enables 3 times faster than that of granular activated carbon in terms of surface diffusion coefficient. This is the first study, to the best of our knowledge, to synthesize GMC as an adsorbent for water purification by using facile granulation method and to investigate the adsorption kinetics and characteristics of GMC. This study introduces a new and simple method for the synthesis of GMC and reveals its adsorption characteristics for large molecular compounds in a water treatment.

1. Introduction

Among various water treatment techniques, adsorption is one of the promising technologies for removal of organic contaminants due to its high efficiency, convenience, and feasibility (Ghorai et al., 2014; Gupta and Ali, 2008; Ma et al., 2012). Activated carbon is one of the most versatile adsorbents and is widely used for removal of organic compounds due to its high surface area and large pore volume (Azizian et al., 2009; Malik, 2004). However, it is only effective for adsorption of small molecular compounds because of its narrow pore size distribution and microporous structure (Ji et al., 2010). Large molecular compounds can block the pores of activated carbon surface or serve as precursors to toxic chemicals in water (Li et al., 2003b; Pelekani and Snoeyink, 1999).

The drawbacks of activated carbon can be overcome by the use of mesoporous carbon, which has meso-sized pores (from 2 to 50 nm). Increasing attention has been focused on mesoporous carbon in water treatment processes for removing large molecular contaminants since the introduction of ordered mesoporous carbon, CMK-1, developed using mesoporous silica MCM-48 as a template by Ryoo in 1999 (Ryoo et al., 1999). For example, macromolecule organic compounds such as natural organic matter, vitamin E, methylene blue, orange II, remazol red 3BS, and reactive black 5 were effectively removed by mesoporous carbon materials because of their mesopores (Asouhidou et al., 2009; Cheng et al., 2012; Hartmann et al., 2005; Liu et al., 2011; Yuan et al., 2007).

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Although mesoporous carbon has great adsorption performance in aqueous phases, it mainly has two limitations that preclude environmental application: 1) only a few studies have been performed to identify the adsorption mechanisms of organic contaminants onto mesoporous carbon in terms of sorption characteristics and dynamics; and 2) mesoporous carbon has inevitable limitations related to engineering applications, such as separation and recovery for reuse and regeneration, severe pressure drop, and retarded mass transfer rate in fixed bed reactors due to its powder form (El-Safty et al., 2005; Kim et al., 2014; Yang et al., 2002).

To overcome the problems of powder-type materials, powder-typed mesoporous carbon needs to be transformed into a granular-type material with higher mechanical strength. However, granulation also has limitations as it can severely reduce or change the physical properties due to the pressure required by the granulation process and the complicated synthesis procedures (Kim et al., 2014; Saini et al., 2011). Therefore, the development of new and improved methods is necessary for the synthesis of granulated mesoporous carbon materials to extend their performance.

In the current study, we introduce a new, facile, eco-friendly, and economical synthesis method for the production of granulated mesoporous carbon (GMC) with three-dimensional spherical mesoporous symmetry structure. It is a one-step synthesis involving a simultaneous carbonization and calcination process that uses as-synthesized mesoporous carbon particles and direct carbonization of silica/surfactant nanocomposites. Granulation of the powdered mesoporous carbon is achieved using polyvinyl alcohol, carboxymethyl cellulose, and microcrystalline cellulose as organic binders. These cheap organic polymers can replace high cost resins and polymers and create extra meso/macropores in the final product upon their removal during the calcination process at extremely high temperature. This generates new pores and pathways for diffusion of the adsorbates into the adsorbent. Also, this new synthesis method results in a decreased energy consumption and lower production cost by reducing the number and duration of calcination steps and by eliminating the need for incorporation of carbon precursors into the pores of a template material. The synthesized GMC is a suitable material that retains its physical properties even after granulation and provides high mechanical stability for application in aqueous phases. Methyl violet is selected as a target large molecule (molecular weight: 393.95 g/mol) that is frequently detected in wastewaters of various industries such as cosmetics, food, textile, and paper manufacturing (dos Santos et al., 2007; Janoš, 2003). The major concern of widespread dyes in water systems is that they are carcinogenic and cause hypersensitivity reactions and behavioral problems in humans (Chung and Stevens, 1993; Vanhulle et al., 2008; Wong and Yu, 1999). The feasibility of using this GMC for water purification was investigated by evaluating the adsorption characteristics of methyl violet dye onto the GMC in terms of adsorption kinetics, isotherms, and dose effects. The adsorption dynamics of GMC was also delineated by a computational modeling approach to determine surface diffusion and external mass transfer. To the best of our knowledge, this is the first attempt to synthesize GMC that maintains physical properties of powder-type mesoporous carbon and to evaluate the adsorption dynamics, mechanisms, and the mesopore effect of a GMC on adsorption processes.

2. Materials and method

2.1. Chemicals

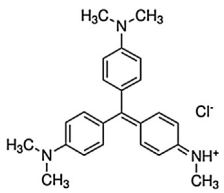
Pluronic P123 (P123, Aldrich) was used as structure-directing agent and carbon source; tetraethylorthosilicate (TEOS 98%, Aldrich) as a silica template; hydrochloric acid (HCl, 37%, Samchun chemical) and trimethylbenzene (TMB 98%, Kanto chemical) as pore forming agents; sulfuric acid (98%, Duksan chemical) as a dehydration catalyst for crosslinking of the polymeric chains by removing the H_2O in P123; polyvinyl alcohol (PVA, 97% (MW: 30,000–32,000), OCI company), and carboxymethyl cellulose (CMC, Aldrich) and microcrystalline cellulose (MCe, Aldrich) as organic binders for the synthesis of GMC carbon adsorbents. Methyl violet (MV, Sigma-aldrich) was used as a target compound because it is widely used and frequently detected in water environment (Mittal et al., 2008). The Physicochemical properties of MV are presented in Table 1. Granular activated carbon (GAC, coal-base, 8–12 mesh, Samchun chemical) was purchased for comparison purposes.

2.2. Synthesis and characterization of mesoporous carbon materials

The direct synthesis of the as-synthesized powdered mesoporous carbon consisting of TEOS/Pluronic P123 triblock copolymer/TMB nanocomposite was described previously (Kim et al., 2004). In detail, 60 g of P123 was completely dissolved in a solution of 1560 ml of deionized water and 252 ml of hydrochloric acid at 313 K for 4 h. The P123 solution was reacted with 51.6 ml of TMB for 1 h and 110.4 ml of TEOS was then added to form TEOS/P123/TMB nanocomposite. The solution was stirred at 250 rpm for 24 h at 313 K and aged at 373 K for 24 h. The resulting white particles were filtered, mixed with a mixture of 280 ml of deionized water and 5.6 ml sulfuric acid for 1 h, and then dried at 373 K. The obtained as-synthesized mesoporous carbon was directly used in the granulation process. PVA, CMC, and MCe, used as organic binders, and 24 ml of DI water were mixed with 60 g of the as-synthesized mesoporous carbon to obtain GMC-PVA, GMC-CMC, and GMC-MCe, respectively. The mixture of TEOS/P123/TMB and organic binder were passed through a twin extruder instrument to create the granular shape. These organic binders can interconnect each as-synthesized mesoporous carbon particle and generate extra meso/macropores upon removal by burning during the calcination step (Kim et al., 2014). The resulting granules were dried at 373 K in an oven and calcined at 1173 K in a box furnace under nitrogen gas to transform the P123 (cross-linked polymer chains) to carbonaceous compounds and to eliminate the TMB and organic binders to form mesopores and new extrapores. The remaining silica template was removed with 10 wt% hydrofluoric acid in a 50:50 mixture of deionized water and ethanol (Fig. 1).

The final granulated mesoporous carbon materials (GMC, 8–12 mesh of granule size) were obtained by this new, facile, direct, and economical synthesis method. It has the main advantages of direct use of the as-synthesized mesoporous carbon particles for

Table 1
Physicochemical properties of MV.

Dye	Methyl violet 2B (MV)
Generic name	Basic violet 1
Molecular weight	393.95
Chemical Formula	$C_{24}H_{28}ClN_3$
Colour index number	42,535
λ_{max}	580 nm
Chemical structure	
	(3.51 nm^2)