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Ciprofloxacin and carbamazepine adsorption on activated carbons produced from leather residues

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ABSTRACT

Ciprofloxacin and carbamazepine adsorption was studied using an activated carbon produced from leather residues (wet white shavings) and a commercially available activated carbon (Norit ROW 0.8) and the effect of pH level was studied. The activated carbon produced from wet white shavings showed better results due to its higher specific surface area, confirming that leather residues are a viable precursor for the preparation of activated carbons for the adsorption of these chemicals. The effect of pH on the AC adsorption capacity was not significant in the case of carbamazepine, however lower pH led to higher adsorption capacities for ciprofloxacin.

Keywords: Activated carbon; Leather residues; Ciprofloxacin; Carbamazepine; Adsorption

1. Introduction

Human activities have led to an increase in the pollution of one of our most valuable resources, water. Removing pollutants from water has been one of humanity's greatest concerns. According to UNESCO, ecosystems and human health are being threatened by new and emerging pollutants. These include both synthetic and natural chemicals, and microorganisms which are not normally monitored or regulated [1]. Some chemicals contained in pharmaceuticals can be considered emerging contaminants. After consumption many of these compounds end up in sewage and wastewater. Although water and wastewater treatment plants remove many compounds, some are still not regulated and they are released into surface waters [2].

Compounds such as beta-blockers, antidepressants, anti-inflammatories, antibiotics and anti-epileptics have been detected in hospital wastewater, even after conventional treatment processes [3]. Since pharmaceuticals were created to trigger a physiological response, their presence in an aquatic environment may pose risks to human and animal life [4].

Ciprofloxacin (CIP, $C_{17}H_{18}FN_3O_3$) is an antibiotic that belongs to the second-generation class of quinolones. Its molecular structure can be found in Fig. 1a. The quinolones are used for the treatment of several bacterial diseases both in humans and animals [5]. Ciprofloxacin concentrations can vary between 3 000 and 28 000 μg/L in pharmaceutical effluents, 0.255–0.568 μg/L in hospital effluents (Switzerland), and in farms from 0.020 to 0.100 μg/L (Central China) [6]. The presence of CIP in aqueous solution, even in low concentrations, can result in the development of antibiotic resistant bacteria, can lower the efficiency of other therapeutic drugs, and can cause symptoms such as nausea [6] and endocrine dysregulation [7].

Carbamazepine (CBZ; $C_{15}H_{12}N_2O$) is a mood stabilizing drug and an anticonvulsant. The molecular structure of CBZ can be found in Fig. 1b. This pharmaceutical is mainly used in the treatment of epilepsy, trigeminal neuralgia, and bipolar affective disorder [8].

Due to its persistence, CBZ is one of the most frequently detected pharmaceuticals in wastewater [11,12]. There are a variety of processes that can be used to treat effluents containing these types of emerging pollutants, such as

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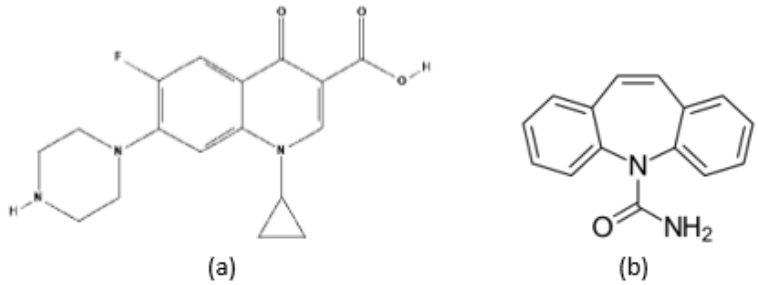

Fig. 1. Ciprofloxacin (a) [9] and carbamazepine molecular structures (b) [10].

nanofiltration, reverse osmosis, ozonisation, and oxidation processes. These treatments are often associated with high costs and high waste production, which is the reason they are not usually applied in effluents treatment [13]. On the other hand, there are cheaper, relatively simple and high efficiency treatments that can be implemented, such as adsorption. Adsorption can be used to remove both organic and inorganic compounds from wastewater [14].

Activated carbon has been widely used in water purification, among others. Although it is an easy-to-use method, the costs associated with adsorption are seen as a drawback [15]. For this reason, the necessity to produce cheaper adsorbents is presented.

There are studies where different types of biomass were used to produce activated carbon which are then used in adsorption tests. Materials such as bamboo [5], sawdust [16], olive stones [17] and forest and agricultural residues [18] were carbonized and activated, thus producing activated carbon. The use of waste materials as precursors to activated carbons helps reduce the quantity of disposed waste, thus reducing pollution and the cost of adsorbent production.

The effectiveness of adsorption is related to the activated carbon surface area. Usually, the larger the carbon's surface area, the greater the amount of adsorbate that can be adsorbed.

There are two methods used to prepare activated carbon: chemical activation and physical activation. Chemical activation is the method most used for preparing activated carbon. It is important to choose an adequate activating agent since it will define the porous structure and the type of functional structure on the surface of the materials. Reagents such as KOH, NaOH, $ZnCl_2$, H_3PO_4 and K_2CO_3 can be used for this [5]. The precursor material is impregnated with the activating agent and then activated by heating at high temperatures. In physical activation, the materials are carbonized and then activated in oxidizing atmospheres (CO_2 and water vapor) at high temperatures. In the present study, residues from the leather industry were used to produce activated carbon and then tested as an adsorbent for ciprofloxacin and carbamazepine.

2. Materials and methods

2.1. Activated carbon preparation and characterization

Wet white shavings were used as activated carbons precursors. The wet white shavings were carbonized at 800°C for 1 h in an inert atmosphere of nitrogen (flowrate of 200 mL/min). The carbonized material was impregnated with potassium hydroxide (KOH) in a 1:1 mass ratio and then heated from room temperature to 900°C (heating rate 5°C/min, inert atmosphere of nitrogen with flow rate of 200 mL/min). The holding time at 900°C was 1 h. After cooling, the activated carbon was washed with demineralized water until neutral pH was reached.

The textural characterization of activated carbons was performed by nitrogen adsorption at –196°C determined in a Quantachrome NOVA 2200e (Quantachrome Instruments – 1900 Corporate Dr, Boynton Beach, FL 33426, United States of America). The activated carbons were previously degassed at 350°C for 3 h and adsorption isotherms at relative pressures between 0.03 and 0.99 were determined. The specific surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method. To calculate micropore volume (V_{mp}) and external surface area (S_t), the *t*-method was used. Total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.95.

2.2. Preparation of ciprofloxacin and carbamazepine solutions, and quantification at different pH

Ciprofloxacin (purity >98%) powder was dissolved using demineralized water. Ciprofloxacin concentration was determined by UV-Vis spectrophotometry using a Perkin Elmer Lambda 25 UV/Visible Spectrophotometer (PerkinElmer, Inc. – 940 Winter St., Waltham, MA 02451, United States of America). The wavelength used varied according to the pH of the solutions in which the ciprofloxacin was dissolved.

Carbamazepine (Alfa Aesar, powder, purity >98%, Shore Road, Port of Heysham Industrial Park, Heysham, Lancashire LA3 2XY, United Kingdom) powder was initially dissolved with methanol to obtain a concentrated solution of 1,000 mg/L. This solution was then diluted to the required concentration by adding demineralized water.

Carbamazepine was quantified by UV-Vis spectrophotometry using a Shimadzu UV-2101PC Spectrophotometer (Shimadzu – 1, Nishinokyo Kuwabara-cho, Nakagyo-ku, Kyoto 604-8511, Japan). The determination was accomplished at a wavelength of 285 nm.

Initially ciprofloxacin was dissolved in solutions with a pH of 3 (by addition of a 0.1 M solution of HCl), 7 and 11 (by addition of a 0.1 M solution of NaOH). These pH values were chosen in such a way that ciprofloxacin could be present in an ionic form, since it is known that it can

display multiple forms [19]. The acidic solutions were stable with no significant pH variations, the antibiotic concentration was kept in solution and larger quantities of ciprofloxacin could be dissolved compared to other pH levels. Neutral and basic pH solutions were not verified because the pH displayed significative variations, and the CIP ended up precipitating. In order to maintain the pH value and avoid CIP precipitation, buffer solutions were used. For neutral pH (6.85) a solution of KH_2PO_4 0.01 M + Na_2HPO_4 0.01 M was used, allowing a stable solution to be obtained. However, for basic pH, even with 0.01 M buffer solutions of Na_3PO_4 (pH = 11.72) and 0.025 M $NaHCO_3$ + 0.025 M Na_2CO_3 (pH = 10.00) CIP precipitation was always present, meaning that the solution was not stable.

Since carbamazepine is almost insoluble in water, methanol was used to prepare a concentrated solution. The different pH levels did not cause any precipitation of this compound.

2.3. Batch adsorption studies

The evaluation of the adsorption capacities of wet white activated carbon (WWAC) and commercial activated carbon Norit ROW 0.8 (ROW_0.8) was conducted by contacting different amounts of the adsorbents (between 0.02 and 0.18 g) with a ciprofloxacin or carbamazepine solution of known concentration. WWAC was used, as produced, in powdered form, whereas ROW_0.8 was used in the form of pellets, to simulate behaviour in industrial applications. The equilibrium times were determined for both materials to assure that the experimental adsorption data are at equilibrium. Therefore, the adsorption capacities will not be affected by particle size. After 48 h of agitation (equilibrium time) in an orbital agitator at 25°C and 150 rpm the solution was removed and filtered, allowing the determination of the amount of adsorbate adsorbed by mass unit of adsorbent, q (mg/g_{AC}) using Eq. (1):

$$q = \frac{\left(C_i - C_e\right)\cdot V}{m_{\text{ads}}} \tag{1}$$

where C_i (mg/L) is the initial concentration of the ciprofloxacin or carbamazepine solution, C_e (mg/L) is the concentration of the ciprofloxacin or carbamazepine solutions after equilibrium was achieved, V (L) is the volume of the ciprofloxacin or carbamazepine solution in contact with the activated carbon, and m_{ads} (g) is the adsorbent mass used.

Adsorption tests were conducted at three pH levels, acidic (pH = 3), neutral and basic (pH = 11). To prepare the acidic and alkaline solutions, hydrochloric acid and sodium hydroxide respectively were added. For neutral pH no chemicals were added, meaning the pH only depended on the amount of ciprofloxacin or carbamazepine in solution.

Langmuir and Freundlich's models were used to fit the experimental equilibrium isotherms data.

Langmuir's model [Eq. (2)] can be described as:

$$q_e = \frac{q_{\max}\cdot C_e \cdot K_L}{1 + K_L \cdot C_e} \tag{2}$$

where q_e is the amount of adsorbate adsorbed by unit of mass of adsorbent when equilibrium is attained (mg/g), $q_{\max}$ is the maximum amount of adsorbate adsorbed by unit of the adsorbent's mass (mg/g), C_e is the equilibrium concentration of the carbamazepine or ciprofloxacin solutions (mg/L), and K_L is the Langmuir constant (L/mg), which is related to the energy of adsorption.

Freundlich's model [Eq. (3)] is commonly used to describe the adsorption process on heterogenous surfaces. This model assumes that adsorption occurs in a multilayer and is described as:

$$q_e = K_F \cdot C_e^n \tag{3}$$

where K_F is the Freundlich constant (mg/g) that approximates the adsorption capacity, and n is the Freundlich constant that represents the adsorption intensity [20].

3. Results and discussion

3.1. Activated carbon textural characterization

In this work two activated carbons were utilized: one produced from leather industry wastes by chemical activation (WWAC) and one commercially available (ROW_0.8). Before adsorption tests, these carbons were characterized texturally using nitrogen adsorption at –196°C. The isotherms obtained are presented in Fig. 2 and the calculated results are presented in Table 1.

As shown in Fig. 2, the isotherms are type I, characteristic of microporous materials. Those isotherms also present hysteresis which is a phenomenon associated with capillary condensation in mesoporous structures. The hysteresis type was determined to be a type IV (according

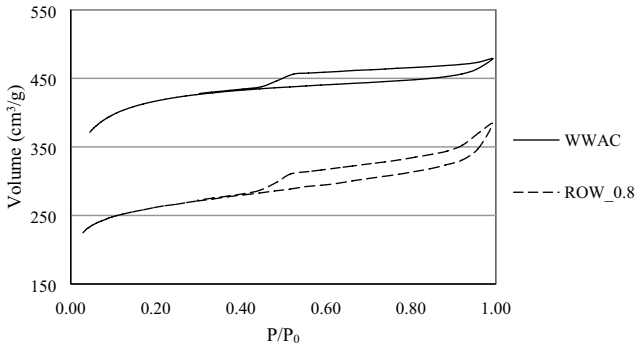

Fig. 2. Nitrogen adsorption at –196°C for the different carbons.

Table 1
Activated carbons textural characterization

	ROW_0.8	WWAC
V_{micro} (cm^3/g)	0.38	0.64
V_p (cm^3/g)	0.54	0.72
S_t (m^2/g)	106	51
S_{micro} (m^2/g)	886.3	1,533.4
S_{BET} (m^2/g)	992.3	1,584.3

to IUPAC's characterization), which is related to narrow slit-like pores [21]. It is also possible to observe, by the shape of the isotherms at relative pressures below 0.1, that WWAC has a wider micropore size distribution. When a carbon has mesopores, the slope of the isotherm at relative pressures greater than 0.3 is higher. The surface area corresponding to pores other than micropores (mesopores, macropores and external surface area) can be evaluated by the slope of the adsorption isotherm. The higher the slope, the higher the external surface area will be.

As can be seen in Table 1, WWAC has a higher specific surface area when compared to ROW_0.8. In addition micropore volume (V_{micro}) and total pore volume (V_p) are larger for WWAC. On the other hand, ROW_0.8 has a higher external surface area. From these results it is expected that WWAC will present higher adsorption capacities due to its textural parameters.

3.2. Adsorption tests

To test the viability of the use of adsorption as a method for removal of ciprofloxacin and carbamazepine, activated carbons were used in adsorption trials. Since pH can influence the adsorption process, three pH levels were tested. The experimental equilibrium adsorption data were fitted with Langmuir and Freundlich models using the minimization of the sum of squared errors (SSE) method.

The ciprofloxacin experimental adsorption results (at acidic pH) on both carbons, as well as the fitting curves from the Langmuir and Freundlich models are represented in Fig. 3. The calculated parameter values for each model and the sum of the squared errors are listed in Table 2.

The results obtained for ciprofloxacin show that WWAC is a better adsorbent for this compound due to its higher specific surface area, which can be seen in Fig. 3. It is also possible to observe that ROW_0.8 has some experimental point dispersion, when compared to WWAC.

Analysing Table 2 it can be observed that WWAC has a higher adsorption capacity than ROW_0.8 (more than 3 times higher). The highest adsorption capacities were obtained, for both materials, at acidic pH. CIP is an amphoteric compound and possesses both acidic and basic characteristics, and at acidic conditions (pH = 3) CIP is cationic [22]. The surface of activated carbons usually contains acid oxygen groups which can promote the adsorption of cations, explaining the higher adsorption capacities for acidic pH. The SSE values show that the model that best fits the experimental data is the Langmuir model at an acidic pH and the Freundlich model for neutral pH. Note that results for basic pH are not shown, due to instability of the solution, resulting in the precipitation of the adsorbate.

The results for the carbamazepine adsorption can be found in Table 3 and a representation of the Langmuir and Freundlich models fitted to the experimental data (at basic pH) is shown in Fig. 4.

From Fig. 4 it is possible to establish that WWAC has a higher adsorption capacity for carbamazepine when compared to ROW_0.8. In a similar manner to CIP adsorption, experimental points dispersion with ROW_0.8 can

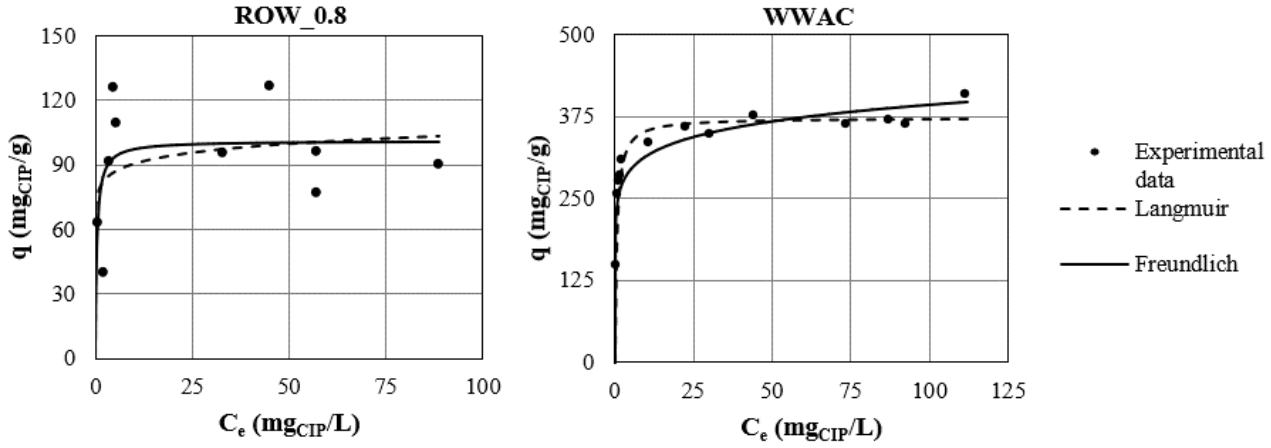

Fig. 3. CIP adsorption isotherms at acidic pH.

Table 2
CIP adsorption isotherm fitting results on activated carbons (Langmuir and Freundlich models)

Activated carbon	pH	Langmuir			Freundlich		
		q_{max} (mg_{CIP}/g)	K_L (L/mg_{CIP})	SSE (mg_{CIP}^2/g^2)	n	K_F (L/mg_{CIP})	SSE (mg_{CIP}^2/g^2)
ROW_0.8	Acid	101	2.50	4,721	0.061	78.7	5,471
	Neutral	66.7	9.83	2,849	0.062	57.5	2,667
WWAC	Acid	373	1.78	5,581	0.096	252	12,664
	Neutral	209	5.29	4,988	0.094	152	3,045

Table 3
CBZ adsorption isotherm fitting results on activated carbons (Langmuir and Freundlich models)

Activated carbon	pH	Langmuir			Freundlich		
		q_{max} (mg_{CBZ}/g)	K_L (L/mg_{CBZ})	SSE (mg_{CBZ}^2/g^2)	n	K_F (L/mg_{CBZ})	SSE (mg_{CBZ}^2/g^2)
ROW_0.8	Acid	177	0.182	17,951	0.183	74.4	21,057
	Neutral	133	0.395	2,151	0.262	49.1	3,017
	Basic	130	0.385	3,044	0.207	59.4	3,203
WWAC	Acid	384	0.156	39,427	0.201	145	7,374
	Neutral	380	0.265	28,279	0.295	109	36,434
	Basic	362	0.152	31,263	0.208	133	5,394

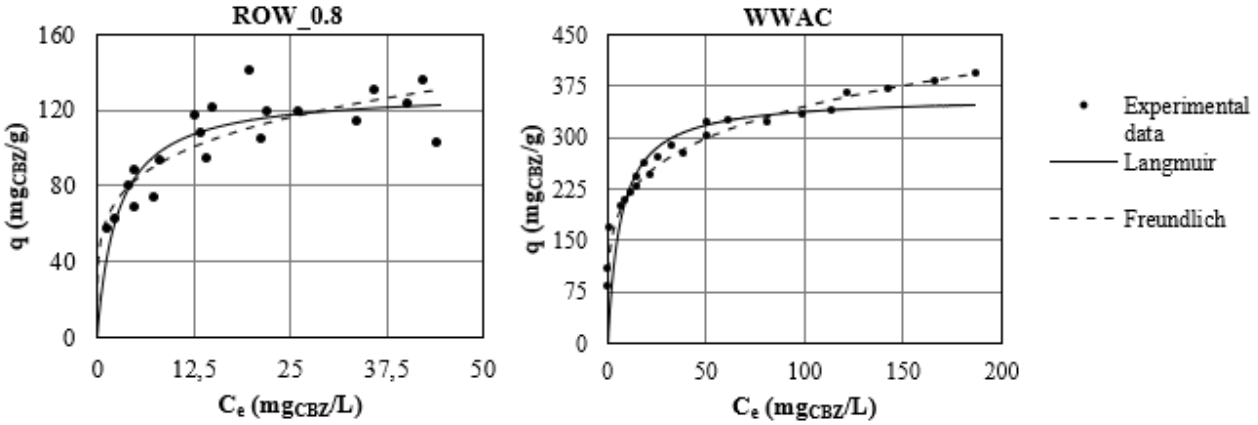

Fig. 4. CBZ adsorption isotherms at basic pH.

be observed. From Table 3 it is clear that the activated carbon produced from leather residues has higher adsorption capacities (q > 300 mg_{CBZ}/g) when compared with the commercial activated carbon (ROW_0.8). These results can be justified by the higher specific surface area of WWAC. It was shown that the Freundlich model offers the best fit for the adsorption isotherms for WWAC, except at neutral pH. The Langmuir model presents the best fitting for ROW_0.8. The adsorption capacity of WWAC presents a small variation (6%) with pH value. This behaviour was expected because CBZ is a neutral compound between pH 3 and 11 [22]. Nevertheless, for ROW_0.8 carbon the adsorption capacity is 30% higher at acidic pH, which may be a consequence of a poorer fitting of the model.

4. Conclusions

This work has shown that residues from leather tanneries can be valorised and that high-quality activated carbon (WWAC) can be produced and used as an adsorbent. This activated carbon is a better adsorbent for ciprofloxacin and carbamazepine when compared to commercially available carbons. The highest adsorption capacity for ciprofloxacin was obtained at pH 3 with WWAC. For carbamazepine, the best capacities were also obtained with WWAC and were not affected by pH level. Adsorption of pharmaceuticals (ciprofloxacin and carbamazepine) is a viable method for the treatment of wastewater containing these compounds.

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