

VALORIZATION OF OLIVICULTURE RESIDUES FOR THE REMOVAL OF ESTROGENS FROM WATER

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INTRODUCTION & MAIN OBJECTIVE

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 into the environment presenting several undesirable effects on aquatic species and human health even when present at very low concentrations (trace levels) [1, 2]. It is also 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, CO₂, 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 can be used to remove efficiently a wide range of micropollutants from water [7].

In this work, an extensive set of experimental results are presented in order to demonstrate the potential for olive stones residues valorization, through the preparation of activated carbon materials applied as adsorbents for the removal of estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) from water.

PREPARATION OF ADSORBENTS

The raw olive stone was milled, thus giving rise to the adsorbent OS. The production of other adsorbents is described in Figure 1.

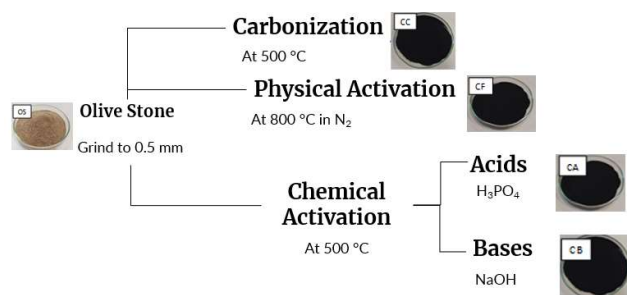


Figure 1. Schematic illustration of the followed methodology for the preparation of adsorbents.

CHARACTERIZATION OF ADSORBENTS

Table 1. Carbonization yield and pH_{pzc} for the prepared adsorbents.

Adsorbent	Yield (%)	pH _{pzc}
OS	nd	5.43 ± 0.13
CC	26.86 ± 0.85	8.46 ± 0.03
CF	23.03 ± 1.81	8.64 ± 0.02
CA	57.45 ± 2.88	3.84 ± 0.05
CB	33.86 ± 1.71	8.92 ± 0.04

Table 2. Surface characterization and removal efficiency for the different adsorbents.

Adsorbents	Area BET (m ² /g)	Pore volume (mL/g)	Micropore volume (%)	Pore diameter (nm)	Removal (%)
OS	4	0.005	0	5.45	24.2
CC	67	0.049	59.2	0.87	51.2
CF	14	0.017	29.4	0.90	24.9
CB	27	0.039	17.9	1.54	36.6
CA	590	0.338	86.4	0.77	96.4

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ADSORPTION KINETICS STUDY

$$\text{Batch method: } q_t = \frac{(C_0 - C_t)V}{m_{ads}} \quad \text{Removal (\%)} = \frac{C_0 - C_e}{C_e} \times 100$$

$$E\% = \sqrt{\frac{1}{n-p} \sum (q_{exp} - q_{teo})^2}$$

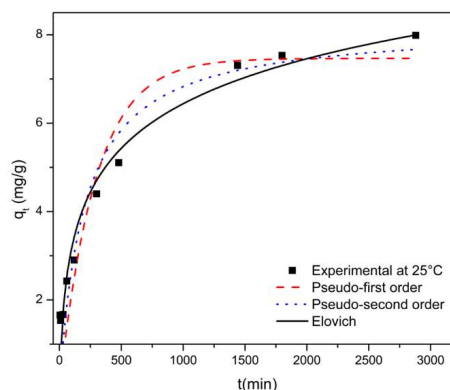


Table 3. Adsorption experimental conditions.

Mass	30 mg
Time	5 – 2880 min
Shaking	150 rpm
Volume	50 mL
Concentration E2, EE2 and E1	2 mg L ⁻¹
pH	7.0
Temperature	25°C

Figure 2. Kinetic models for the adsorption of total estrogens onto CA adsorbent. Comparison between experimental results (points) and models (lines).

Pseudo-first order	Pseudo-second order	Elovich
$q_t = q_e(1 - e^{-k_1 t})$	$q_t = q_e - \frac{q_e}{k_2 q_e t + 1}$	$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$

Table 4. Kinetic constants for adsorption of E2, EE2 and E1 by CA activated carbon.

Kinetics	E2	EE2	E1
q _{e, exp} (mg g ⁻¹)	2.81	2.55	2.62
Pseudo-first order			
k ₁ (min ⁻¹)	0.0034	0.0031	0.0037
q _e (mg g ⁻¹)	2.67	2.30	2.51
E%	0.46	0.37	0.24
Pseudo-second order			
k ₂ (g mg ⁻¹ min ⁻¹)	0.0016	0.0020	0.0019
q _e (mg g ⁻¹)	2.94	2.50	2.77
E%	0.24	0.32	0.19
Elovich			
α (mg g ⁻¹ min ⁻¹)	0.036	0.049	0.034
β (mg g ⁻¹)	1.83	2.45	1.93
E%	0.17	0.23	0.14

CONCLUSIONS

- Acid activation increased carbonization yield (57.45%), decreased pH_{pzc} (3.84), and increased the surface area (590 m²/g).
- Activated carbons are promising for the removal of estrogens (96.4 %) by adsorption from aqueous solutions.
- Adsorption equilibrium reached after 1440 min.
- The model that best fit to the experimental data was the Elovich model, then the pseudo-second order model. This indicates that the adsorption of estrogens on this adsorbent occurs by a chemisorption process.

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