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Role of activated carbon properties in atrazine and paracetamol adsorption equilibrium and kinetics

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ABSTRACT

Adsorption of two widespread emerging water contaminants (atrazine and paracetamol) onto three different activated carbons was investigated. The carbons were characterized and the influence of their physicochemical properties on the adsorption performance of atrazine and paracetamol was evaluated. The adsorption equilibrium data were fitted to different adsorption isotherm models (Langmuir, Freundlich, and Dubinin–Radushkevich) while the adsorption rates were described using three different kinetic models (pseudo second order, intraparticle diffusion and a new approach based on diffusion-reaction models). The results indicated that hydrophobic character of the compounds does not affect the sorption capacity of the tested carbons but does influence the uptake rate. The model proposed, based on mass balances, lead to interpret and compare the kinetic of different adsorbents in contrast to classical empirical models. The model is a simple and powerful tool able to satisfactorily estimate the sorption capacities and kinetics of the carbons under different operation conditions by means of only two parameters with physical meaning. All the carbons studied adsorbed paracetamol more effectively than atrazine, possibly due to the fact that sorption takes place by H-bonding interactions.

1. Introduction

The emission of so-called "emerging contaminants" has arisen recently as an environmental problem. This group is mainly composed of compounds used in large quantities in everyday life, such as human and veterinary pharmaceuticals, personal care products, surfactants, pesticides and different industrial additives. Removal of some emerging contaminants in wastewater treatment plants (WWTP) was found to be rather low due to the fact that most of them are resistant to biological degradation. Consequently sewage effluents are one of the main sources of these compounds and their metabolites, which can potentially end up in finished drinking water (Petrovic et al., 2003; De Ridder et al., 2010).

One effective way to eliminate these recalcitrant compounds could be to introduce an adsorption step before dumping WWTP effluents. Activated carbons are widely used to adsorb organic substances from gases or liquids. They are commonly obtained from various organic precursors such as bituminous coal, peat, wood, coconut shell (Marsh and Rodriguez-Reinoso, 2006). In recent years, there has been a growing interest in converting organic waste materials with high carbon content into activated carbon (Schröder et al., 2011). Sludge is waste material produced in large volumes in

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the sewage treatment plants. It can be recycled by composting and used in agricultural land, incinerated or used in landfills. Nowadays, new environmentally benign alternatives for this residue are being sought. In this sense, sewage sludge has been investigated as an attractive precursor for activated carbon production (Smith et al., 2009).

The adsorption capacity of an activated carbon depends on its physic-chemical characteristics (e.g. surface area, pore size, functional groups) and the nature of the adsorbate (e.g. molecular weight and size, hydrophobicity, polarity, functional groups) (Mohamed et al., 2011). In the literature, several solute properties that influence organic solute adsorption onto activated carbon have been discussed. Some authors have tried to directly relate octanol–water coefficient (K_{ow}) to adsorption capacity (De Ridder et al., 2010). A good relation between this property and adsorption was found for most of the hydrophobic contaminants onto activated carbons. However, a poor correlation was shown when the solutes were small and hydrophilic (Westerhoff et al., 2005) or when they were aromatic compounds (Chen et al., 2007). In the case of aromatic compounds several authors have suggested that they can be adsorbed on activated carbons by dispersion interactions between the π-electrons of the aromatic ring and those of the graphene layers (Li et al., 2009). Functionalization of either the adsorbent or the adsorbate profoundly affects these dispersion interactions. On the other hand, if the aromatic compounds have hydrogen-bonding functional groups, hydrogen bonding can contribute to the compound adsorption (Moreno-Castilla, 2004; Terzik, 2000). However, the specific mechanisms, through which adsorption of aromatic compounds occur are still not well established.

In this work, we study the adsorption of two widespread water emerging contaminants, atrazine (1,3,5-triazine-2,4-diamine, 6-chloro-N-ethyl-N′-(1-methylethyl)) and paracetamol (N-acetyl-p-aminophenol) onto different activated carbons prepared from various raw materials: a bituminous coal, a lignite and sewage sludge. To understand interactions between the sorbents and the target contaminants, the texture and chemical properties of active carbons were characterized. This research aims to provide new information for a better understanding of the factors and the mechanism involved in the adsorption process. Moreover, a new kinetic model, based on mass balances and description of transfer processes, has been proposed to describe with physical interpretation the sorption kinetic, overcoming the limitation of classic kinetic empirical models.

2. Materials and methods

2.1. Adsorbates

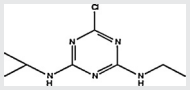
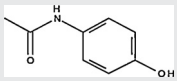
The adsorbates used were a pesticide, atrazine (Sigma–Aldrich, Germany) and a pharmaceutical, paracetamol (Fagron, Spain). Table 1 shows physico-chemical properties of these two compounds.

Paracetamol stock solution (200 mg/L) was prepared with ultra-pure water (Milli-Q). Atrazine stock solution (1000 mg/L) was prepared with acetone (Scharlau, Spain). From these solutions, samples for calibration and sorption experiments were obtained by dilution.

2.2. Adsorbents

Three activated carbons were evaluated. Two of them were commercial activated carbons. Filtrasorb-400 (F-400) was supplied by Chemviron (Belgium) and obtained from a bituminous coal. Norit PK 1-3 (NPK) was produced from peat by Norit Americas Inc. (USA). The third carbon was a sludge-based activated carbon-like material (SBC) prepared from sludge from WWTP through the methodology described by Smith and Fowler (2011).

Table 1 – Physico-chemical properties of atrazine and paracetamol.

Compound	Atrazine	Paracetamol
Molecular structure		
Molecular formula	$C_8H_{14}ClN_5$	$C_8H_9NO_2$
Molecular weight (g/mol)	215.69	151.16
Log K_{ow}	2.43	0.46–0.49
pK_a	2.27	9.86
Molar volume (cm^3/mol)	169.8	120.9

2.3. Textural and chemical carbons characterization methods

The texture of the three carbons was characterized by N_2 adsorption isotherm at −196 °C, in a conventional volumetric apparatus (ASAP 2420 from Micrometics). Before each experiment, the samples were outgassed under vacuum at 120 °C overnight to remove any adsorbed moisture and/or gases. The N_2 isotherms were used to calculate the specific surface area (S_{BET}), total pore volume (V_{TOT}), at a relative pressure of 0.95, and pore size distribution. The pore size distribution (PSD) was evaluated using the density functional theory (DFT), assuming slit-shape pore geometry.

The carbons were further characterized for their elemental analysis using a LECO CHN-2000 and a LECO Sulphur Determination S-144-DR. The ash content and humidity were determined according to the methods described in ISO 1171 and ISO 5068.

FTIR technique was applied in order to determine the main functional groups on the surface carbons. For this purpose spectra were determined between 4000 and 400 cm^{-1} using an FTIR spectroscope (Spectrum 65 FT-IR, PerkinElmer).

2.4. Adsorption assays

For kinetics studies, 50 mg of adsorbent were added to 250 mL of 40 mg/L atrazine or paracetamol solutions. Mixtures were stirred at 25 °C in a multipoint agitation plate. At different times (from 1 to 48 h), samples were taken and filtered through a cellulose acetate filter (0.2 μm diameter pore) and the remaining concentrations were analyzed in a UV/Vis spectrophotometer (Lambda 25 PerkinElmer) at 242 nm for paracetamol and 224.9 nm for atrazine. The detection limit for paracetamol was 144 ppb and for atrazine 220 ppb. The paracetamol and atrazine uptake (q_t) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where q_t is the amount (mg/g) of atrazine or paracetamol adsorbed at time t, C_0 is the initial concentration (mg/L), C_t is the concentration at time t (mg/L), V is the volume (L) of the adsorbate solution and W is the weight (g) of carbon used.