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Instituto Politécnico de Bragança & Ordem dos Engenheiros

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Title

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Simão Pedro de Almeida Pinho

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Removal of estrogens from water using activated carbon adsorbent materials prepared from olive stones

E.C. Milani[1,2,3]*, *M.L. Menezes*[3], *J.L. de Tuesta*[4], *A.E. Ribeiro*[1,2], *P. Brito*[1,2], *A. Queiroz*[1,2]

[1]*Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;* [2]*Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;* [3]*Universidade Tecnológica Federal do Paraná (UTFPR-AP), 86812-460 Apucarana, PR, Brasil;* [4]*Department of Chemical and Environmental Technology, ESCET, Rey Juan Carlos University, Tulipán s/n, 28933 Móstoles, Madrid, Spain.*

*eduriqueerick@gmail.com

Estrogens are a type of hormones that are continuously released to environment presenting several undesirable effects on aquatic species and human health even when present at very low concentrations. With the present work we will present an extensive set of experimental results that presents the valorization of olive stones residues to prepare activated carbons to be used as adsorbent for the removal of estrogens by adsorption from water. Five different adsorbents were produced and characterized. The carbonization yield, the pH at point of zero charge, BET surface area of the carbonaceous materials were measured. Additionally, FTIR analysis was also performed. The simultaneous removal of the three estrogens from water was evaluated for all five prepared adsorbents. For the adsorbent with the best removal performance, a kinetic study was carried out. The obtained results show that olive stones exhibit potential for the production of activated carbons with high surface area used to remove estrogens from water.

Introduction

Estrogens belong to the class of water micropollutants named as endocrine disrupting chemicals and are considered persistent substances in the environment. Estrogens are a type of hormones that are continuously released to environment presenting several undesirable effects on aquatic species and human health even when present at very low concentrations (trace levels) [1, 2]. Additionally, it is known that traditional sewage and drinking water treatment plants are not able to remove or degrade these compounds and additional treatments are required [3, 4].

Activated carbons (ACs) are low-cost carbonaceous materials with a high surface area. ACs undergo an activation process in order to increase its adsorption performance. Activation can be performed by physical treatment, in which the organic material is thermal treated with an atmosphere of air, CO_2, and water vapor, or also by applying some chemical treatments using generally, strong acids, chloride salts or strong bases [5].

As carbon source for ACs preparation, many precursors have been tested, mainly biomass wastes (olive stones, rice husk, coconut shell, among others). According to the Instituto Nacional de Estatística (INE), in 2021, Portugal produced more than 1.3 million tons of olives and it is estimated that more than 500,000 tons of residues were generated per year [6]. Currently, there is an effort to produce bio-based adsorbents that are able to remove efficiently a wide range of micropollutants from water [7].

Objectives

The main objective of this work is to prepare and characterize different types of adsorbents from olive stones. The selection of the better material is based on the highest removal performance of estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) from water matrices using adsorption process.

Methods

Five different adsorbents were produced, namely powdered olive stone (OS), physical activated at 800°C for 1h, with a heating rate of 10°C/min with N_2 flow of 20 cm^3 min^{-1} (CF), carbonized at 500°C for 1.5h with a heating rate of 10°C min^{-1} in a sealed crucible (CC), chemical activated using phosphoric acid (CA) and chemical activated with sodium hydroxide (CB). The carbonization yield was calculated and the pH at point of zero charge (pH_{PZC}), BET surface area (S_{BET}) of the carbonaceous materials were determined (see Table 1). FTIR analysis of all materials was performed (Figure 1). The simultaneous removal of the three estrogens (E1, E2 and EE2) from water was evaluated for all the five prepared adsorbents. For the adsorbent with the best removal performance, a kinetic study was also carried out.

Results

The carbon production method significantly influences the carbonization yield. Acid activation was the method that allowed the highest yield (57.45%). The adsorbent's production method also has a significant impact on the adsorbents' pH_{PZC}, which is shown by the fact that the acid activation provides the material with the lowest pH_{PZC} (3.84). Acid activation was also the one that promoted the greatest increase in surface area with S_{BET} of 590 m^2 g^{-1}.

Table 1. Some surface properties and estrogen removal using five olive stone adsorbents.

Adsorbents	Yield (%)	pH_{PZC}	S_{BET} (m^2/g)	Total estrogens removal (%)
OS	-	5.43	4	24.2
CF	23.0	8.64	14	24.9
CC	26.9	8.46	67	51.2
CA	57.5	3.84	590	96.4
CB	33.9	8.92	27	36.6

In Figure 1, the band at 3438 cm^{-1} indicates the O-H stretching of alcohol and phenols [4]; the activated carbons suffered a drastic reduction in relation to the OS, due to the high temperatures (500 and 800°C) submitted. The band located at 2923 cm^{-1} indicates the stretching and bending of the C–H of the OS carbon chain [4]; activated carbons did not obtain a visible band in this region, showing that the carbonization process promoted the thermal decomposition of the C–H bonds and formation of carbon structures.

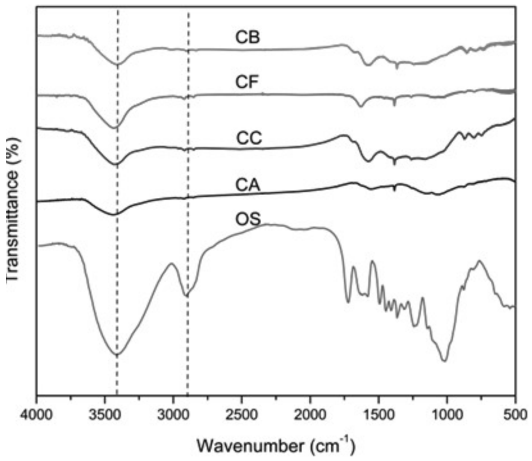

Figure 1. FTIR analysis of the five prepared adsorbents.

The adsorbent selection was performed by simultaneous adsorption of E2, EE2 and E1 at 25°C for 24h with an initial concentration of 2 mg L^{-1} of adsorbents at pH 7. Removal was proportional to surface area, thus the adsorbent with greater removal was the CA with 96.4% removal and was chosen to perform a kinetic study.

The kinetic study was carried out at temperatures of 25, 35 and 45°C. Pseudo-first order, pseudo-second order and Elovich models were used to fit to experimental results obtained for the removal of total estrogens, as presented in Figure 2.

The equilibrium time was found to be 1800 min. The adsorption capacity at the equilibrium increased with the increase of temperature. The models that best fit to the experimental data was first the Elovich model, then the pseudo-second order and finally the pseudo-first order. This indicate that the adsorption of estrogens in this adsorbent occurs by a chemisorption process, since the Elovich and the pseudo-second order models describe a chemical adsorption process.

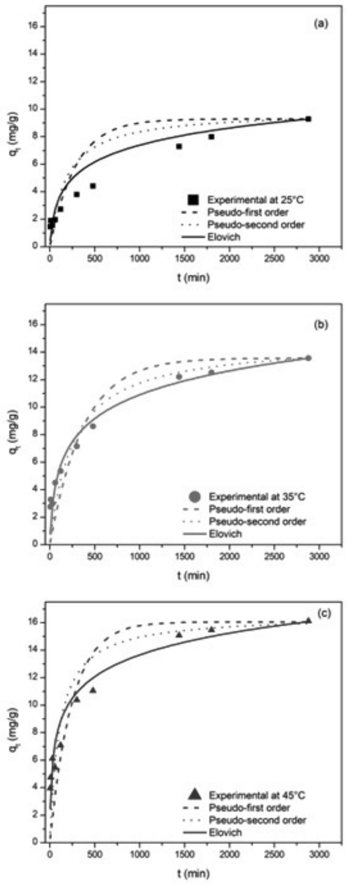

Figure 2. Adsorption kinetics of total estrogens for 15 mg of AC activated charcoal from 5 to 2880 min, with stirring at 150 rpm in 50mL of solution with an initial concentration of 2 mg L^{-1} of each estrogen at pH 7.0. Temperature of 25°C (a), 35°C (b) and 45°C (c).

Conclusions

The results obtained show that acid activation (AC) prepared material is the adsorbent presenting the better removal performance. The overall results, confirm that olive stones exhibit potential for the production of adsorbents with high surfaces used to remove estrogens from water.

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