Chemical Engineering Journal 294 (2016) 353–361

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Preparation of regenerable granular carbon nanotubes by a simple heating-filtration method for efficient removal of typical pharmaceuticals

Danna Shan [a], Shubo Deng [a,*], Tianning Zhao [a], Gang Yu [a], Judith Winglee [b], Mark R. Wiesner [b,*]

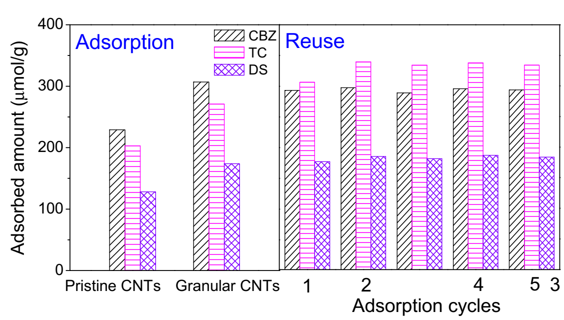
[a] School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Tsinghua University, Beijing 100084, China

[b] Department of Civil and Environmental Engineering, Duke University, P.O. Box 90287, Durham, NC 27708-0287, USA

HIGHLIGHTS

- Novel granular carbon nanotubes are prepared by a simple heating-filtration method.
- Granular CNTs have more available surfaces for adsorption than CNTs powder.
- Granular CNTs exhibit enhanced adsorption capacity for pharmaceuticals.
- The spent granular CNTs can be successfully regenerated at 400 °C in air.
- The regenerated CNTs can be reused without loss of adsorption capacity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 January 2016
Received in revised form 27 February 2016
Accepted 29 February 2016
Available online 4 March 2016

Keywords:
Granular carbon nanotubes
Heating treatment
Carbamazepine
Tetracycline
Diclofenac sodium
Thermal regeneration

ABSTRACT

A simple and convenient method was used to prepare novel granular carbon nanotubes (CNTs) for enhanced adsorption of pharmaceuticals. By heating CNTs powder at 450 °C in air, followed by filtration, the obtained granular adsorbent exhibited high surface area and pore volume since the heating process produced some oxygen-containing functional groups on CNT surface, making CNTs more dispersible in the formation of granular cake. The porous granular CNTs not only had more available surfaces for adsorption but also were more easily separated from solution than pristine CNTs (p-CNTs) powder. This adsorbent exhibited relatively fast adsorption for carbamazepine (CBZ), tetracycline (TC) and diclofenac sodium (DS), and the maximum adsorption capacity on the granular CNTs was 369.5 μmol/g for CBZ, 284.2 μmol/g for TC and 203.1 μmol/g for DS according to the Langmuir fitting, increasing by 42.4%, 37.8% and 38.0% in comparison with the pristine CNTs powder. Moreover, the spent granular CNTs were successfully regenerated at 400 °C in air without decreasing the adsorption capacity in five regeneration cycles. The adsorbed CBZ and DS were completely degraded, while the adsorbed TC was partially oxidized and the residual was favorable for the subsequent adsorption. This research develops an easy method to prepare and regenerate granular CNT adsorbent for the enhanced removal of organic pollutants from water or wastewater.

* Corresponding authors. Tel.: +86 10 62792165; fax: +86 10 62794006.
E-mail addresses: dengshubo@tsinghua.edu.cn (S. Deng), wiesner@duke.edu (M.R. Wiesner).

http://dx.doi.org/10.1016/j.cej.2016.02.118
1385-8947/

1. Introduction

Various adsorbents have been developed to remove pollutants from water and wastewater during the past decades [1]. Nanomaterials such as carbon nanotubes (CNTs) and graphene have recently shown great promise for the removal of pharmaceuticals and other aromatic pollutants [2–5]. Despite many decades of work on the topic, there remains considerable room for improvement in increasing adsorption capacity, efficiency of separation and improved regeneration and reuse [6].

CNTs have attracted tremendous attention due to their excellent properties such as high surface area, uniformity, mechanical strength and chemical stability. When introduced to water from a powdered form, CNTs are usually prone to aggregation as bundles because of the strong van der Waals interaction and hydrophobic interactions. Aggregation would undesirably decrease the specific surface area and thus reduce the adsorption capacity of CNTs [7].

Surface functionalization is among the approaches used to improve the dispersion of CNTs in water. It has been proved that functionalized CNTs can disperse well in water by chemical functionalization, such as heating oxidation and acid treatment [8–10]. However, it is also of great importance to collect and reuse these materials after forming the dispersion in water. One strategy for separating CNTs is to introduce magnetic particles onto the CNTs [11,12], but the disadvantage of this approach include incomplete separation and the decrease of adsorption capacity due to the surfaces occupied by the magnetic materials [13]. Other major concern of the powdered CNTs is the health and environmental risks posed by CNTs once they enter the environments with their significant increase of use and manufacture [14]. CNTs may also be presented as paper-like membrane filters (buckypaper) that are flexible and mechanically stable. These materials have found application in radio frequency filters, cold field emission cathodes and strain sensors [15,16]. CNT membranes have also been created to exploit the electrochemical properties of CNTs as well as their mechanical properties, thermal stability, high chemical resistance and good electrical conductivity [17,18]. A highly porous network and tunable electrochemical reactivity suggest that there may be attractive applications for CNT filters made as adsorbents with good adsorption capacity and simultaneously easy degradation of contaminants.

Bulk CNTs configured as CNT sponges and CNT granules have received much attention because of their easy separation, good electrical properties and adsorption behavior [19,20]. The CNT sponges are a sponge-like bulk materials consisting of self-assembled, interconnected CNT skeletons, three-dimensional macroporous structure and were also used to adsorb a wide range of organic solvents and oils [21]. However, the relative large pore sizes (0.08–500 μm in diameter) of CNT sponge is too big for conventional pollutants, and it tends to float on water surface due to the low density, resulting in favorable adsorption of contaminants on water surfaces and maybe ineffective for those in water [21,22]. After the adsorbed oils or solvents were squeezed out or burned in air, the adsorption capacity decreased dramatically in the next adsorption process [22,23]. To resolve these drawbacks, the structure enhanced and pore size controlled granular CNT/Al_2O_3 hybrid adsorbent was synthesized by a sol–gel method and applied to the removal of pharmaceuticals in our previous work [2]. The granular adsorbent showed both good adsorption and regeneration properties. Although many pores were produced in this hybrid adsorbent, the adsorption capacity was not greater than that of the aggregated p-CNTs. The reason for this might be that the Al_2O_3 covered some adsorption sites and blocked the pores of the adsorbent. To the best of our knowledge, the high-performance and low-cost granular CNTs prepared based on the increase of CNTs dispersion have not been reported by now.

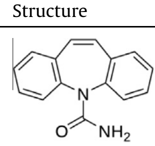
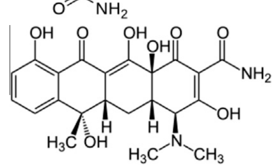
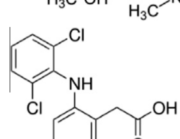
The objective of this paper is to prepare a novel granular CNT adsorbent with the combined advantages of high adsorption capacity, easy separation and simple regeneration. We used a simple heating-filtration method to prepare the efficient granular CNTs. The heating process partially oxidized the CNTs that could be more easily dispersed and then used to create intertwined CNT networks formed through self-supporting forces that yield cakes with a strong and porous structure after the filtration. Three typical pharmaceuticals of practical relevance, among the most frequently detected pharmaceuticals in wastewater [24,25], were selected to evaluate the efficacy of granular CNTs in removing such micropollutants, and especially they have obvious difference in molecular size and functional groups. Both contaminant adsorption and thermal regeneration of the adsorbent were investigated.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (outer diameter: 8–15 nm, length: 10–50 μm, purity > 95%, and ash < 1.5%) were purchased from Cheap Tubes Inc. (Cambridgeport, USA) and used as received. The three typical pharmaceuticals, carbamazepine (CBZ, purity > 97%), tetracycline (TC, purity > 98%) and diclofenac sodium (DS, purity > 98%), were purchased from J & K Scientific Co. (Beijing, China). The physicochemical properties of CBZ, TC and DS are listed in Table 1. All chemical solutions were prepared in ultrapure water produced by a Milli-Q system (Millipore, USA).

Table 1
Physicochemical properties of CBZ, TC and DS.

Pharmaceutical	Molecular formula	Structure	MW	Size (nm)	pK_a	Boiling point (°C)
Carbamazepine (CBZ)	$C_{15}H_{12}N_2O$		236	0.9	2.3 13.9	411
Tetracycline (TC)	$C_{22}H_{24}N_2O_8$		444	1.4	3.3 7.7 9.7 12.0	791
Diclofenac sodium (DS)	$C_{14}H_{10}C_{12}NNaO_2$		318	1.1	4.1	410