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Pharmaceuticals removal by activated carbons: Role of morphology on cyclic thermal regeneration

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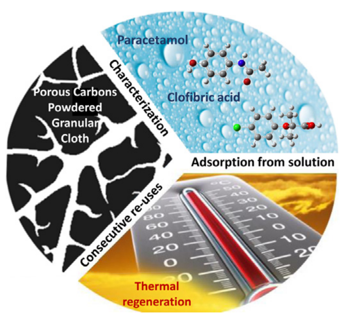
HIGHLIGHTS

- Cloth, granular and powder carbons were tested as adsorbents of paracetamol and clofibric acid.
- Adsorption mechanism of both compounds is ruled by the carbons' supermicropores volume.
- Higher and quicker removal of the pollutants are achieved with cloth and powder samples.
- Thermal regeneration cloth and granular carbons at 400 °C recovered high paracetamol uptake.

GRAPHICAL ABSTRACT



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ABSTRACT

This work aims to evaluate the performance of activated carbons as reusable adsorbents of pharmaceutical compounds. To achieve this objective, the behaviour of carbons with different morphologies (powdered, granular and cloth) in the adsorption of paracetamol and clofibric acid from aqueous solution was studied; as well as the thermal regeneration of paracetamol saturated activated carbons at 400 and 600 °C. For that, the properties of the carbon materials were characterized by N_2 and CO_2 adsorption, pH_{PZC}, XPS, TG, XRD and SEM. Kinetic results showed the importance of supermicropore volume for the diffusion of the probe molecules towards the adsorption active sites, and the negative effect of granular form which led to significantly lower adsorption rates. Paracetamol adsorption followed a Langmuir mechanism in almost all cases, whereas clofibric acid adsorption generally occurred through a more complex mechanism. This behaviour was explained considering the nature of the clofibric acid species present in solution. This compound was always the most adsorbed molecule, reaching a maximum adsorption capacity of $\sim$500 mg dm^{-3} in the case of carbon cloth.

Thermal regeneration proved to be an efficient methodology to recover the porosity of the granular and cloth paracetamol exhausted activated carbons. After the second regeneration treatment at 400 °C both activated carbons retained around 57% of their initial paracetamol uptake.

The conjugation of the adsorption and regeneration results pointed out the benefits of the carbon cloth (in felt form) morphology which, being an easy handling sample, gathered the performance of the best powdered sample assayed in adsorption experiments, with the behaviour of granular carbon upon regeneration.

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1. Introduction

Pharmaceuticals are compounds with biological activity, developed to promote human health and well-being. Nevertheless, only a fraction of the pharmaceutical active compound present in, for example, a painkiller tablet, is metabolized by the organism. Therefore, a great amount of medicines is excreted, finding their way into the environment, as it is demonstrated in several monitoring studies [1–6]. For the scientific community the detection of pharmaceutical compounds in several sort of water bodies is a long time recognized problem [7], and the recent inclusion of some medicines (namely diclofenac) in the Watch List of 2015/495/EU directive reveals that this issue is now calling the attention of legislative authorities [8].

The present study is focused on paracetamol and clofibric acid which are among the most detected pharmaceutical compounds in the aquatic environment. Paracetamol is one of the most consumed analgesic and antipyretic medicines worldwide, being a major ingredient in numerous cold and flu tablets formulation. Because of its relatively high solubility in water, it is frequently detected in the aquatic environment [9–11]. Clofibric acid is the metabolite and active principle of several blood lipid regulators, being considered a potential endocrine disruptor; it is nowadays regarded as one of the most persistent drug residues in the environment [12,13]. The first data regarding the detection of this pollutant were reported in the 70's when it was found in raw and treated wastewater at concentrations up to 2 $\mu g\, dm^{-3}$ [14,15]. In 1993, this chemical was detected in groundwater, in the Berlin area and, a year later, its presence was confirmed in ground, river and even in tap water [16].

Activated carbons are versatile adsorbent materials that have been employed in a large number of industrial processes, including technologies for the removal of organic pollutants from water (*i.e.*, purification of drinking water and wastewater treatment) [1,17,18]. This thematic has been explored by our research group in several studies regarding the preparation and use of biomass derived activated carbons which proved to be efficient adsorbents for the removal of various pharmaceutical compounds from aqueous solutions [19–23].

When activated carbons reach their saturation limit they fail to adsorb the targeted pollutants. The exhausted materials are, in many cases, simply disposed in a landfill or incinerated. However, aiming to a more sustainable society, and to prevent environmental contaminations, the regeneration of these materials has become an important issue both from academic and industrial perspectives, as well as from an economic point of view. In this context, companies like Cabot-Norit provide reactivation of granular activated carbons through a thermal treatment of the exhausted material [24].

Besides thermal regeneration [25–28] other regeneration procedures have been proposed in the literature, such as, desorption induced by microwave radiation [29,30], solvent extraction [31], and by chemical and catalytic decomposition [26], or microbial processes [32]. The most attractive option is the one that gathers the best compromise among the cost, the regeneration efficiency and the number of saturation-regeneration cycles that allows the recovery of a considerable degree of carbon's porosity.

Thermal treatment is the most used method for regeneration of activated carbons due to its simplicity and versatility since, as mentioned above, it consists in heating the exhausted carbon, usually under inert atmosphere, to degrade the adsorbate and so recover the largest possible fraction of the porosity. However, it must be stressed that the choice of the more adequate operational conditions to perform regeneration depends on the system formed by carbon and pollutant(s). In the literature, there are several studies in this thematic, as for example those developed by Ledesma *et al.* [27], and by Sabio *et al.* [28] both focused on the regeneration of granular carbons exhausted with *p*-nitrophenol. Ledesma *et al.* [27] promoted five regeneration cycles by heating the exhausted samples at 900 °C which caused a progressive and accentuated loss of the textural properties. Sabio *et al.* [28] extended the study to more moderated temperatures (300–800 °C) promoting only a single regeneration cycle. The results showed that temperatures lower than 500 °C led to less efficient recoveries of the *p*-nitrophenol upload. The best result was obtained with 800 °C, allowing the recovery of 75% of the initial *p*-nitrophenol uptake.

Considering the regeneration of activated carbons exhausted with pharmaceutical compounds, fewer studies are available in literature. Examples are the works developed by Ania and co-workers over carbons exhausted with salicylic acid which were submitted to 6 regeneration cycles of microwave assisted treatment [30], or thermal treatment at 850 °C [25]. In this last case the final sample retained half of the salicylic acid capacity of the fresh sample. More recently, Batista *et al.* [33] reported the regeneration of rapeseed derived carbons exhausted with caffeine through regeneration at 400, 500 and 600 °C demonstrating that after two regeneration cycles for 1 h, at the highest temperature, around 95% of the initial adsorption capacity for caffeine was recovered.

To the best of our knowledge the studies focused on the thermal regeneration process of carbons are made over only one type of morphology, generally, powder [25,33,34] or granular [27–29] carbons. However, as the regeneration of exhausted activated carbons is becoming a reality in several processes, and carbons with novel morphologies have improved performances in industrial processes, to evaluate the role of the carbons morphology on the feasibility of the regeneration process is of fundamental importance. So, in the present study the performance of activated carbons with different morphologies – granular, powdered and cloth (felt form) – for the adsorption of two pharmaceutical compounds (clofibric acid and paracetamol) was evaluated. Consecutive re-uses of thermal regenerated paracetamol exhausted carbons were also addressed to evaluate not only the impact of the heating temperature but also to shed light on the influence of sample morphology in the regeneration process.

2. Materials and methods

2.1. Activated carbons

The lab-made activated carbon felt, herein named Activated Carbon Cloth, ACC, was prepared from 5.0dtex polyacrylonitrile (PAN) heavy tow textile fibers following the procedure detailed described in Ref. 35. Briefly, the textile fibers were submitted to a two-step air thermal oxidation process in a laboratory scale oven that operate at temperatures between 200 and 300 °C. The oxidized textile PAN fiber was converted in felt form by standard textile process. The oxidized PAN fiber in felt form was then carbonized and activated in the same electrical furnace. In the first step the material was carbonized under argon flow at 900 °C for 20 min (heating ramp 30 °C min^{-1}). For the activation the argon gas was shifted to CO_2 and the temperature rised at 30 ºC min^{-1} up to 1000 °C, this temperature was maintained during 50 min. In parallel with this sample three activated carbons commonly used in wastewater treatment were also assayed:

- NS, powdered carbon commercialized by Norit as SAE SUPER, with 97% (wt./wt.) of particles with dimensions <0.15 mm.
- VP, powdered carbon V Plus from ChiemiVall, obtained by steam activation of pine wood. According to the technical report 90% of the particles are smaller than the n° 325 US Standard Sieve, *i.e.*, smaller than 44 μm.