



# Polyol derived sulfonated solvothermal carbon for efficient dye removal from aqueous solutions

Ali Can Zaman

Science and Technology Application and Research Center, Yildiz Technical University, 34349 Yildiz-Besiktas, Istanbul, Turkey



## ARTICLE INFO

### Article history:

Received 19 July 2017

Received in revised form 15 October 2017

Accepted 20 November 2017

Available online 22 November 2017

### Keywords:

Solvothermal synthesis

Sulfonation

Carbon nanoparticle

Methylene blue

Water purification

Dye removal

## ABSTRACT

Solvothermal carbonization of ethylene glycol was employed for the synthesis of nanostructured sulfonated carbon in which sulfuric acid was used as the synthesis medium. The existence of sulfonic acid ( $\text{SO}_3\text{H}$ ), carboxylic acid ( $\text{COOH}$ ), and many other functional groups was determined by FTIR and TG-FTIR (Thermogravimetric Analysis-Fourier Transform Infrared Spectroscopy). Synthesized bulk material consisted of  $68.46 \pm 20.19$  nm sized quasi-spherical carbon particles according to Scanning electron microscopy (SEM) observations. X-ray diffraction (XRD) analysis revealed that the material was a turbostratic type carbon. Formation mechanism of sulfonated solvothermal carbon (SSC) is believed to involve ethylene and ethylene glycol oligomers. Namely, carbon carbon bond forming reactions take place between aliphatic intermediate molecules under high temperature-high pressure conditions by constituting randomly oriented carbon aromatic frameworks connected by aliphatic short chains, meanwhile functionalization (e.g., sulfonation) processes take place. Experimentally maximum adsorption capacity for methylene blue (MB) under basic conditions (pH 11) was determined to be  $1472.61 \text{ mg g}^{-1}$  while initial MB/carbon weight ratio was  $1500 \text{ mg g}^{-1}$  and over 96% removal was achieved within <240 min. It was demonstrated that SSC is an excellent adsorbent for the removal of dye pollutants from aqueous systems.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Carbonaceous materials are versatile. Because they may find use in many applications including pollutant removal [1], supercapacitor applications [2], Li-ion batteries [3] and catalysis [4–7]. Activated carbon is among those materials. For a specific purpose the production methods of carbon materials need to be carefully chosen since they have to possess suitable chemical and physical properties. Classical carbonization method is pyrolysis of carbon precursors like coal, lignin, saw dust etc., which is the elimination of non carbon species using thermal decomposition [1]. Pyrolysis is energy-consuming [8]. And frequently activation is needed for these materials. In addition, among many functionalized carbons, sulfur containing (thiolated, sulfonated) carbons are becoming attractive because they are promising in applications like water treatment and catalysis [7]. Presence of  $-\text{SO}_3\text{H}$  groups along with the presence of other functional groups like  $-\text{COOH}$  and  $-\text{OH}$  is known to cause carbonaceous materials to possess high catalytic performance and high adsorption capacity even though these materials exhibit small specific surface areas [9]. For example, Z. Jia et al. produced PVA microspheres treated with concentrated  $\text{H}_2\text{SO}_4$  under solvothermal method with carbonization of microspheres [10]. The produced sulfonated material exhibits  $925.9 \text{ mg g}^{-1}$  MB adsorption efficiency at  $45^\circ\text{C}$ . Shen et al.

produced sulfonated graphene nanosheets by sulfonation of graphene oxide with the aryl diazonium salt of sulfanilic acid [11]. They reached  $906 \text{ mg g}^{-1}$  adsorption maximum over MB for sulfonated graphene, the efficiency was limited to  $623 \text{ mg g}^{-1}$  for graphene oxide in the same study. Imaizumi et al. reached  $943.1 \text{ mg g}^{-1}$  adsorption capacity for MB with synthesized sulfonated carbon nanofibers [12]. As an example of importance of presence of sulfonic acid groups, He et al. reached similar specific surface area with carbon monoliths [13], but they couldn't reach MB removal efficiency ( $127 \text{ mg g}^{-1}$ ) of sulfonated carbon fibers due to limited amount of functional groups, and especially due to lack of  $-\text{SO}_3\text{H}$  groups.

Preparation of thiolated or sulfonated carbon is generally conducted by post-processing of a carbon material (synthetic carbon or coke etc.), by subjecting it to activation with sulfur compounds [8]. Frequently used sulfonation compounds are oleum, sulfuric acid, and free sulfur trioxide, halogen derivatives of sulfuric acid which all are derived from sulfur trioxide [14]. These processes require acquiring or synthesizing the carbon material firstly, and subsequently sulfonation of the material is carried out such as in the production of sulfonated carbon/nano-metal oxide composites in the study of Kour et al. [15]. Multi steps for preparations are prerequisite and time-consuming.

As opposed to pyrolysis, Hydro(solv)thermal synthesis could be used to synthesis carbons under mild conditions. Hydrothermal carbonization is well-known example of one step preparation route: a synthetic

E-mail address: [alicanzaman@gmail.com](mailto:alicanzaman@gmail.com).

way to produce functional carbons by using carbohydrates studied by many authors such as Titirici and co-workers [16]. Using specific precursor materials (carbohydrates) and using aqueous solvents may limit attachment of desired functional groups on evolved carbons under subcritical conditions. However, as an example of multi-step preparation, there are studies of successful functionalization of these materials with sulfonic acid groups by post treatments such as in the work of Sevilla et al. [17]. Though there are examples of using water as medium for preparation of functionalized (sulfonated) carbons in one step [18], by selecting an appropriate precursor and non-aqueous medium combination for carbonization-functionalization may open new possibilities such as in the work of Wang et al. [19]. Therefore solvothermal carbonization (more energy-saving than pyrolysis and subsequent activation) could be used as a one step process for the preparation of functionalized carbons.

Hydrothermal synthesis has some drawbacks compared to solvothermal synthesis. Namely, sulfonation reaction of benzene is reversible under the presence of water, thus hydrothermal synthesis may not be suitable to synthesize sulfonated carbons in one step if one wants to decorate the surface of the synthesized material with high density of sulfonic acid groups. Sulfonated activated carbons are potential substitutes for solvothermal carbons. They are generally obtained from natural raw materials, and they may contain large amounts of mineral impurities which may severely affect the catalytic performance [7] or adsorption properties.

In solvothermal synthesis, under subcritical conditions dehydration of the precursor is accompanied by sulfonation and thiolation of evolved carbon framework. Different precursors could affect the synthesized materials' properties drastically. Therefore, it is appropriate to put forward the notion that each precursor combination and process condition may end up with a different carbon material possessing different properties. Thus, the motivation behind this study is to work on one suitable precursors for production of a sulfonated carbon, characterization and determination of applicability of the material to pollutant removal from water. And with regard to synthesis of sulfonated carbons, to the best of the author's knowledge there is no study on the production of ethylene glycol derived sulfonated carbons under solvothermal conditions, and investigation of its MB removal efficiency from aqueous solutions.

In the present work, it is found necessary to reveal the properties of ethylene glycol derived solvothermal carbon, which is synthesized in concentrate sulfuric acid environment. Synthesized material was characterized by FTIR, XRD, TG-FTIR, SEM, EDS, DLS and Volumetric gas ( $N_2$ ) adsorption and a structural model is proposed based on observations with the assistance of literature data. Finally, adsorption measurements were carried out in water to reveal the potential of the material in water purification applications. It was found that synthesized material is a superb adsorbent for MB removal ( $1472.61 \text{ mg g}^{-1}$ ) from aqueous systems.

## 2. Experimental methods

### 2.1. Sample preparation

Sulfonated carbon material was produced by solvothermal synthesis as shown in Fig. 1. Sulfuric acid (95%–98%) was used as a sulfur source and dehydrating agent. Sulfuric acid ( $H_2SO_4$ ) and ethylene glycol ( $C_2H_6O_2$ ) were purchased from Merck. In a typical synthesis, prior to synthesis ethylene glycol and sulfuric acid were mixed at room temperature. For 1 mol of ethylene glycol 4 mol of sulfuric acid was added. The mixture is white viscous liquid which may possess a yellowish color due to impurities or absorption of moisture. The reaction mixture was placed in a Teflon lined stainless steel autoclave having 85 mL volume. The liquid occupied 12.6% of the total volume. Reaction mixture in autoclave was kept for 12 h. at  $200^\circ\text{C}$  in a laboratory oven. Subsequently, carbon material was ground in an agate mortar and sieved ( $106 \mu\text{m}$ ) and washed repeatedly with deionized water by using a ceramic gooch crucible (POR 3) to totally remove sulfate anions. Filtration was carried out till no sulfate ion detection upon mixing of filtrate with Potassium chloride ( $BaCl_2$ ). As shown in Fig. 1, synthesized nanoparticles could be obtained in colloidal form after ultrasonication, centrifugation and filtration. Products could be dispersed in various solvents such as water or acetonitrile.

### 2.2. Characterization

#### 2.2.1. Thermogravimetric analysis - Fourier transform infrared spectroscopy (TG-FTIR) and FTIR analysis

IR spectrum of the sample was recorded using Perkin Elmer Spectrum 100 series equipped with diamond ATR operating in the range  $4000\text{--}650 \text{ cm}^{-1}$  and analysis was conducted by averaging 250 scans at resolution of  $0.5 \text{ cm}^{-1}$ . The spectrum was obtained with respect to background. For TG-FTIR analysis thermogravimetric analyzer (Hitachi SII6000 Exstar TG/DTA) was connected with Perkin Elmer Spectrum 100 by a connection tube (Pike Technologies) with a gas cell having KBr infrared windows. The connection tube and gas cell were heated to  $200^\circ\text{C}$  prior to analysis to avoid possibility of condensation of species. Around 30 mg of sample powders were poured into alumina ( $Al_2O_3$ ) ceramic crucibles and heated up to  $1100^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$  (up to  $1000^\circ\text{C}$  is presented in figures.). The system was purged with nitrogen gas at a flow rate of  $250 \text{ mL min}^{-1}$ . The time delay for reaching of evolved gasses in TG to FTIR gas cell was neglected by taking into consideration of high purge rate and small transfer line diameter, delay is on the order of 1 or 2 s. FTIR spectrometer was configured to collect spectrum at every 30 s with a resolution of  $4 \text{ cm}^{-1}$ . Evaluations on evolved gas products: baseline corrections and peak deconvolution processes were conducted using Origin software.

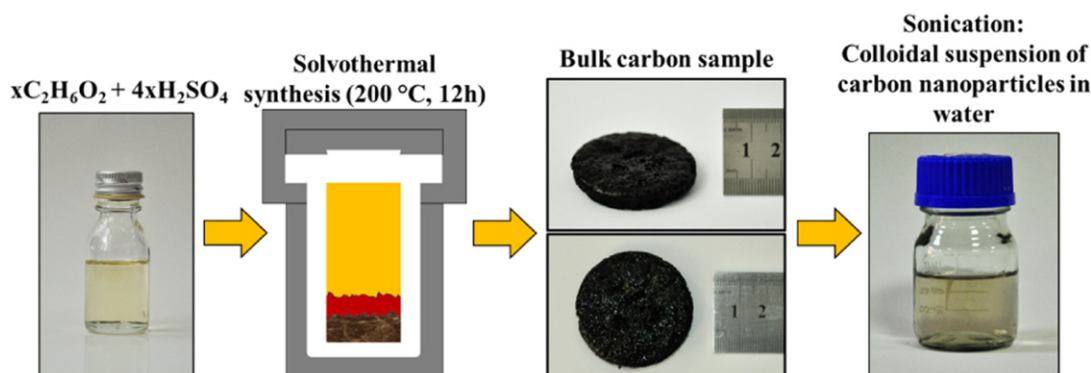


Fig. 1. Synthesis sequence of solvothermal carbon monolith and prepared colloid.

Download English Version:

<https://daneshyari.com/en/article/7843920>

Download Persian Version:

<https://daneshyari.com/article/7843920>

[Daneshyari.com](https://daneshyari.com)