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Adsorption of emerging pollutants on functionalized multiwall carbon nanotubes

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HIGHLIGHTS

- Adsorption of emerging pollutants on functionalized carbon nanotubes.
- Functionalization of carbon nanotubes tunes adsorption properties.
- Different functional groups tested (N- and O-containing groups), and compared with parent MWCNTs.
- Main factors affecting these effects: hydrophobicity, π–π interaction, and morphology.

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ABSTRACT

Adsorption of three representative emerging pollutants – 1,8-dichlorooctane, nalidixic acid and 2-(4-methylphenoxy)ethanol- on different carbon nanotubes was studied in order to determine the influence of the morphological and chemical properties of the materials on their adsorption properties. As adsorbents, multiwall carbon nanotubes (MWCNTs) without functionalization and with oxygen or nitrogen surface groups, as well as carbon nanotubes doped with nitrogen were used. The adsorption was studied in aqueous phase using batch adsorption experiments, results being fitted to both Langmuir and Freundlich models. The adsorption capacity is strongly dependent on both the hydrophobicity of the adsorbates and the morphology of the adsorbents. Thermodynamic parameters were determined observing strong interactions between the aromatic rings of the emerging pollutant and the nitrogen modified adsorbents.

1. Introduction

Emerging pollutants are defined as those no regulated pollutants presenting a significant risk for aquatic environments, and requiring future regulation (NORMAN, 2014). Emerging pollutants include not only compounds or substances in active or past production, but also their metabolites and other transformation products and chemical by-products generated during their production and use. European Union has prioritized the identification, prevention, monitoring and processing of pollutants and pathogens in European water bodies in order to protect human health and keep ecosystems quality (IRSTEA, 2014). In this way, the Water Framework Directive (EU, 2000) established Environmental Quality Standards (EQS) for 33 priority pollutants. According to the directive, member states should implement measures to control their emissions in order to achieve “good chemical status” and accomplish the EQS for the priority pollutants in all water bodies before 2015. However, add to the priority pollutants, emerging pollutants may be included in the updated versions of the WFD. In fact, a working group of the European Commission (the sub-group on Chemical Monitoring and Emerging Pollutants) is focused on topics related to emerging pollutants, including analytical methods, levels in the environment and hazard information (Carere et al., 2012). The prevention of priority and emerging pollutants emissions through wastewater treatment plants effluents into the aqueous environment requires the development of treatment technologies that ensure the quality of receiving water bodies.

Unlike traditional priority pollutants, some emerging contaminants may not be toxic, persistent or bioaccumulative, but may

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produce subtle ecological effects, and there is uncertainty about their adverse ecological effects. These "emerging pollutants" are commonly derived from municipal and industrial wastewater treatment plants, which cannot eliminate it completely with conventional treatment technologies (Carballa et al., 2004; Rivera-Utrilla et al., 2013). Conventional biological wastewater treatment processes will attenuate at least some emerging pollutants, depending on the conditions (Omil et al., 2010). Alahmad and Alawi (2010) measured micropollutants concentrations in effluents from wastewater treatment plants, finding treatment efficiencies, which ranged from 25% to 100%, depending on the biological treatment facility. The use of membrane bioreactors (Sipma et al., 2010), photocatalysis and photolysis (Gamage and Zhang, 2010), or enzymatic treatments (Majeau et al., 2010) could be other options. Membrane separations have been widely studied, obtaining efficiencies of even 90% by nanofiltration (Dixon et al., 2010) or 100% by reverse osmosis (Boleda et al., 2010). An interesting alternative are the physicochemical separations by coagulation or adsorption, which could be a valuable pretreatment processes able to concentrate the emerging pollutants prior to further abatement treatments, decreasing in these way the cost of the overall treatment. Coagulation have been studied without significant removal for pharmaceuticals (Adams et al., 2002) or with removal rates lower than 30% (Huerta-Fontela et al., 2011), whereas adsorption on activated carbons are the most extended and known operation (Iwasaki et al., 2001; Nevskaia and Guerrero-Ruiz, 2001; Rigobello et al., 2013; Ruiz et al., 2010; Yu et al., 2008).

Recently, the use of carbon nanotubes (CNTs), mainly the multi-walled CNTs (MWCNTs), for the adsorption of these emerging pollutants (Wang et al., 2010; Zhang et al., 2013) has gained interest for the removal of different pollutants in the aqueous streams. They have been used for the sorption of a large number of contaminants, both inorganic (Fang and Chen, 2012; Yan et al., 2014) and organic (Bai et al., 2010; Joseph et al., 2011; Zhang et al., 2013). However, add to their chemically inert surface for physical adsorption and high specific surface area comparing with other carbon adsorbents (Kondratyuk and Yates Jr., 2007), CNTs presents surface sites, which can be tuned incorporating heteroatoms in their structure. In this way, nitrogen atoms are incorporated when the scope is the increase of basic properties (Faba et al., 2013), whereas oxygen surface groups, usually by oxidant treatments, are introduced with the aim of increasing the wettability properties of the surface, improving the adsorption properties for polar compounds (Chinthaginjala et al., 2007). Thus, CNTs allow the surface modification in order to maximize the selectivity of adsorption through families of compounds, add to improve the desorption behavior.

The aim of this work is to explore the sorption behavior and mechanism of the three emerging pollutants selected on different CNTs. Four types of CNTs, including functionalized CNTs – MWCNT, MWCNT-COOH, MWCNT-NH_2, N-CNT – were selected for studying the effect of the different chemical and surface properties on their adsorption performance. As emerging pollutants, three different compounds, representative from three groups (pharmaceuticals, surfactants and plasticizers), were chosen: a chlorinated paraffin (1,8-dichlorooctane), a quinolone (nalidixic acid) and an alkylphenoletoxilate (2-(4-methylphenoxy)ethanol).

2. Materials and methods

2.1. Materials

The three compounds used in this work as representative of emerging pollutants are: a chlorinated paraffin, 1,8-dichlorooctane (DCO, Sigma–Aldrich, 98%); a quinolone, nalidixic acid (NAL, Duchefa, Biochemie B.V., 99.4%); and an alkylphenoletoxilate, 2-(4-methylphenoxy)ethanol (MPET, TCI Europe NV, 98%).

As adsorbents, four multiwalled carbon nanotubes have been used. Three of them are manufactured by DropSens: multi-wall non-functionalized nanotubes (MWCNT), functionalized with —COOH groups (MWCNT-COOH) and functionalized with —NH_2 groups (MWCNT-NH_2). Likewise, a fourth sample of carbon nanotubes was synthesized at laboratory scale by chemical vapor deposition in a fluidized bed reactor on Fe/SiO_2 catalyst from acetonitrile vapor at 1123 K (N-CNT) (Faba et al., 2013).

2.2. Characterization of carbon nanotubes

All the samples were characterized by N_2 adsorption at 77 K in an automatic Micromeritics ASAP 2010 volumetric system. The BET equation was applied to the N_2 isotherms to obtain surface area values. The mesopore volumes and pore size distributions were obtained by application of the Barret, Joyner and Halenda method (BJH) to the desorption branch of the N_2 isotherm. TEM micrographs were performed on a JEOL JEM-2100F microscope at 200 kV, the samples were prepared by grinding and ultrasonic dispersal in an acetone solution. Zeta potentials were measured in a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK), with the carbon nanotubes suspensions at different pH. Thermogravimetric analyses (TGA) were conducted under He in an apparatus CI Electronics microbalance (MK2-MC5). The sample was heated with a 10 K/min ramp up to 1273 K, followed by an isotherm stage at that temperature for 30 min.

The surface functional groups were analyzed by temperature programmed desorption coupled with mass spectrometer (TPD–MS) experiments under vacuum in a conventional volumetric apparatus connected to a SRS RGA-200 mass spectrometer. The sample was evacuated for 30 min at room temperature and then, the temperature was increased until 1023 K at a 10 K/min. Considering that the gases evolved during the TGA experiment are CO_2 and CO, as it is evidenced from the TPD–MS, and that the range of temperatures at which the evolution takes place is different; the amount of carboxyl can be estimated by the weight loss up to 723 K while phenol–carbonyl groups correspond to the mass loss from 723 K up to 1100 K.

Elemental analysis of samples containing nitrogen was performed with a LECO CHNS-932 Chemical Analyzer. XPS analysis was performed with an ESCA-PROBE P (Omicron) spectrometer by using non-monochromatized Mg-K radiation (1253.6 eV). All binding energies (BE) were referenced to the C 1s line at 284.6 eV.

2.3. Adsorption experiments

Adsorption isotherms on CNTs were obtained using a batch equilibration technique at 298, 303 and 308 K for individual target compounds. The adsorption was carried out at neutral pH ($pH = 7 \pm 0.5$) because this is a typical pH of water in treatment plants (Choi et al., 2005; Yu et al., 2008) and it is the pH for which the highest adsorption capacity values for this kind of pollutants were obtained in previous works (Bai et al., 2010; Peng et al., 2012). In all the reported experiments, measured pH values did not change during the adsorption experiment. A volume of 50 mL of each solution with different concentration (20–80 mg L^{-1}) were added to 50 mL glass bottles containing a weighed quantity of sorbents (1 mg for DCO and MPET and 10 mg for NAL), according to previous data on the influence of adsorbent dosage (Patiño et al., 2015). The bottles were shaken at 100 opm (oscillations per minute) for 72 h – time required to reach equilibrium. Preliminary experiments showed that the equilibrium was achieved for all