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Single, binary, and mixture adsorption of nine organic contaminants onto a microporous and a microporous/mesoporous activated carbon cloth

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ABSTRACT

The adsorption kinetics of nine contaminants (ibuprofen, carbamazepine, ofloxacin, bisphenol-A, diclofenac, mecoprop, pentachlorophenol, benzotriazol and caffeine) on a microporous and a microporous/mesoporous activated carbon cloth were studied in single, two-component and complete mixture at pH 7.5. Adsorption capacities at equilibrium were highest for the highly microporous carbon material, showing that pollutant adsorption mainly takes place in the micropores. This effect was more pronounced for small size adsorbates. Adsorption kinetics were increased for small size adsorbates thanks to their easy diffusion in the narrow porosity. Same behaviors were observed in the complex mixture containing the nine pollutants. Competition and sieving effects were observed in two-component mixtures, while considering two adsorbates having different molecular volumes, as for example caffeine and diclofenac. Moreover, the desorption of the co-adsorbates having the highest Gibbs energy value of adsorption determined from adsorption isotherms at 298 K (caffeine, mecoprop and benzotriazol) was observed for the kinetics of the complex mixture of the nine contaminants and of the two-component mixture. This desorption was provoked by the competition with the contaminants having lower Gibbs energy variation in single adsorption and thus strongly attracted at the adsorbent surface.

1. Introduction

Numerous studies have shown that a variety of pharmaceutical molecules, solvents or pesticides are frequently detected in water at trace concentrations (ng L^{-1} to μg L^{-1}) [1,2]. These organic micropollutants (OMPs) are not entirely removed by waste water treatment plants [3,4] and may thus become highly toxic due to their accumulation in the environment. Among different methods to remove these molecules from water is adsorption. Granular and powdered activated carbons (PACs) are widely used as adsorbents as they possess high surface areas and wide pore size distributions [5,6]. However, these materials present the disadvantage of releasing fine particles and dusts, which is not the case for activated carbon cloths (ACCs) or felts whose special shape facilitates their manipulation and recovery. ACCs usually exhibit rapid adsorption kinetics in comparison with powdered or granular activated carbons [7–10]. Moreover, some pollutants adsorbed on ACCs can be reversibly desorbed through electrochemical methods [11] allowing a fast regeneration of the adsorbent. Recently, ozonation was compared to adsorption on powdered activated carbons for the removal of micropollutants from waste water treatment plant effluents by Margot et al. [12]. The authors concluded that while ozone acted specifically on a few OMPs, removing them more efficiently, adsorption on PACs removed a larger spectrum of OMPs. PAC-ultrafiltration was recommended as the most suitable treatment technology, especially for the treatment of sensitive receiving waters, such as recreational waters or drinking water resources.

However, ozonation processes can produce by-products that are undesirable for water treatment [13] and bioassays on waste water treated through ozonation are not conclusive. To avoid the production of toxic by-products, ozonation needs more time to be

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completed [14]. Thus, an activated carbon fiber (ACF) seems to be the safer solution regarding waste water treatment.

Since the competition between OMPs and organic matter was identified as the most important factor impacting OMP adsorption in real effluents [15], most of the studies related to competition have focused on organic matter [16,17]. A few authors tried, however, to understand the competitive effect between the OMPs [18–20] which cannot be neglected in order not to overestimate the activated carbon adsorption capacity [21].

Aside from the environmental applications, understanding the competition of OMPs on ACC can throw light on some aspects of the adsorption mechanisms. This has been studied in the biological field, especially on interfaces between proteins and different types of surfaces. The importance of electrostatic interactions and solvation of proteins on maximum adsorbed capacity was shown by van der Veen et al. [22] and Barnthip et al. [23]. Thermodynamic studies can also be helpful to understand the adsorption and solvation phenomena [24] in order to better understand the competition behavior of each pollutant.

The purpose of this study is to better understand the competitive adsorption kinetics of nine micropollutants: ibuprofen (IBP), carbamazepine (CBZ), ofloxacin (OFX), bisphenol-A, (BPA), diclofenac (DFN), mecoprop (MCP), pentachlorophenol (PCP), benzotriazol (BZT) and caffeine (CAF) onto a microporous and a microporous/mesoporous activated carbon cloth at a pH value characteristic of waste water treatment plant effluents (i.e. between 6.5 and 8.5).

The adsorbents were finely characterized and the kinetics of each OMP were studied at 25 °C and compared. To investigate the competitive adsorption between the molecules, two kinds of experiments were performed on the ACCs: binary adsorption kinetics of PCP, OFX and DFN along with co-adsorbates, and the adsorption kinetics of a mixture of the nine pollutants. The adsorption kinetics have been correlated to the adsorbent and pollutant characteristics. They were interpreted in relation with the Gibbs isosteric free energy of each pollutant, determined from the adsorption isotherms on the microporous ACC, in order to better understand the competition phenomenon.

2. Material and methods

2.1. Reagents and chemicals

HPLC grade acetonitrile and orthophosphoric acid (85 mass. %) were purchased from VWR international. Most of the reagents were purchased from Sigma-Aldrich and were of reagent plus Purity, i.e., ≥98%. Mecoprop of Pestanal® grade was purchased from Fluka.

2.2. Targeted pollutants characteristics

OMPs were selected according to specific criteria related to their nature and occurrence. The chosen molecules are frequently found in water treatment plants and cover a wide variety of micropollutants: a pesticide (mecoprop), a solvent (pentachlorophenol), an anti-corrosive (benzotriazol), a natural marker (caffeine), and different pharmaceutical products such as two non-steroidal anti-inflammatory drugs (diclofenac and ibuprofen), an antibiotic (ofloxacin), a neuroleptic (carbamazepine) and an endocrine disruptor (bisphenol A). At pH 7.5, some molecules were negatively charged (MCP, PCP, DFN and IBP), while others were neutral (CBZ, CAF, BPA and BZT) or zwitterionic (OFX) (Fig. 1).

Furthermore, they possessed different physico-chemical properties in terms of water solubility, polarity and molecular volumes (Table 1). Water solubilities and octanol/water partition coefficients (Log K_{ow}) were calculated using Marvinsketch (version 6.3.1, www.chemaxon.com, 2015). Volumes were calculated using Chemsketch (ACD/ChemSketch, version 12.01, Advanced Chemistry Development, Inc., Toronto, ON, Canada, www.acdlabs.com, 2015), by measuring the width, length and height of a parallelepiped surrounding the molecule. The smallest molecules were BZT and PCP and the largest ones were OFX and DFN (Table 1). The most hydrophobic ones were BPA and CBZ and the most hydrophilic ones were CAF and OFX. The diversity of the targeted pollutants represents a complete and complex system, and should allow us to define the weight of parameters involved in the adsorption process.

2.3. Textural and chemical characterization of the adsorbents

The activated carbon cloths referenced KIP 1200 (resin phenolic precursor) and BBV 800 (viscose precursor) used in this study were supplied by DACARB (Asnières sur Seine, France). These two adsorbent materials were selected because of their different characteristics in terms of chemical functionalities and nanotextural properties. In order to remove traces of dissolved contaminants coming from the carbonization and/or activation steps, the pristine materials were washed with water using a Soxhlet extractor; the washing cycle was applied during one – two days and the materials were then dried under vacuum (150 mbar) at 120 °C.

2.3.1. Textural characterization of the adsorbents

The ACC samples were analyzed by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX, Hitachi S4500 FEG, with an electron beam of 15 kV). Furthermore, the ACCs were outgassed overnight at 393 K under vacuum (10 mbar) before being characterized by N_2 and CO_2

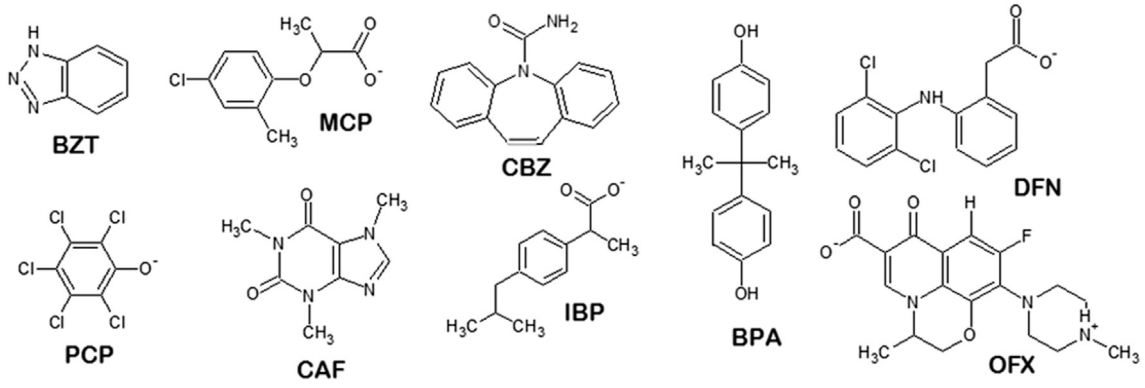

Fig. 1. Adsorbate formulae and speciations at pH 7.5.