



## Enhanced clofibric acid removal by activated carbons: Water hardness as a key parameter

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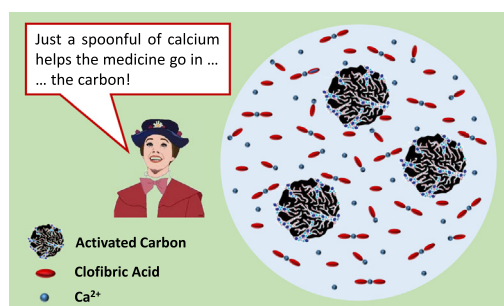
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### HIGHLIGHTS

- Supermicropore network allows higher adsorption of clofibric acid at pH 3 and 8.
- Lower removals at pH 8 are due to higher stability of clofibric acid in solution.
- Hard water enhances clofibric acid adsorption onto activated carbons.
- Simulation and experimental data reveal formation of Ca<sup>2+</sup>–clofibric acid complexes.
- Complex species adsorption explains higher clofibric acid adsorption in hard water.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Clofibric acid is the metabolite and active principle of blood lipid regulators, it represents the class of acidic pharmaceuticals, and is one of the most persistent drug residues detected in the aquatic environment worldwide. This interdisciplinary work evaluates the effect of solution pH and water hardness in clofibric acid adsorption onto commercial activated carbons. Kinetic and equilibrium assays revealed that the highest clofibric acid removal efficiencies (>70%) were attained at pH 3, and that at pH 8 water hardness degree plays a fundamental role in the adsorption process. In hard water at pH 8 the removal efficiency values increased by 22 or 46% points depending on the carbon sample. Adsorbents' textural properties also affect the adsorption process since for the microporous sample (CP) the increase of water hardness has a great influence in kinetic and equilibrium data, while for the micro + mesoporous carbon (VP) the variation of the water hardness promoted less significant changes. At pH 3 the increase of water hardness leads to changes in the adsorption mechanism of clofibric acid onto CP carbon signaled by a transition from an S-type to an L-type curve. At pH 8 the change from deionized water to hard water doubles the maximum adsorption capacity of sample CP (101.7 mg g<sup>-1</sup> vs 211.9 mg g<sup>-1</sup>, respectively).

The adsorption enhancement, with water hardness under alkaline conditions, was reasoned in terms of calcium complexation with clofibrate anion exposed by molecular modeling and conductivity studies. Ca<sup>2+</sup> complexation by other acidic organic compounds may also occur, and should be considered, since it can play a fundamental role in improved design of water treatment processes employing activated carbons.

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## 1. Introduction

Natural waters contain soluble and insoluble materials of organic or inorganic origin. The later contribute to water hardness degree and calcium and magnesium salts are the most abundant species, with a profile dependent on the geological characteristics of each region [1]. The adsorption efficiency reduction of activated carbons due to pore blocking by humic acids is well known [2–4]. However only few studies analyze the effect of water hardness on organic micro-pollutant adsorption onto activated carbons [5,6], and both report the decrease of maximum adsorption capacity when changing from deionized to hard water (due to competitive adsorption or salting-in effect). So, a deeper understanding of the influence of water hardness on the adsorption of micro-pollutants onto nanoporous carbon materials is pertinent and useful for the design of more efficient water treatment plants.

Contamination of water bodies by emergent pollutants, which include pharmaceutical compounds, has been attracting increasing attention from the scientific and governmental entities. Pharmaceutical compounds detected in ambient water matrixes include antibiotics, steroid hormones, antiepileptic drugs, painkillers (analgesics and anti-inflammatories), blood lipid regulators, beta-blockers, among other classes [7,8]. Recently, pharmaceutical compounds appear in a Watch List in the 2013/39/EU directive and, for now, activated carbons, are presented as one of the best available decontamination technologies for their removal.

Clofibric acid is the metabolite and active principle of the blood lipid regulators, being considered a potential endocrine disruptor, since it interferes with the synthesis of cholesterol [8]. Clofibric acid has a recalcitrant behavior in conventional and advanced water treatment technologies [2,9–12] being frequently detected in environmental monitoring of pharmaceuticals. The association of continuous consumption (1–2 g/day for long periods, attaining annual consumptions of thousands of tons) and high resistance to degradation, renders this metabolite a widespread presence in wastewater treatment plants, and as one of the most persistent drug residues detected in the aquatic environment [8,13–15]. In the literature, there are reports of concentrations of clofibric acid as high as hundreds of nanograms per liter in surface water, ground water [16] and even more worrying in tap water [8,13–15].

Clofibric acid also represents a class of pharmaceuticals, the acidic drugs that include several over-the-counter medicines: ibuprofen, diclofenac, ketoprofen, naproxen or acetylsalicylic acid. All the acidic drugs share a common functional group – carboxylic group – and similar  $pK_a$ . So, clofibric acid is usually selected as target compound to represent both lipid regulators and acidic drugs.

In a previous study published by Mestre et al. [17] the isotherms of clofibric acid onto activated carbons (solutions with 10% of methanol) were sigmoidal type curves, indicative of a cooperative adsorption process, and the solution pH was considered a critical parameter due to its effect on the speciation of this organic molecule. Other literature studies using alcohol-free aqueous solutions also identified lower clofibric acid adsorption onto activated carbons [2,18,19] or graphene sheets [20] when solution  $pH > pK_a$  (3.6). Regarding the effect of ionic strength in the adsorption of clofibric acid onto graphene sheets at pH 4.3, Zhang et al. [20] found that a salting-out effect was likely to be involved, overcoming the influence of competitive sorption and resulting in nearly constant sorption amount at high salt concentrations. Rioja et al. [21] evaluated the competitive removal of pharmaceutical compounds, including clofibric acid, from environmental water by a combined adsorption-photolysis treatment using two activated carbons and  $TiO_2$ . The authors found that pharmaceuticals removal in seawater was comparable to that attained in deionized water (~90%), while

tests made with tap water, river water or wastewater presented lower values (55–65%) [21].

The main objective of the present work was to evaluate the effect of pH (3 and 8) and water hardness on the adsorption of different clofibric acid species onto activated carbons with distinct textural properties. Besides, pH 8 was chosen since this is the effluents' pH after secondary treatment [21], when activated carbon adsorption is usually employed. To the best of our knowledge, there are no studies concerning the effect of water hardness on the adsorption of acidic pharmaceutical compounds onto activated carbon materials. As we will show, specific interactions between clofibric acid species in solution and cations present in hard waters have an important role in the explanation of the experimental behavior found for the adsorption onto activated carbons.

The deeper understanding of the adsorption mechanism of clofibric acid onto activated carbons was possible due to a multidisciplinary approach, which besides materials characterization, included molecular simulation and experimental validation (conductivity measurements) of the complex liquid phase systems.

## 2. Materials and methods

### 2.1. Nanotextural and chemical characterization of activated carbons

Two commercial activated carbons commonly used in water treatment and obtained from physical activation of coconut-shell, CP, and wood, VP, were selected for the adsorption of clofibric acid from aqueous phase. The activated carbons from ChiemiVall were used as received and their commercial references are CP 900 (sample CP) and VPLUS (sample VP). The samples were characterized by  $N_2$  and  $CO_2$  adsorption at  $-196$  and  $0$  °C, respectively. The  $N_2$  adsorption isotherms were obtained in an automatic apparatus Micromeritics ASAP 2010 while the  $CO_2$  adsorption experiments were made in a conventional volumetric apparatus equipped with an MKS-Baratron (310BHS-1000) pressure transducer (0–133 kPa). In any case, before the isotherms acquisition the samples ( $\approx 50$  mg) were outgassed overnight at  $120$  °C under vacuum better than  $10^{-2}$  Pa.

From  $N_2$  adsorption data the apparent surface area,  $A_{BET}$ , was determined through BET equation ( $0.05 < p/p^0 < 0.15$ ) [22]. The microporosity was analyzed applying the  $\alpha_s$  method, taking as reference the isotherm reported by Rodríguez-Reinoso et al. [23]. The total micropore volume ( $V_{\alpha \text{ total}}$ ), was obtained by back extrapolation of the linear region of the  $\alpha_s$  plots at high relative pressure ( $\alpha_s > 1$ ). The ultramicropore (width  $< 0.7$  nm) volume,  $V_{\alpha \text{ ultra}}$ , was evaluated by the intercept of the linear range defined by the experimental points determined at  $p/p^0$  between 0.02 and, about, 0.4. The volume of the larger micropores, supermicropores,  $V_{\alpha \text{ super}}$ , is the difference between  $V_{\alpha \text{ total}}$  and  $V_{\alpha \text{ ultra}}$ .

The net surface charge of the materials was evaluated by the determination of the pH at the point of zero charge ( $pH_{PZC}$ ) by reverse mass titration following the method proposed by Noh and Schwarz [24] and using a Symphony SP70P pH meter for the pH measurements.

### 2.2. Liquid phase adsorption

In this work, the effect of water hardness on clofibric acid (Alfa Aesar GmbH, lot G1266B) adsorption onto two activated carbons commercialized for water treatment purposes was evaluated by kinetic and equilibrium studies. For this purpose, solutions prepared with deionized water (W) and with water of different hardness levels:  $80 \text{ mg dm}^{-3}$  (W80) and  $200 \text{ mg dm}^{-3}$  (W200) of equivalent  $CaCO_3$ , were used.

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