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Synthesis of carbon xerogels and their application in adsorption studies of caffeine and diclofenac as emerging contaminants

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ABSTRACT

This work involves the application of carbon xerogels in the removal of two emerging contaminants, caffeine and diclofenac, from aqueous solutions. Textural characterization of the carbon xerogels prepared by polycondensation of resorcinol with formaldehyde (with a molar ratio of 1:2) has been investigated using N₂ adsorption–desorption at –196 °C. Chemical surface groups were analyzed by FTIR spectroscopy, elemental microanalysis and determination of isoelectric point. The equilibrium tests were carried out using different weights of adsorbent and the experimental data were best correlated by Sips isotherm equation. The kinetic experimental data were described using pseudo-first and pseudo-second order kinetic models, being well described by a pseudo-second order model. The maximum adsorption capacity was observed for adsorption of caffeine onto a xerogel treated with urea solution (182.5 mg g⁻¹), due to the presence of Lewis bases on its surface, which increase the adsorption affinity for organic compounds. On the other hand, the higher extent of diclofenac adsorption was obtained with a carbon xerogel treated with sulfuric acid (80.0 mg g⁻¹), mainly due to electronic interactions. Comparing these results with other data reported in the literature, the carbon xerogels employed in our study were found to exhibit comparable adsorption capacities and higher kinetic properties.

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1. Introduction

An increasing number of emerging contaminants have been detected in surface waters of Europe, which is a topic of actual concern for international scientific and legislative communities. Generally, these compounds, e.g., pharmaceuticals, surfactants, pesticides, brominated flame retardants and personal care products are not totally removed by conventional wastewater treatment plants (WWTP), due to its ubiquitous and non-biodegradable character. Many of these substances

are suspected to have endocrine-disrupting effects, possibly at long-term, in living organisms, including humans (Nikolaou et al., 2007).

In these categories, pharmaceuticals are a group of substances of high relevance, since it has been reported that 3000 different pharmaceutical compounds are on the market throughout European Union. Among these, several classes, such as antibiotics, anti-inflammatory and analgesic drugs, lipid regulators, beta-blockers, steroids and hormones, antiepileptic drugs, diuretics and cancer therapeutics have

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been detected in wastewater, groundwater and even drinking waters (Halling-Sørensen et al., 1998; Ternes, 1998; Kümmerer et al., 2000; Kolpin et al., 2002).

Caffeine is one of the most widespread pharmaceuticals, usually proposed as tracer of human pollution, since it can be almost entirely human-related. The presence of caffeine has been detected in water from wells (Seiler et al., 1999), in Boston Harbor seawater (Siegener and Chen, 2002) and in Swiss lakes and rivers (Buerge et al., 2003), indicating that this compound can be used as indicator of domestic pollution. It is generally present in WWTP effluents and surface waters, having been detected in U.S. streams at maximum levels of $6.0 \mu\text{g L}^{-1}$ (Kolpin et al., 2004).

Diclofenac is an anti-inflammatory drug, extensively used to treat inflammation and pain in pathologies as rheumatoid arthritis. Diclofenac is the compound having the highest acute toxicity within the non-steroidal anti-inflammatory drugs (NSAID), showing EC_{50} values lower than 100 mg L^{-1} for all the tests performed (Cleuvers, 2003).

This drug has been frequently detected in wastewater at a median concentration of $0.81 \mu\text{g L}^{-1}$, and the maximal value in wastewater and surface water is up to $2 \mu\text{g L}^{-1}$. Due to its evidenced ecotoxicity and low removal percentages in WWTP, this compound has been recently included in the List of Priority Contaminants, regulated by 2013/39/EU Directive (Oaks et al., 2004; Triebskorn et al., 2004).

Advanced oxidation processes are efficient technologies to degrade recalcitrant contaminants; however, intermediates of acute toxicity may be generated during the process. So, adsorption can be presented as an efficient alternative in the removal of micro-pollutants from wastewaters (Faria et al., 2008; Sotelo et al., 2013a,b). Commercial adsorbents, usually showing microporous character, have been tested in the removal of these compounds, leading to extensive operation times. On the other hand, mesoporous carbons can adsorb larger molecules, such as dyes or organic compounds, providing better kinetic performance.

To the best of our knowledge, there are not many studies focused on the elimination of emerging contaminants by synthesized materials with extended mesoporosity. In this sense, the synthesis of carbon xerogels and their application as adsorbents of micro-pollutants have been carried out. In 1989, Pekala et al. (Pekala, 1989; Pekala and Kong, 1989) demonstrated that some chemical reactions by sol-gel transitions lead to nanoporous organic gels. The polymerization reaction of resorcinol (1,3-dihydroxybenzene) and formaldehyde generates the formation of organic gels with high porosity (>80%), large specific surface area ($400\text{--}900 \text{ m}^2 \text{ g}^{-1}$) and low density (0.03 g cm^{-3}) (Pekala and Schaefer, 1993).

Previous works have shown that polymerization conditions, e.g. [resorcinol]/[formaldehyde] ratio, dilution ratio, pH of solution, and synthesis temperature affect the structure and properties of these organic xerogels. The high specific surface areas and conductivity obtained make these materials good candidates for the preparation of electrodes for fuel cells (Figueiredo et al., 2006); therefore, their well-developed pore texture is a great advantage in the fields of adsorption and catalysts supports. Their applications as adsorbents are recently increasing and present promising results for the removal of several dyes (Girgis et al., 2011; Figueiredo et al., 2011; Han et al., 2000; Ribeiro et al., 2012) and metals (Girgis et al., 2012).

From our knowledge, few relevant studies about adsorption of micro-pollutants onto carbon xerogels have been reported. Examples are the works of Carabineiro et al. (2011, 2012) in

which they studied the removal of the antibiotic ciprofloxacin. Therefore, in the present work, a carbon xerogel was prepared and subsequently subjected to several treatments in order to modify the nature and quantity of surface functional groups, leading to four carbon adsorbents with different textural and chemical properties. These materials were evaluated in the adsorption of two pharmaceuticals (caffeine and diclofenac), by performing kinetic studies and determining equilibrium adsorption isotherms, allowing to assess the effect of the surface chemistry on the adsorption of the selected micro-pollutants.

2. Materials and methods

2.1. Reactants

Caffeine and diclofenac were provided by Sigma-Aldrich (Steinheim, Germany), in analytical purity (>99.99%) and used in the experiments directly. The caffeine/diclofenac solutions were prepared by diluting stock solutions to the required concentrations.

Resorcinol (99 wt.%) and formaldehyde solution (37 wt.% in water, stabilized with 15 wt.% methanol) were purchased from Sigma-Aldrich. Sulfuric acid (96–98 wt.%), nitric acid (65 wt.%) and urea (65 wt.%) were obtained from Riedel-de-Haën. Sodium hydroxide (98 wt.%) was obtained from Panreac.

2.2. Synthesis procedure

A carbon xerogel (CX) was prepared by polycondensation of resorcinol with formaldehyde (with a molar ratio of 1:2), following the procedure described elsewhere (Gomes et al., 2008): 9.91 g of resorcinol was added to 18.8 mL of deionized water in a glass flask. After complete dissolution, 13.5 mL of formaldehyde solution was also added. In order to achieve the desired initial pH of the precursor solution (6.1), sodium hydroxide solution was added drop wise under continuous stirring and pH monitoring. The gelation step was allowed to proceed at 85°C during 3 days.

After this period the gel was dark red and the consistency of the material allowed the sample to be grounded to obtain particle sizes in the range 0.106–0.250 mm. The gel was then dried in oven during several days from 60°C to 150°C , defining a heating ramp of $20^\circ\text{C day}^{-1}$. After drying, the gel was calcined under a nitrogen flow ($100 \text{ cm}^3 \text{ min}^{-1}$) at 120°C , 400°C and 600°C during 60 min at each temperature and then at 800°C for 240 min, defining a heating ramp of 2°C min^{-1} , resulting in the CX material.

2.3. Modification of the carbon xerogel

The original CX material was modified by liquid phase, thermal and hydrothermal treatments, resulting in the production of three additional carbon xerogel samples, with different chemical properties and very similar textural features. These treatments were performed adapting the procedures reported elsewhere (Molina-Sabio et al., 1991; Gomes et al., 2010): a 50 g L^{-1} mixture containing CX in concentrated sulfuric acid solution (18 mol L^{-1}) was kept for 3 h at 200°C in a 500 mL round-bottom flask heated by an oil bath; the recovered solids were thoroughly washed with distilled water until the neutrality of the rinsing waters was reached, and further dried in oven for 18 h at 110°C , resulting in the CXS material. A 50 g L^{-1} mixture containing CX in nitric acid (5 mol L^{-1}) was kept for 3 h

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