Chemosphere 146 (2016) 113–120

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Application of a multiwalled carbon nanotube-chitosan composite as an electrode in the electrosorption process for water purification

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HIGHLIGHTS

- Multiwalled carbon nanotube-chitosan composite electrodes were prepared.
- The composite electrode had good capacitive properties of double-layer capacitors.
- The composite electrode was a good candidate for capacitive deionization.
- Electro-enhanced adsorption of aniline was achieved by the anodic polarization.

ARTICLE INFO

Article history:
Received 14 September 2015
Received in revised form
2 December 2015
Accepted 7 December 2015
Available online 20 December 2015

Handling Editor: E. Brillas

Keywords:
Carbon nanotube
Chitosan
Composite electrode
Electrosorption
Capacitive deionization
Aniline

ABSTRACT

In this study, a multiwalled carbon nanotubes-chitosan (CNTs-CS) composite electrode was fabricated to enable water purification by electrosorption. The CNTs-CS composite electrode was shown to possess excellent capacitive behaviors and good pore accessibility by electrochemical impedance spectroscopy, galvanostatic charge–discharge, and cyclic voltammetry measurements in 1 M H_2SO_4 electrolyte. Moreover, the CNTs-CS composite electrode showed promising performance for capacitive water desalination. At an electric potential of 1.2 V, the electrosorption capacity and electrosorption rate of NaCl ions on the CNTs-CS composite electrode were determined to be 10.7 mg g^{-1} and 0.051 min^{-1}, respectively, which were considerably higher than those of conventional activated electrodes. The improved electrosorption performance could be ascribed to the existence of mesopores. Additionally, the feasibility of electrosorptive removal of aniline from an aqueous solution has been demonstrated. Upon polarization at 0.6 V, the CNTs-CS composite electrode had a larger electrosorption capacity of 26.4 mg g^{-1} and a higher electrosorption rate of 0.006 min^{-1} for aniline compared with the open circuit condition. The enhanced adsorption resulted from the improved affinity between aniline and the electrode under electrochemical assistance involving a nonfaradic process. Consequently, the CNT-CS composite electrode, exhibiting typical double-layer capacitor behavior and a sufficient potential range, can be a potential electrode material for application in the electrosorption process.

1. Introduction

With rapid population growth combined with unsustainable use of water resources, water scarcity has become a major challenge in the world. It is imperative to develop efficient technologies for water purification. Carbon materials, such as activated carbons, carbon nanotubes (CNTs), and graphene, have been widely used electrochemically for energy storage and water treatment technologies (Frackowiak and Beguin, 2001; Simon and Gogotsi, 2008; Humplik et al., 2011; Bose et al., 2012; Kemp et al., 2013). In particular, CNTs have been demonstrated to be promising electrode materials because of their superior conductivity, excellent chemical inertness, high surface area, and large sorption capacity (Chen et al., 2002; Simon and Gogotsi, 2008; Goh et al., 2013). In addition, adsorption is recognized as an effective method for the removal of environmental contaminants from aqueous solutions. Researchers have intensively studied the use of CNTs to electrochemically remove pollutants, and the adsorption capacity and adsorption rate

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http://dx.doi.org/10.1016/j.chemosphere.2015.12.012
0045-6535/

of these CNTs can be significantly enhanced through electrochemical assistance (Li et al., 2011, 2014; Liu et al., 2014; Fan et al., 2015).

The electrosorption process, which is a potential-induced adsorption of unwanted ions and contaminants on the surface of charged electrodes, has drawn much attention due to its environmental friendliness and low energy consumption (Ban et al., 1998; Gabelich et al., 2002; Ying et al., 2002; Huang et al., 2014). More specifically, capacitive deionization (CDI) is a promising alternative process to remove salt ions and can compete with reverse osmosis (RO) as a method for brackish water desalination, i.e., salt concentration < 5000 mg L^{-1}. (Anderson et al., 2010; AlMarzooqi et al., 2014). In principle, the CDI process involves the use of electrical double-layer (EDL) capacitors, associated with capacitive charge storage, to turn salt water into fresh water (Hou et al., 2013; Porada et al., 2013). Upon applying an electrical potential (0.8–1.4 V) between two oppositely placed nanoporous carbon electrodes, cations and anions are removed by electrosorption at the surface of the charged electrodes. Hence, ions are temporarily stored at the electrode/electrolyte interface via EDL formation. It is noted that high performance desalination can be achieved using nanoporous carbon electrodes with a high specific capacitance (Kim and Yoon, 2013; Yeh et al., 2015).

Recently, CNTs have been successfully introduced as CDI electrode materials due to their remarkable electrochemical properties (Dai et al., 2005; Tofighy and Mohammadi, 2010; Goh et al., 2013; Yang et al., 2013). By taking advantage of the physical and chemical merits of two different constituent materials, CNTs-based composite electrodes, including CNTs-nanofibers (Wang et al., 2006; Pan et al., 2009), CNTs-activated carbon (Dai et al., 2006; Zhang et al., 2006), and CNTs-mesoporous carbon (Peng et al., 2012), have been applied in CDI systems and have exhibited excellent desalination capabilities. In addition, the development of carbon-polymer composite electrodes for CDI has received attention (Liu et al., 2015). For example, Yan et al. (Yan et al., 2012) proposed single-walled CNTs and polyaniline (PANI) composites by in situ polymerization of aniline in a CNTs suspension. It was found that the packing of PANI outside the CNTs resulted in an increase in mesoporosity, which facilitated ion transport and resulted in improved electrosorption of salt ions. Our group also synthesized CNTs-poly(vinyl alcohol) (PVA) composites as CDI electrodes for the removal of NaCl (Hou et al., 2014). It was demonstrated that CNTs combined with PVA yielded a porous surface with high wettability and a large ion-accessible surface area, leading to improved electrosorption capacity.

Efforts dedicated to exploring the electrosorption process with conventional porous carbon materials (e.g., activated carbon, activated carbon fiber, and activated carbon cloth) to absorb organic pollutants (e.g., phenol, bentazone, polycyclic aromatic dyes, and aniline) continue to grow for the purification of wastewater (Ban et al., 1998; Ayranci and Conway, 2001; Han et al., 2006a, b; Ania and Béguin, 2007; Bayram and Ayranci, 2010, 2012) because the polarization of the carbon electrodes can noticeably improve the adsorption of these organic pollutants. A recent investigation further showed that multiwalled CNTs had a great potential for removing emerging contaminants, such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), by electrochemical assistant adsorption, in which both the adsorption capacity and the adsorption rate could be enhanced at a low polarization of 0.6 V (Li et al., 2011). It is worth noting that aniline, which is a potential carcinogen and causes teratogenesis in aquatic species, is widely distributed in aquatic environments. In this regard, Han et al. (Han et al., 2006a) reported that activated carbon fibers with electrochemically enhanced adsorption properties could achieve aniline removal from aqueous solutions.

Furthermore, chitosan (CS) has received much attention as a hydrophilic, biodegradable, and non-toxic polysaccharide biopolymer. For example, CNT-CS composites have been used as electrochemical sensors (Zhang et al., 2004; Liu et al., 2005; Wu et al., 2007). Notably, activated carbon cloths modified by CS were utilized as electrodes to remove Cu^{2+} ions from wastewater by electrosorption at 0.3 V (Huang and Su, 2010). Moreover, it has been reported that CNTs-CS composite electrodes, prepared by the covalent functionalization of CNTs with CS, effectively removed Cu^{2+} ions at 1.2 V (Zhan et al., 2011). However, studies regarding the applications of CNTs-CS composite electrodes for water purification based on the electrosorption process are still limited at the current stage.

The main objective of this work is to fabricate a composite electrode based on CS-grafted multiwalled CNTs and to study its applicability in the electro-enhanced removal of unwanted species from aqueous solutions under electrochemical assistance. The electrochemical properties of a CNTs-CS composite electrode were analyzed by electrochemical impedance spectroscopy, galvanostatic charge–discharge, and cyclic voltammetry measurements. Batch-mode electrosorption experiments were performed to investigate the potential of the CNTs-CS composite as an electrode material for capacitive water desalination and enhanced adsorption of aniline during the electrosorption process.

2. Experimental

2.1. Preparation of electrode

Pristine multiwalled CNTs (CNano Technology Ltd., China) were purified using the following procedures. The powdered CNTs were immersed in 3 M HNO_3 by ultrasonic processing for 1 h. Subsequently, the mixture of powder CNTs and HNO_3 was refluxed at 105 °C for 3 h to remove impurities. Afterwards, the multiwalled CNTs were collected by filtration, washed with deionized water until the pH of the filtrate was nearly neutral, and dried in an oven at 105 °C for 24 h. The resulting CNTs were mixed with CS (molecular weight of 140,000–220,000, Sigma–Aldrich) at a weight ratio of 8:2 in an aqueous solution with 2 wt% acetic acid and stirred for 28 h. Finally, the CNTs-CS mixed solution was painted onto a titanium plate, followed by drying at 120 °C for 2 h, to obtain the CNTs-CS composite electrode.

2.2. Characterization methods

The specific surface area and the pore size distribution of carbon materials were determined by the N_2 adsorption/desorption method using a Micromeritics ASAP 2020M gas sorption analyzer. Specific surface areas of the samples were calculated by the Brunauer–Emmett–Teller (BET) method at a relative pressure (P/P_0) of 0.99. The pore size distributions were determined from the desorption branches using the Barrett–Joiner–Halenda (BJH) method. Scanning electron microscopy (SEM, JEOL, Inc., JSM-6500F) and transmission electron microscopy (TEM, Hitachi H-7650) were used to characterize the surface morphology and structure of the samples. The contact angle of water on the surface of the electrode was analyzed using a drop shape analysis system (Krüss, DSA100).

2.3. Electrochemical measurements

The electrochemical properties of the CNTs-CS composite electrode were analyzed using a three-electrode electrochemical cell at room temperature. The working electrode was a piece of the prepared carbon material with an area of 10 mm × 10 mm, while the