Multivariate analysis of pharmaceutical pollutants adsorption in aqueous media with tailored waste-based carbonaceous adsorbent materials and commercial activated carbons

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Introduction

Human activity in the domestic, commercial, or industrial sphere is the main cause of waste generation, this being one of the serious environmental problems that today's society must face through new production processes that generate less waste or by recycling and reusing them. Leather industry generates a large volume of biocollagenic wastes that sometimes end up to the landfills or incineration. Researchers are looking for new alternatives to revalorize these wastes. One of these alternatives could be the production of activated carbons used to eliminate pharmaceutical pollutants in aqueous media.

Chemical activation has been proved to be an efficient method to obtain activated carbons. The use of carbonates (K_2CO_3) as activating agents reduces the environmental impact respect hidroxides (KOH) (Gil, R.R. et al. 2014).

Nowadays, the emission of pharmaceutical pollutants has been causing environmental problems in aqueous media. These contaminants have found in water treatment plants (Lladó et al. 2016). One methodology to eliminate them is using an adsorption process with activated carbon. The success of this technology depends on the development of an adsorbent with high adsorption capacity (high micropores development) and compound selectivity.

The objective of this work is to evaluate twenty experimental and commercial carbonaceous adsorbent materials in the process of adsorption of pharmaceutical contaminants in aqueous media. In addition, principal component analysis is applied to elaborate multiple lineal regression models to predict maximum adsorption capacities for future new waste based-activated carbons.

Methodology

A total of fourteen experimental carbonaceous porous materials were used in this study: eight biocollagenic waste-based activated carbons (BWAC), a sludge biochar (SBC), three carbon xerogels (CX) and two coal-based activated carbons. In addition, six commercial activated carbon of different origin (coco shell wastes, petroleum pitch and coal) were included.

BWACs were sustainably obtained from biocollagenic industrial wastes by chemical activation using diferent amount of an alkali agent (KOH, K_2CO_3); the biowaste and the activating agent were mixed in solid state (physical mixture) and the thermochemical process took place at different activation temperatures (750 and 900 °C) (Gil, R.R: et al (2014)).

An exhaustive and complete study of the chemical, morphological and textural properties of all adsorbent materials was made. Texture of the adsorbents were characterized by N_2 adsorption at 77 K: BET specific surface area (S_{BET}), total pore volume (V_{TOT}), micropore volume (V_{ULTRAM}: volume corresponding to pore width <0.7 nm, V_{SUPERM}: volume corresponding to pore width 0.7–2 nm, V_{TMICRO}: volume corresponding to total micropore) and mesopore volume (V_{MESO}: volume corresponding to pore width 2-50 nm). The adsorbents were further characterized for their elemental analysis (C, H, N, S, O), ash content, humidity, and pH.

Five different pharmaceutical adsorbates were selected according to their molecular size and physico-chemical properties: phenol, salicylic acid, paracetamol, diclofenac sodium and iodixanol. The presence of these organic contaminants in surface waters is common. Equilibrium adsorption studies were determined with batch experiments. Isotherms experimental data were fitted to two-parameters isotherms model Langmuir and Freundlich using MATLAB.

The multivariate method principal component analysis (PCA) was used to observe the possible influences of texture and elemental composition of the adsorbent materials on the adsorption process of the adsorbates. PCA was run using Minitab 17 (computer program designed for studies of statistical analysis). The most important variables will be used to elaborate a multiple lineal regression model to predict the maximum adsorption capacities of the 5 molecules for new adsorbents.

Results

The experimental BWACs displayed good chemical characteristics in the form of a high carbon (82-93%) and oxygen (2-10%) content and a moderate nitrogen content (up to 2.9%); their ash content is low (0.8-5.5%) Their textural properties showed high BET surface areas (up to 1665 m2 g-1) and a high pore volume in which micropores predominate (>70%). SBC was characterized by a low carbon and a high ashes content (41.62 and 55.37%, respectively). The rest of adsorbents were characterized preferably by a high carbon content (from 88 up to 98%) and a high range of BET surface (from 782 up to 1839 $m^2\ g^{-1}$).

In the adsorption process different results were obtained according to the different adsorbents and the pharmaceutical adsorbed. Maximum adsorption capacity of phenol was observed on most of the BWAC's (up to 2.78 mmol g^{-1}) suggesting that la presence of oxygenated groups influenced on the process. In the case of adsorption of salicylic acid, acid-base nature of adsorbents affected the process increasing or decreasing the amount adsorbed. In the case of adsorption of paracetamol, lower chemical influences were observed, and texture properties started to be more predominant. Adsorption of paracetamol on BWAC's were values between 1.46 and 2.2 mmol g^{-1} approximately. Finally, maximum adsorption capacity of diclofenac and iodixanol were obtained in adsorbents with higher textural development. Good values of q_{max} of diclofenac were observed on BWAC's (up to 1.07 mmol g^{-1}), while for iodixanol, they were for carbon xerogels.

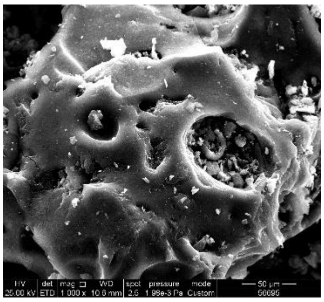

Fig. 1- K_2CO_3 biocollagenic waste-based activated carbon

Principal component analysis reduced the dimensionality of the data set. With the final data, different models were proposed according to the influences on the adsorption process (chemical, textural or both process). In the following table is shown some of the obtained multiple lineal regression models.

Pharmaceutical	Model	r^2
Phenol	$Q_{phenol} = 0.059 + 0.02496 \cdot C - 1.101 \cdot H - 0.0565 \cdot O + 0.863 \cdot V_{SUPERM}$	87.71%
Diclofenac	$Q_{diclofenac} = 0.998 - 0.00445 \cdot C - 0.861 \cdot H + 0.0243 \cdot O + -1.76 \cdot V_{SUPERM} + 0.672 \cdot V_{MESO}$	71.31%

Conclusions

In this study biocollagenic waste-based activated carbon were compared with different adsorbent on the adsorption process of different pharmaceutical in aqueous media. Chemical and textural characteristics of BWAC's (high oxygen content and high BET) enhance the adsorption of the pharmaceutical compounds in comparison to the rest of adsorbent studied. These properties affected in different ways on the adsorption of the five pharmaceuticals pollutants. The present of oxygenated group enhanced the adsorption of phenol. Salicylic acid and paracetamol adsorption was affected by functional groups and pH of the adsorbent. While diclofenac and iodixanol adsorption was preferably physical due to high volume of molecule. BWAC's has shown that it can be expected to have a positive impact on the circular economy in the future.

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