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Performance of different carbonaceous materials for emerging pollutants adsorption

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HIGHLIGHTS

- Micropollutants are removed from waters by adsorption on carbonaceous materials.
- Adsorbents tested: activated carbons, carbon nanofibers and nanotubes, and graphites.
- Equilibrium modeling and thermodynamic analysis.
- Morphology and physic-chemistry of pollutants determine their adsorption parameters.

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ABSTRACT

The adsorption of three representative emerging pollutants over different kinds of carbonaceous adsorbents has been studied in this work. The adsorbates were nalidixic acid (NAL, representative of a pharmaceutical), 1,8-dichlorooctane (DCO, a chloroparaffin) and methyl-phenoxy-ethanol (MPET, a surfactant). Activated carbons, carbon nanofibers, carbon nanotubes and high surface area graphites have been tested as adsorbents. Adsorption isotherms, carried out in a batch system, were fitted using both a Langmuir and a Freundlich model. It was shown that the capacity of adsorption follows the order DCO $\gg$ NAL > MPET for all the adsorbents, and among the adsorbents, the external morphology (surface area and mesoporous volume) is the key parameter. The results from thermodynamic analysis show, however, that both morphological and chemical properties of both adsorbates and adsorbents influenced their behavior.

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1. Introduction

Emerging pollutants are a group of unregulated compounds presented in water, which are considered to be very harmful both for the human health and for the environment (Virkutyte et al., 2010). The origins of the emerging pollutants are very different, some of them having low reactivity- such as perfluorinated compounds-, which leads to relatively high exposure periods in the environment. Furthermore, they are water- and lipid-soluble enough to be introduced in natural waters and trophic cycles (Barceló and López de Alda, 2008). Their release into the environment is diverse and includes agricultural uses, municipal and industrial wastewater discharge or accidental spills (Mompelat et al., 2009). After the discharge, these compounds can be degraded or distributed between different phases. Thus, different effects on organisms have been reported such as chronic toxicity, endocrine disruption, and bioaccumulation (Barceló and López de Alda, 2008; Bolong et al., 2009; Virkutyte et al., 2010).

The emerging pollutants have been divided into five groups: pharmaceuticals, steroid hormones, perfluorinated compounds, surfactants and personal care products (Virkutyte et al., 2010). In the group of pharmaceuticals alone, over a hundred compounds (excluding their metabolites) have been detected in effluents and surface waters: analgesics, anti-inflammatories, antidepressants, anti-epileptics, lipid metabolism regulators, several classes of antibiotics, β-blockers, antineoplastics, and hormones (Monteiro and Boxall, 2009). Furthermore, since wastewater treatment plants are designed to remove organic matter and nutrients present at higher concentrations ($g\,L^{-1}$), these treatments are inefficient for the elimination of many emerging pollutants (Rivera-Utrilla et al., 2013). Partially, these compounds can

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be removed in conventional primary or secondary treatments or even by interaction effects, such as adsorption of emerging pollutants by biological sludge or into emulsified oils. However, a fraction of these compounds will be finally released into the environment and, via drinking water, constitute a major exposure pathway for humans (Bergman et al., 2012). In fact, recent works have evidenced the presence of these compounds in the treated drinking water (Vieno et al., 2007; Kumar and Xagoraraki, 2010; Wu et al., 2013). Furthermore, some transformations can occur through the different treatments, with the resulting chemicals exhibiting even higher toxicity than the parent ones (Farré et al., 2008). Thus, the importance of efficient technologies to remove these compounds in the wastewater treatment plants is evident.

In order to remove these pollutants, biological (Chang et al., 2009; Park et al., 2010), physico-chemical treatments, and hybrids techniques have been proposed. Among the physico-chemical procedures, the most common are membranes (Yoon et al., 2006) and coagulation (Kim et al., 2007); however these methods are not very effective in the removal of emerging pollutants. Other advanced methods, such as the UV irradiation in presence of H_2O_2 or advanced catalytic oxidation based either on cavitation, ozonation or Fenton processes have been studied with reasonable results (Esplugas et al., 2007). However, the main drawback is the low concentrations of the compounds to be removed.

In this way, adsorption has emerged as a feasible method for either the removal of the emerging pollutants from the water stream or as a method of concentrating the pollutants for further destructive treatments. Emerging pollutants adsorption has already been extensively studied, mainly on activated carbons (Nevskaia and Guerrero-Ruiz, 2001; Iwasaki et al., 2002; Yu et al., 2008; Ruiz et al., 2010; SlodobaRigobello et al., 2013) because of their good adsorption properties: high surface area and microporous structure. More recently, works on the adsorption of these emerging pollutants on carbon nanotubes (Wang et al., 2010; Zhang et al., 2013) have demonstrated their potential to control the presence of several contaminants in the environment due to unique physicochemical and electrical properties. From these works, the unique properties as adsorbents of carbonaceous materials stand out, indicating the possibility of tuning both the morphology and the surface chemistry. However, to the best of our knowledge, there are not systematic studies comparing the adsorption properties of these different kinds of carbon adsorbents.

The scope of this work is to explore the adsorption behavior on different carbonaceous materials (activated carbons, carbon nanofibers, carbon nanotubes and high surface area graphites) for emerging pollutants in waters. As emerging pollutants, three compounds representative of three groups (pharmaceuticals, surfactants and plasticizers) were chosen. More concretely, a quinolone, an alkylphenoletoxilate and a chlorinated paraffin. Quinolones are a group of antibacterial agents used as a human and veterinary drug. Among them, the nalidixic acid is an antibiotic which is effective against most Gram-negative bacteria (Velaga et al., 2008; Ulu, 2009). Chlorinated paraffins are flame retardants and chemical stabilizers in polymers and paints. They are usually considered as chloroparaffins molecules with a number of carbon atoms between 10 and 30 and a chlorine content ranging from 30% to 70% by mass (Zitko, 1980; Tomy et al., 1998). However, in this work, the 1,8-dochlorooctane molecule was chosen due to the easiness of the analysis. The alkylphenoletoxilates are used as detergents, pesticides and industrial products. One common compound of this family is the Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$), used frequently as detergent. In this work, we have choose a very similar molecule, 2-(4-Methylphenoxy)ethanol, due to the easiness of analysis.

2. Materials and methods

2.1. Materials

The three compounds used in this work as adsorbates are 1,8-dichlorooctane (Sigma–Aldrich, 98%), nalidixic acid (Duchefa, Biochemie B.V., 99.4%) and 2-(4-Methylphenoxy)ethanol (TCI Europe NV, 98%). The molecular structures of each adsorbate, as well as the physicochemical properties, are listed in Table 1.

The adsorbents used in this work were of carbonaceous nature, and were selected to be representative of the different morphologies: two activated carbons differing in morphology and surface chemistry (AC), carbon nanotubes (CNT), carbon nanofibers (CNF) and high surface area graphites (HSAG). The textural characterization of the materials was based on N_2 adsorption isotherms, measured in a Micromeritics ASAP 2000 surface analyzer. The point of zero charge was measured in a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK), based on electrophoretic mobility measurements of aqueous suspensions of the catalysts at different pH values (Smoluchowski approximation). Table 2 summarizes the characterization data of the adsorbents (further details are given in Díaz et al., 2005; Cuervo et al., 2008, 2009). In all cases, the adsorbents were washed with distilled water to remove contaminants, and then dried at 373 K for 24 h before storage under vacuum in a desiccator until use. The experiments were conducted employing the particle diameter interval: $250\ \mu m < D < 355\ \mu m$. This interval was previously optimized in order to achieve the maximum adsorption capacity and avoid the flotation of the particles due to its low density.

2.2. Batch adsorption experiments

Batch adsorption experiments were performed in 50 mL glass bottles shaken in a water bath for 72 h at 100 opm (oscillations per minute). Preliminary tests were conducted at 298 K to determine the equilibrium time and to fix the optimum adsorbent amount, varying the amount of adsorbent between 1 and 10 mg in 50 mL of solution.

Adsorption isotherms were conducted at 298, 303 and 308 K for individual target compounds. A fixed amount of adsorbent – determined in preliminary studies-, was put in contact with 50 mL of solution of emerging pollutants of concentrations between 20 and 80 mg L^{-1}. Blank experiments were run under the same conditions to verify the losses by volatilization or adsorption on the bottle walls. After equilibration, the supernatants were filtered using a 0.22 μm glass fiber filter prior to analysis. Each adsorption experiment was repeated twice, with a deviation lower than 7%.

The initial and final concentrations of DCO and MPET were analyzed by GC–MS in a calibrated Shimadzu GC/MS QP2010 Plus instrument, using a 30 m long TRB-5MS capillary column as stationary phase. The samples, once filtered, were extracted in chloroform (using a volume ratio of 1:1). NAL solutions were analyzed using a HPLC apparatus (Agilent 1200 with an UV–vis detector and a 150 mm Zorbax SB-Aqcolumn).

3. Results and discussion

3.1. Influence of the adsorbent amount

The influence of adsorbent amount on the adsorption of the three chosen compounds is shown in Fig. 1A. The amount of adsorbate retained per unit of adsorbent decreased for DCO and MPET with increasing adsorbent mass, as it could be expected, due to the reduction in the adsorbate/adsorbent ratio. The amount of DCO retained (mg g^{-1}) is nearly the same for all the adsorbents,

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