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Adsorption behavior of estrogenic compounds on carbon nanotubes from aqueous solutions: Kinetic and thermodynamic studies

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ABSTRACT

In this study different estrogenic compounds, estrone (E1), 17β-estradiol (E2), and 17a-ethinylestradiol (EE2), were removed from the model and real solution by the newly emerged multi-walled carbon nanotubes. The effects of different factors which affect the removal process were studied and optimized for efficient removal. The kinetics of E1, E2, and EE2 adsorption on MWCNTs were analyzed using different kinetic models and the results showed that the removal was mainly a pseudo-second-order process. The thermodynamic study showed the spontaneity and exothermic nature of the removal process, with negative entropy.

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1. Introduction

Recently, compounds categorized as endocrine disrupting chemicals (EDCs) have drawn attention as emerging pollutants in sources of drinking water. EDCs are a structurally diverse group of compounds that may adversely affect the health of humans, wildlife and fishes, or their progenies, by interaction with the endocrine system [1]. They include chemicals used heavily in the past, in industry and agriculture, such as polychlorinated biphenyls, bisphenol A, organochlorine pesticides, and estrogens, including estrone (E1), 17β-estradiol (E2), as well as the synthetic estrogen, 17a-ethinylestradiol (EE2). Recent research showed that natural and synthetic estrogens are effective endocrine disrupters as they cause endocrine alterations on aquatic organisms at sub ng/L levels [2,3]. Hence effective treatments are needed for estrogen remediation. Currently, there are different traditional methods of water treatment, such as activated sludge treatment [4], adsorption by solid adsorbent [5], ozonation [6], filtration membranes [7,8], or photocatalytic oxidation [9]. Among the above mentioned methods, adsorption is regarded as a promising method for the removal of estrogens as it removed all the estrogens effectively without producing by-products, which in most cases could be as harmful as the original pollutants [10,11], and recycle of both the solid adsorbent and estrogens could be optimized. Recently, many newly emerged solid adsorbents were used for the removal of estrogens from polluted water such as carbonaceous resin and high-silica zeolites [12], molecularly imprinted polymer [13], and carbon nanotubes [14,15].

Carbon nanotubes have come under intense multidisciplinary study because of their unique physical and chemical properties. These characteristics allow them to be used in a broad range of applications [16–20]. Many research studies showed the ability of CNTs for the removal of different pollutants such as heavy metals [21,22], lipase [23], resorcinol [24], tetracycline [25], aniline [26], pentachlorophenol [27] and many other pollutants [28] from aqueous solution. However, the studies on the adsorption of EDCs such as estrogens by MWCNTs are still scarce in literature [8,15,29]. Further investigations on the adsorption/removal of the most common EDCs; estrone, 17β-estradiol, and 17a-ethinylestradiol, by multi-walled carbon nanotubes as a newly emerging and promising adsorbent, are essential for aquatic environment remediation. In this manuscript, MWCNTs were used for the effective removal of targeted estrogens from aqueous solutions. The effects of different adsorption conditions such as solution pH, temperature, estrogens concentration, and adsorption time, were studied and optimized. Also, the adsorption process was studied from the kinetics and thermodynamics point of view in order to achieve a better understanding of the adsorption process. Kinetic studies are crucial to understanding the factors and means of transport for estrogens from the aqueous phase to the solid MWCNTs phase. Thermodynamics calculation of the adsorption process is required to understand the mechanism of adsorption and its spontaneity by calculating the different thermodynamic parameters.

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2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) were obtained from Shenzhen Nano-Technologies, China. The MWCNTs were sonicated in acetone for 2.0 h as a pre-treatment step in order to remove any organic compounds adsorbed previously on the MWCNTs surface during the production or storage, then the MWCNTs were filtered and washed with acetone many times and dried in an oven at 110 °C, in order to evaporate the acetone. Estrone, 17β-estradiol, and 17a-ethinylestradiol, were laboratory reagent grade and obtained from Sigma–Aldrich, Canada. All other chemicals were obtained from Sigma–Aldrich (analytical grade) and all solutions were prepared using deionized water.

2.2. Characterization techniques

A transmission electron microscope (TEM) (type JEOL JEM-1230 operating at 120 kV attached to a CCD camera) was used to characterize the MWCNTs for their morphological structure. The specific surface area of the different MWCNTs was determined from nitrogen adsorption/desorption isotherms measurements at 77 K using a model NOVA 3200e automated gas sorption system (Quantachrome, USA).

2.3. Analytical method

Estrone, 17β-estradiol, and 17a-ethinylestradiol concentrations were determined using HPLC (Hewlett Packard 1100 series liquid chromatograph (Avondale, CA)) equipped with pump, auto injector, and diode array detector set at 200 nm and ChemStation for data collection and analysis, using different percentage of acetonitrile/water at 1 ml/min as the mobile phase. The samples (10 μl) were injected. The stationary phase was Zorbax Eclipse column (XDB-C18, 5 μm, 150 mm × 4.6 mm ID).

2.4. Adsorption experiments

Kinetic experiments were carried out to identify the adsorption rate and to find the effect of time and temperature on the adsorption process. The experimental procedures could be described as follows: (1) a series of 10.0 ml solutions containing 5 mg L^{-1} of E1, E2, and EE2 was prepared in 25 ml glass bottle and kept at a certain temperature, (2) the pH of the solution was adjusted to 6.0 using universal pH buffer (Britton–Robinson buffer), (3) 100.0 mg of MWCNTs was added into the solution, (4) the solution was shaked continuously for a certain period of time, (5) after the completion of preset time intervals, the solution was taken and immediately filtered through a filter paper to collect the supernatant, (6) the residual of E1, E2, and EE2 concentrations in the aqueous solution were then determined by HPLC and the amounts adsorbed were calculated as follows:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

where q_t is the amount of E1, E2, and EE2 adsorbed by the MWCNTs (mg/g), C_0 is the initial concentration (mg L^{-1}), C_t is the final concentration after a certain period of time (mg L^{-1}), V is the initial solution volume (L) and m is the MWCNT dose (g). The percentage of removed in solution was calculated using Eq. (2):

$$\%\,\text{Removed} = \frac{C_o - C_t}{C_o} \times 100 \quad (2)$$

The adsorption of E1, E2, and EE2 on the walls of the glass flasks and the filter paper was determined by running a blank experiment without MWCNTs and was found to be negligible.

2.5. Real water samples

Two real samples were used to study the efficiency of MWCNTs for the removal of the estrogenic compounds under investigation. A tap water sample (TWS) was collected from our lab after allowing the tap water to flow for 10 min. The wastewater sample (MBR 6000 STP) was collected from the Membrane Bio-Reactor Technology Waste Water Treatment Plant – King Abdulaziz University (KAUWW), Jeddah City (Latitude deg. North 21.487954, Longitude deg. East 39.236748). Both samples were filtered through 0.45 μm Millipore filter paper and kept in Teflon® bottles at 5 °C in the dark. 100 mg MWCNTs were packed inside a glass column as was explained previously [30], and 25 ml of the real sample solution was allowed to flow inside the column with a flow rate of 1.7 ml/min.

3. Results and discussion

3.1. Characterization of multi-walled carbon nanotubes

Fig. 1 shows the transmission electron microscope image of the MWCNTs. The MWCNTs were long and entangled around each other with an average diameter between 30 and 60 nm and an average length between 2 and 5 μm. The TEM analysis verified the hollow structure of MWCNTs used and showed that the inner diameter was between 6 and 9 nm. The Nitrogen adsorption/desorption isotherms were determined from N_2 adsorption measured at 77 K and specific surface area was calculated using the Brunauer–Emmett–Teller equation and was found to be 84.3 $m^2\,g^{-1}$.

3.2. Optimization of the removal parameters

The effects of different parameters which affected the removal of E1, E2, and EE2, by MWCNTs from an aqueous solution were investigated and optimized. The effect of the contact time on the removal of E1, E2, and EE2 by MWCNTs from solution was studied and the results are shown in Fig. 2. It is clear from the figure that the % removed was increased sharply within the first 5 min as the % removed reached 83.2, 89.2, and 91.2% for E1, E2, and EE2, respectively. Further increase in the contact time to 180 min associated with a slight increase in the % removed to 85.9, 94.4, and

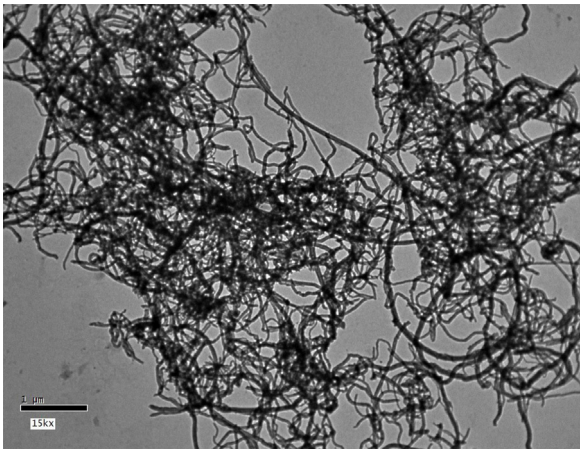

Fig. 1. Transmittance electron microscope images for the MWCNTs.

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