



Rapid Communication

Removal of Caffeine and Diclofenac from Aqueous Solution by Adsorption on Multiwalled Carbon Nanotubes

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ABSTRACT

A commercial multiwalled carbon nanotube has been used to adsorb caffeine and diclofenac, which are representative anthropogenic markers for wastewater contamination of surface waters. The effect that several parameters, such as the initial concentration of organic molecules, the mass of adsorbent and the contact time, may have on the adsorption behavior of the solid has also been studied. In addition, the adsorption kinetics were studied and found to best fit pseudo-second-order and intraparticle-diffusion models. Equilibrium, which was usually achieved after a contact time of 30 min, is described using various isotherm equation models. After treatment with HCl, the adsorbent was found to maintain its adsorption capacity after one cycle of reuse.

Emerging contaminants are defined as chemicals not currently subject to any discharge limitations or regulatory requirements and whose effects on human health and the environment are not yet sufficiently known. This type of contaminant includes a wide variety of compounds, such as pharmaceutical products, drugs, pesticides, personal care products and industrial additives [1], and some of them can be considered as anthropogenic markers for wastewater contamination [2]. Several methods can be applied to reduce the concentration of these types of contaminants in wastewater. Of these, adsorption processes on porous materials are simple to design and operate and do not contribute to the formation of undesirable by-products. As such, adsorption has been reported to be an effective treatment for removing organic compounds [3].

Since their discovery, carbon nanotubes have generated a significant amount of research interest due to their high electrical conductivity, high specific surface area, and high mechanical, thermal and chemical stability [4]. These properties mean that, if used as fillers in nanocomposites, they can increase the mechanical, rheological and electrical properties of the resulting nanomaterials. For example, a better catalytic performance is observed in the case of Fenton-type catalysts combined with carbon nanotubes, [5]. To gain a better understanding of the mechanisms involved in the degradation of organic molecules, the interaction of carbon nanotubes used as a filler in catalysts for the adsorption of organic molecules as contaminants could be studied. In this regard, the use of carbon nanotubes as adsorbents in environmental pollution management, and in the particular case of the removal of organic contaminants, has gained interest in recent years

(see Table S-1). All these findings are a strong indication that carbon nanotubes are very interesting adsorbents for further study and development for use in environmental applications.

The chemicals considered in the present study are frequently found in wastewater and are also considered to be potential chemical markers of domestic wastewater contamination in surface waters. The concentration levels of these chemicals are in the range of $\mu\text{g-ng/dm}^3$ [6]. To the best of our knowledge, despite the importance of the organic molecules considered in this work, studies of their adsorption using carbon nanotubes as adsorbents are very limited. Consequently, the objective of this work was to examine the effectiveness of commercial multiwalled carbon nanotubes for the removal of caffeine (CF) and diclofenac (DF) from aqueous solution at a concentration of up to 15 mg/dm^3 by adsorption.

The multiwalled carbon nanotubes used as the adsorbent are commercial material obtained from Sigma-Aldrich. All chemical reagents were supplied by Sigma-Aldrich and used without further purification. The chemical structures and main characteristics of the organic molecules are shown in Table S2. The contaminant solutions were prepared using ultrapure water obtained with a Milli-Q apparatus (Millipore).

Determination of the point of zero charge (pHpzc) indicates the net charge of the adsorbent surface in the solution. Thus, the net charge on the adsorbent surface is negative when the equilibrium pH of the solution is higher than the pHpzc of the solid, whereas a positive net surface charge is observed when the equilibrium pH of the solution is lower than the pHpzc. The pHpzc of the carbon nanotubes used in the present study was determined according to a method described

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previously [7].

Textural analyses were based on nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyzer). Prior to analysis, the adsorbent was degassed for 24 h at $200\text{ }^{\circ}\text{C}$ at a pressure of less than 0.133 Pa .

The adsorption kinetics were determined by performing a series of batch mode experiments. In each experiment, 10 cm^3 of aqueous solution with an initial concentration of $5, 10$ or 15 mg/dm^3 was placed in a glass tube and mixed with $25, 50$ or 100 mg of carbon nanotubes at pH 7. After shaking for a predetermined time, the suspension was filtered through $0.45\text{ }\mu\text{m}$ Durapore membrane filters and the concentration of the contaminant in the aqueous solution measured using a UV–Vis spectrometer (Jasco V-730). The absorbance was measured at the experimentally determined maximum absorbance wavelength and used to calculate the concentration of the contaminant remaining in solution. The quantity of organic compound adsorbed by the carbon nanotubes was calculated from the difference between the initial and remaining concentrations according to the following equation:

$$q_{t,e} = V \cdot (C_0 - C_{t,e}) / m \quad (1)$$

where C_0 and C_t (mg/dm^3) are the initial and final concentrations of organic compound in solution, respectively, V (cm^3) is the volume of the solution and m (g) is the adsorbent mass.

The equilibrium adsorption capacity of the adsorbent was determined by varying the initial concentration of the contaminant. In this case, 50 mg of adsorbent was added to a glass tube containing 10 cm^3 of solution with a concentration ranging from 0 to 50 mg/dm^3 . After shaking for 2 h , the solution was separated from the solid by filtration and the remaining concentration determined by UV–visible spectrophotometry as in the case of the adsorption kinetics. The quantity of organic compound adsorbed per unit mass of adsorbent at equilibrium was determined according to Eq. (1), where C_e (mg/dm^3) is the concentration of that compound at equilibrium. All adsorption

experiments were performed twice and the reported results are the average of these two measurements.

The nitrogen adsorption isotherm for the multiwalled carbon nanotubes used in this work was type II in the Brunauer, Deming, Deming and Teller (BDDT) classification [8]. The BET specific surface area was found to be $13\text{ m}^2/\text{g}$, the total pore volume obtained at a relative pressure of 0.98 was $0.002\text{ cm}^3/\text{g}$ and the external specific surface area, as estimated using the t -plot method [8], was $10\text{ m}^2/\text{g}$. According to these results, these carbon nanotubes are a nonporous material. The pH_{pzc} value determined for the multiwalled carbon nanotube was 4.5 . Moreover, the adsorbent had a negative charge as the equilibrium pH of aqueous solutions was higher than the pH_{pzc} value, thus meaning that electrostatic attractions between the negatively charged surface and the positively charged organic molecules could favor adsorption. However, the experimental results indicate that the effects of van der Waals and π - π interactions cannot be neglected [9]. For example, Zhang et al. [10] attributed their experimental results for tetracycline adsorption on carbon nanotubes to non-electrostatic π - π dispersion interactions and hydrophobic interactions.

Various factors, such as adsorbent dose and initial organic compound concentration, may play an important role in the adsorption process. The adsorbent dose is an important parameter that strongly influences the process since adsorption capacity depends mainly on the specific surface area and the availability of binding sites on the solid. As such, various doses of multiwalled carbon nanotubes were used in this study, and the results are summarized in Fig. 1. As the amount of adsorbent added to the contaminant solution increased from 25 to 100 mg , the adsorption capacity decreased from 3.21 to 1.41 mg/g in the case of CF, and from 3.32 to 1.36 mg/g in the case of DF. This was probably the result of particle interactions, such as the partial overlapping or aggregation of adsorption sites, thus resulting in a reduction of the effective adsorbent surface area available to the organic molecules.

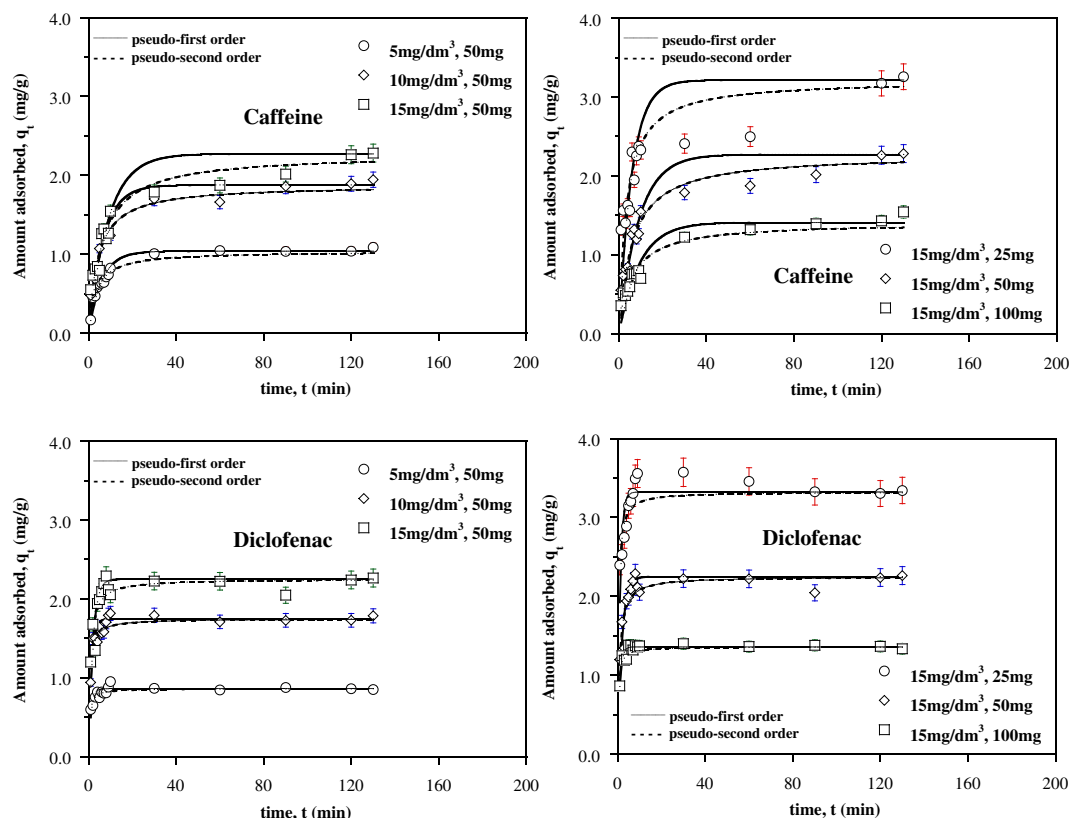


Fig. 1. Kinetic adsorption data for caffeine and diclofenac on the multiwalled carbon nanotubes considering various compound concentrations and adsorbent amounts. $T = 25\text{ }^{\circ}\text{C}$. The lines represent a pseudo-first-order model (—) and a pseudo-second-order model (---).

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