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Activated Carbon Produced from Tanning Industry Residues Used to Remove Carbamazepine from Wastewater

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ABSTRACT
According to UNESCO, emerging pollutants are posing a threat to ecosystems and human health. These compounds can be either synthetic or natural chemicals or microorganisms, that are not usually regulated, and can be found in hospital wastewater, even after conventional treatment processes. Carbamazepine is a mood stabilizing drug and an anticonvulsant. Due to its persistence, carbamazepine is one of the most frequently detected pharmaceuticals in wastewater. Though there are many methods to remove such pollutants, adsorption is one of the most effective treatments. To remove carbamazepine from solution, an activated carbon prepared from leather residues and a commercial activated carbon were used as adsorbents.
The adsorption tests show that the leather residue derived activated carbons have higher specific surface area (> 1500 m^2/g) and higher adsorption capacity ($q > 300$ mg_{CBZ}/g) for carbamazepine when compared to commercial activated carbon (992 m^2/g and $q < 180$ mg_{CBZ}/g, respectively).

Keywords: Activated Carbon; Adsorption; Carbamazepine; Leather Residues

1. INTRODUCTION
As our world continues to develop, human activities lead to an increase in pollution on one of our most valuable resources, water. The elimination of water pollutants has been one of humanity's greatest concern. Compounds such as beta-blockers, antidepressants, anti-inflammatory and antiepileptics have been detected in hospital wastewater, even after conventional treatment processes [1].
Since pharmaceuticals were created to trigger a physiological response, their presence in an aquatic environment may pose risks to human and animal life [2]. Carbamazepine (CBZ; $C_{15}H_{12}N_2O$) is a mood stabilizing drug and an anticonvulsant. This pharmaceutical is mainly used in the treatment of epilepsy, trigeminal neuralgia, and bipolar affective disorder [3]. Activated carbon (AC) has been widely used in water purification, as it can remove dyes, heavy metals, and some pharmaceuticals. Although being an easy-to-use method, adsorption presents cost as a drawback [4]. Therefore, there is a necessity to produce cheaper adsorbents. Using waste materials as activated carbon precursors reduces the disposed waste quantity and pollution, giving added value to the waste material.

2. MATERIALS AND METHODS
Residues from leather tannery (wet white and finished leather shavings) were used as precursors and chemically activated at 900 °C with a 1:1 mass ratio (potassium hydroxide : carbonized precursor). The textural characterization of carbon materials was based on N_2 adsorption isotherms at 77 K using a Quantachrome Instruments Nova 2200e.
The carbamazepine solution used was prepared by dissolving carbamazepine (Alfa Aesar, powder, purity >98%) with methanol to obtain a concentration of 1000 mg/L. Then, this solution was diluted with demineralized water to prepare the required concentration for the adsorption tests.
Carbamazepine concentration was quantified by UV-Vis spectrophotometry using a Shimadzu UV-2101 PC spectrophotometer, at a wavelength of 285 nm. The evaluation of the adsorption capacity of wet white activated carbon (WWAC), finished leather activated carbon (FLAC) and commercial activated carbon Norit ROW 0.8 (ROW_0.8) was conducted by contacting different masses of the adsorbents (between 0.02 and 0.18 g) with a carbamazepine solution of known concentration, during 48 hours at 25 ºC and 150 rpm. Three pH levels were tested, acidic (pH=3, addition of HCl solution), alkaline (pH=11, addition of NaOH solution) and neutral (pH=6/7).

3. RESULTS AND DISCUSSION
In this work activated carbons prepared from leather tannery residues were used for CBZ adsorption and compared to a commercial activated carbon. FLAC and WWAC were prepared by KOH activation and have a specific surface area of 1516 and 1584 m^2/g, respectively whereas ROW_0.8 had a specific surface area of 992 m^2/g.
To determine the effect of pH in the CBZ adsorption, WWAC and ROW_0.8 were used as adsorbents. From the

obtained results it was observed that solution pH did not significantly affect the AC capacities, thus FLAC was only tested at basic pH. Figure 1 shows the experimental adsorption isotherms on WWAC, FLAC and ROW_0.8 and the Langmuir and the Freundlich models fitting curves. The parameters values for each model and sum of squared errors (SSE) are listed in Table 1.

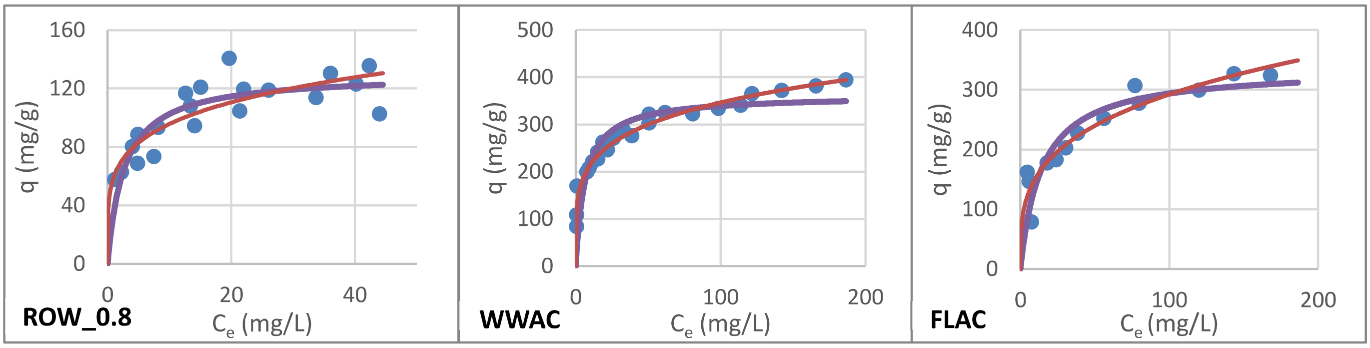

Figure 1 – CBZ adsorption isotherms at basic pH; points – experimental data, red line – Freundlich model, blue line – Langmuir model.

As it can be seen from Figure 1 and table 1, the activated carbons produced from leather residues have a higher adsorption capacity ($q > 300$ mg_{CBZ}/g) when compared with the commercial AC (ROW_0.8), being the highest adsorption capacity obtained with WWAC. It was shown that Freundlich model offers the best fit for the adsorption isotherms for WWAC and FLAC, since the values of SSE obtained are smaller, except for WWAC, at neutral pH.

Table 1 – Adsorption isotherm fitting results on activated carbons (Langmuir and Freundlich models)

	pH	Langmuir			Freundlich		
		q_{max} (mg_{CBZ}/g)	K_L (L/mg)	SSE (mg_{CBZ}^2/mg^2)	n	KF (L/mg)	SSE (mg_{CBZ}^2/mg^2)
ROW_0.8	Acid	177	0.182	17951	0.183	74.4	21057
	Neutral	133	0.395	2151	0.262	49.1	3017
	Basic	130	0.385	3044	0.207	59.4	3203
WWAC	Acid	384	0.156	39427	0.201	145	7374
	Neutral	380	0.265	28279	0.295	109	36434
	Basic	362	0.152	31263	0.208	133	5394
FLAC	Basic	336	0.0696	13226	0.286	78.4	7433

4. CONCLUSION

Residues from leather tanneries are good precursors to produce activated carbons. These carbons are better adsorbents for carbamazepine ($q > 300$ mg_{CBZ}/g) when compared to commercially available carbons ($q < 180$ mg_{CBZ}/g). The effect of pH is not significant for the adsorption of carbamazepine on these activated carbons.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support from the project FCT- UID/04730/2020

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