VALORIZATION OF OLIVICULTURE RESIDUES TO PRODUCE BIOCHARS FOR THE REMOVAL OF NAPROXEN FROM WATER

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INTRODUCTION & MAIN OBJECTIVE

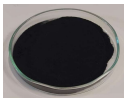
The presence of pharmaceutical drugs, their metabolites and degradation products in the environment requires significant research and monitoring studies to assess the potential risks to human health and to ecosystems. Due to the extremely low concentrations of these chemicals in the environment in the trace levels of µg/L or even ng/L the removal processes must be optimized in order to make them easier, quicker, less expensive, and more environmentally friendly than traditional techniques [1]. Adsorption is a treatment process based on accumulation of the adsorbate (pollutant) on the adsorbent surface that has been successfully used for the optimization of wastewater treatment plants (WWTPs).

Carbon based materials (CBMs), such as activated carbons, chars, carbon black, carbide-derive and nanostructured carbons have shown incredible efficiency as adsorbents. Of considerable interest is the possibility of using biomass wastes to prepare an effective adsorbent and its use in the removal of pharmaceuticals [2]. This work presents the main experimental results for the removal of naproxen from water by adsorption using activated carbon obtained from olive stones [3,4]. Four types of activated carbon materials were prepared from olive stones, the olive pits were powdered to an average diameter of 0.25 mm (type 1), then chemically activated with a strong acid (type 2) and then carbonized at 500ºC (type 3) or pyrolyzed at 800°C (type 4). The batch method was applied to experimentally measure the equilibrium adsorption isotherms. The most significant adsorption parameters were optimized, such as the solution pH, mass of the adsorbent used, adsorption contact time and adsorption temperature.

This work aims to study the removal of naproxen from aqueous solutions using activated carbon obtained from olive stones.

PREPARATION OF ADSORBENTS (OSAC)





OLIVE STONES → GRINDING (0.25 mm) → ACTIVATION (H_2SO_4, 10%) → WASHING (Ultrapure water) → DRYING (AMBIENT & OVEN) → CARBONIZATION (550°C) → PYROLYSIS (800°C) → CHARACTERIZATION

CHARACTERIZATION OF THE ADSORBENTS

Table 1. Textural properties of the OSAC (type 4).

S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	S_{ext} (m^2/g)	$S_{microporos}$ (m^2/g)	$V_{microporos}$ (mm^3/g)	V_{mic}/V_{Total} (%)	$W_{microporos}$ (nm)
409	608	16	393	213	92	2.2

Table 2. Physicochemical properties of OSAC (type 4).

Acidic sites (µmol H^+/g adsorbent)	Basic sites (µmol OH^-/g adsorbent)	pH_{ZC}
877.4	44.7	3.17

QUANTIFICATION BY HPLC CHROMATOGRAPHY

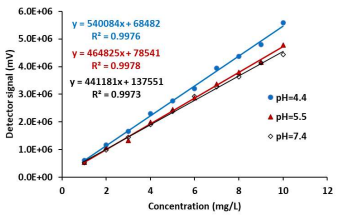


Fig. 1. Effect of pH in the calibration curve.

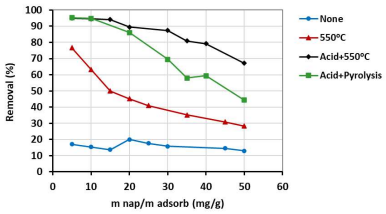
INITIAL CONDITIONS FOR ADSORPTION STUDIES

Temperature	25 °C
Agitation	150 rpm
Sertraline initial concentration	20 mg/L
Volume	50 mL
Adsorbent mass	50 mg

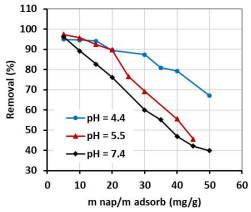
ADSORPTION EQUILIBRIUM AND KINETICS

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

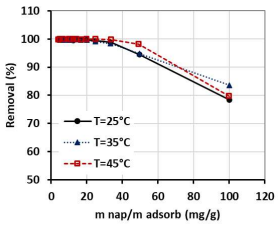
EFFECT OF ADSORBENT TYPE



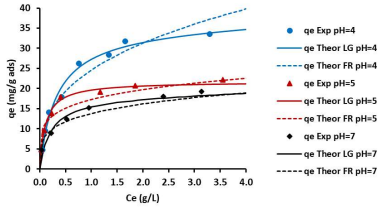
EFFECT OF pH SOLUTION



EFFECT OF TEMPERATURE



ADSORPTION EQUILIBRIUM



Langmuir model $q_e = q_m \frac{K_L \times C_e}{1 + K_L \times C_e}$ $\quad$ **Freundlich model** $q_e = K_F \times (C_e)^{\frac{1}{n}}$

KINETIC STUDY

PSO model

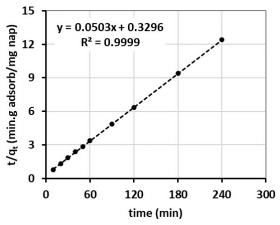
$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

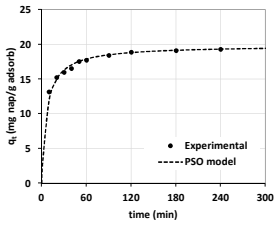
PSO model after linearization

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$$

$q_e = 19.87\ mg_{naproxen}/g_{adsorbent}$

$k_2 = 0.00769\ M^{-1}s^{-1}$





CONCLUSIONS

- From olive stones raw material, four types of adsorbents were prepared, characterized and studied for the removal of naproxen from waters.
- The produced adsorbents present a considerable volume of micropores (84% of the total volume) and significant superficial (BET) area of 411 m^2/g. The type 3 adsorbent material presented the higher adsorption capacity of 37.0 mg of naproxen/g of adsorbent.
- The best adsorption conditions were found to be 24 h adsorption time, 150 rpm agitation, a temperature of 25°C and a pH value of 4.4.
- The Langmuir model was selected to better describe the adsorption behaviour of naproxen in the OSAC adsorbent. Finally, the pseudo-second order model was found to better describe the kinetic adsorption behaviour of naproxen into the OSAC adsorbent.
- The results presented in this work clearly indicate that the olive stone activated carbon is an excellent material for naproxen removal from waters, when compared with other bio-based materials or even when compared with commercial adsorbent materials.

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