


Proceeding Paper

Biowaste Valorization for Emerging Pollutant Abatement in Aqueous Phase [†]

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Abstract: The use of raw chemical- or thermal-modified pine bark (10 g/L) as a biosorbent to remove fluoxetine hydrochloride (FLX), carbamazepine (CRB) and atrazine (ATZ) from water at 5 mg/L each was explored in this work. The adsorption efficiency onto raw pine was as follows: FLX > ATZ > CRB. Pine oxidized with HNO₃ revealed to be the best modified biosorbent in terms of overall sorbate entrapment capacity (1.95 mg/g). The performance of raw pine (as the most sustainable biosorbent) was assessed in a pre-pilot air-lift-type reactor as a rehabilitation system to treat contaminated water for upscale purposes.

Keywords: biowaste; emerging pollutants; biosorption; cost analysis; circular bioeconomy



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1. Introduction

Environmental water pollution caused by emerging pollutants has become a challenging and growing problem worldwide due to their ineffective treatment in wastewater treatment plants [1]. Pharmaceuticals, such as FLX and CRB, and pesticides, such as ATZ, have been frequently detected in different water streams [2–4]. Due to their persistence in the environment and threat to aquatic and terrestrial biodiversity and human health [5], new and effective techniques to reduce their input on water systems is urgent.

The removal of pharmaceuticals and pesticides by adsorption has shown to be a cost-effective option in wastewater treatment [6,7]. The use of organic wastes as alternative biosorbents has been explored. With waste valorization, the dependency on natural resources is reduced, and a circular bioeconomy can be promoted [8]. Among them, pine bark has encouraged several authors to assess its efficiency due to its high potential sorption capacity by ion exchange and chelating processes [9–11]. To enhance its adsorptive capacity, acid or basic chemical modifications or thermal treatments (as hydrothermal carbonization) can be performed [12–14]. For large-scale use, the adsorption process can be performed in reactors, such as the air-lift-type. This kind of reactor is a viable alternative to column reactors because once the sorbent is forced to move by a gas flow it leads to a more effective use [15].

For a more realistic evaluation of the adsorption capacity of pine bark, the present research investigates the adsorption process in multiaqueous solutions (FLX, CRB and ATZ in mixtures as model compounds). The goal is to compare the adsorption capacity of raw chemical- and thermal- modified pine bark in batch experiments. The operation of a pre-pilot air-lift reactor was also investigated as an effective adsorption rehabilitation system for upscale use.

2. Materials and Methods

2.1. Chemicals

FLX (>98%), CRB (98%) and ATZ (PESTANAL[®] analytical standard, 99.1%) were purchased from Sigma-Aldrich. Table 1 summarizes the major physicochemical properties

of selected compounds. For the determination of pH of zero point of charge (pH_{zpc}), 1.0 M H_2SO_4 (95%, Fisher Chemical, Waltham, MA, United States), 1.0 M NaOH ($\geq 97\%$, Fisher Chemical) and 0.01 M NaCl (99.5%, Panreac, Barcelona, Spain) solutions were prepared. HPLC-grade acetonitrile (Fisher Chemical), orthophosphoric acid (analytical reagent grade, Fisher Chemical) and ultra-pure water, obtained from a Milli-Q Millipore system (Sigma-Aldrich, Burlington, MA, United States), were used to prepare the mobile phases for FLX, CRB and ATZ quantification by ultra-high performance liquid chromatography with diode array detector (UHPLC-DAD). A total of 2.5 M NaOH (98%, Labkem, Dublin, Ireland), 1 M H_2O_2 (30%, Fisher Chemical) and HNO_3 (69%, Fisher Chemical) were prepared for chemical surface modification procedures. A total of 1.0 M and 3.0 M NaCl, 50% HPLC-grade methanol (Fisher Chemical), acetonitrile or ethanol (99.8%, Fisher Chemical) aqueous solutions were prepared for desorption assays.

Table 1. Selected physicochemical properties of FLX, CRB and ATZ.

Chemical Name	Molecular Formula	Molecular Weight (g/mol)	pKa	Log K_{ow}	Water solubility (mg/L at 25 °C) [16]
FLX	$\text{C}_{17}\text{H}_{18}\text{F}_3\text{NO}\cdot\text{HCl}$	345.79	9.8 [9]	1.22 [9]	14,000
CRB	$\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$	236.269	13.9 [16]	2.45 [16]	18
ATZ	$\text{C}_8\text{H}_{14}\text{ClN}_5$	215.69	1.68 [17]	2.6–2.71 [17]	33

2.2. Preparation of Waste Biosorbents

Pine bark (*Pinus pinaster*) collected from a pine forest located in Braga (Portugal) was first ground into smaller particles, sieved (ranging from 1 mm to 2 mm) and washed with deionized water to remove impurities and powder particles. Afterwards, it was placed in an oven at 30 °C for 24 h to dry and then stored in a desiccator. Pine bark surface was chemically modified with alkali- and acid-modifying agents for further adsorption capacity evaluation. A total of 2.5 M NaOH aqueous solution was used as reducing agent for alkali modification, and 1 M of HNO_3 and 1 M H_2O_2 aqueous solutions were used for oxidizing modification. For both alkaline and oxidant treatments with HNO_3 , 10 g of raw pine was weighed and transferred to 1 L beaker with 300 mL of the respective modifying agent solution. For the treatment with 1 M H_2O_2 , a 1% of solid ratio was used instead. Mixtures were stirred thoroughly for 24 h at 180 rpm and 25 °C. Then, modified materials were filtered and washed with distilled water until no color was observed on supernatant and there was a constant pH. The solid was filtered and dried in an oven at 50 °C for 48 h. Pine bark hydrochar was prepared in a 500 mL reactor loaded with 25% of solid ratio and deionized water, in a final volume of 200 mL. The temperature of the reaction was set at 220 °C for 150 min. The experimental conditions were established based on the reported literature concerning agricultural residue hydrochars for adsorption process purposes [14]. The reactor was cooled to room temperature, and the solid was collected and washed with deionized water. Hydrochar was recovered by filtration and finally dried 12 h at 105 °C.

2.3. Biosorbent Characterization

The pH_{zpc} of selected biosorbents was determined as it helps to explain the electrostatic interactions between the target sorbates and adsorbent material. It was obtained using the pH drift method, following the procedure given in [10]. The surface chemistry of the biosorbents was studied by means of Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy. FTIR spectra were recorded with an ALPHA II-Bruker spectrometer (Bruker, Karlsruhe, Germany) using a diamond-composite cell. The measurements were recorded over the range from 4000 to 400 cm^{-1} , with a resolution of 4 cm^{-1} and 24 scans per sample. The surface morphology of pine bark was examined by scanning electron microscopy (SEM). Samples were evaluated by a Phenom ProX scanning electron microscope (Phenom-World BV, Eindhoven, Netherlands). All data were processed using

the ProSuite software v2.9.0. (ProSuite, Lievegen, Belgium). The observation of samples was performed with gold coating.

2.4. Sorbate Quantification by UHPLC-DAD

To increase total water solubility, FLX, CRB and ATZ were dissolved separately in acetonitrile (HPLC grade) and different stock solutions of 1 g/L were stored. Diluted solutions of each chemical were prepared from the respective stock solution adding ultrapure water. The mixture quantification was performed by UHPLC-DAD, using a Shimadzu Nexera X2 and a Kinetex C18 column (Phenomenex, Torrance, CA, United States) (1.7 μm \times 100 \AA \times 2.1 mm) operating in gradient mode. Eluents used were 0.1% phosphoric acid in ultrapure water (eluent A), acetonitrile (eluent B) and ultrapure water (eluent C) at a flow rate of 0.5 mL/min. The autosampler was operated at 4 °C, and the column temperature was kept at 50 °C, with an injection volume of 5 μL . The gradient elution started with 10% of eluent B, increasing to 100% B in 6.5 min, decreasing to 10% B in 1.0 min and then maintained the initial conditions during 1.5 min. The chromatograms were registered at a maximum adsorption wavelength of 227 nm. The linearity of the method was assured by setting a calibration curve over the concentration range of 0.3–10 mg/L. Detection limits (0.1 mg/L) were determined as the minimum detectable concentration of analytes in the test sample that can be reliably distinguished from zero. The quantification limits (0.3 mg/L) were set as the concentration above which the analytical method operates with precision. Two replicates of each standard were obtained, and the average peak areas were used for quantification. Data were processed by Lab Solutions software (version 5.71, Shimadzu Corporation, Kyoto, Japan).

2.5. Removal Capacity of Biosorbents

The adsorption potentiality of biosorbents was evaluated to compare them to the raw biomass. After the establishment of equilibrium time (previously established for each target molecule) onto raw pine bark, the adsorption capacity, q_t (mg/g) of the other studied biosorbents was determined. Biosorbent doses of 10 g/L each were used in amber Erlenmeyer flasks with 50 mL of a mixture of FLX, CRB and ATZ at 5 mg/L each. The flasks were shaken in a temperature-controlled incubator at 140 rpm and 25 °C until equilibrium was reached. At equilibrium time, samples were taken to determine the remaining FLX, CRB and ATZ concentration by UHPLC-DAD. A blank test at the same operational conditions but without biosorbent material was also monitored during the experiment.

2.6. Upscale Rehabilitation System

FLX, CRB and ATZ adsorption effectiveness at 5 mg/L each was assessed with raw pine under flow conditions in an air-lift-type acrylic reactor. The reactor (total volume = 5 L) has a circular cross-section ($\Phi = 0.07$ m) and is 1 m high. A 0.6 m long partition was mounted inside the reactor. The air supplied ensured the circulating motion of the contaminated solution and the biosorbent around the partition. The assay was conducted at batch mode for 6 days, using 3 L as working volume, a biosorbent concentration of 15 g/L, and the airflow was fixed at 2 L/min (optimized value). This flow rate enabled the biosorbent mixing in the entire reactor's volume and prevented sedimentation at the reactor's bottom. Periodically, samples were taken from the middle of the reactor height for UHPLC determination of each pollutant concentration.

2.7. Statistical Analysis

GraphPad Prism[®] software (version 8.0; GraphPad Software, Inc., San Diego, CA, USA) was used for statistical analyses. The level of significance was determined by two-ways ANOVA followed by post run test for multiple comparisons (Dunnett's test). Significance was accepted at $p < 0.05$.

3. Results and Discussion

3.1. Characterization of the Biosorbents

The pH_{zpc} corresponds to the pH where the net surface charge of the adsorbent reaches a zero-point value. This parameter is of fundamental importance in adsorption processes since it explains the electrostatic interactions between adsorbates and adsorbent. The pH_{zpc} of natural pine bark presents a value around 5. The alkali modified pine presented a pH_{zpc} of 6.5, and for the oxidant modified, values of 3 and 3.8 were obtained for the treatment with HNO_3 and the H_2O_2 , respectively. The pH_{zpc} of the hydrochar was determined to be 2.8.

The ATR-FTIR spectra of the biosorbents were recorded in the region of 400–4000 cm^{-1} and are shown in Figure 1. FTIR measurements revealed the availability of functional groups on the cell walls of *Pinus pinaster* in relation to the performed chemical and treatment processes. The FTIR spectra of the original samples is described in a previous work of this research group [10]. All samples exhibit a vibration at 1600 cm^{-1} that can be assigned to an aromatic ring stretching mode, representative of the aromatic nature of the samples. The FTIR spectra of the sample oxidized with H_2O_2 did not show relevant differences in terms of functional groups compared to the raw material. The raw pine presents bands at 2910 and 2844 cm^{-1} due to asymmetric and symmetric C–H stretching vibrations in the aliphatic chains –CH, –CH₂ and –CH₃. The oxidized pine with HNO_3 does not reveal the existence of these bands. In the alkali-modified pine, the carbonyl group (band at 1700 cm^{-1}) is not so evident as in the other samples. Pine hydrochar retained considerable oxygen-containing functional groups after hydrothermal treatment. Peaks between 3200 and 3600 cm^{-1} correlated with O–H stretching of hydrogen-bonded hydroxyl groups and were still evident in the hydrochar compared to raw pine bark. The peak at approximately 2906 cm^{-1} , which can be explained as –C–H stretching of the methylene groups, is present [18]. Peaks about 1100 and 1200 cm^{-1} appear in the hydrochar and not in the raw biomass. The peaks at ~1100 and 1200 cm^{-1} correspond to C–O stretching and O–H bending modes of alcoholic, phenolic and carboxylic groups [19]. The bands at 1719 cm^{-1} can be assigned to the C=O stretching vibration from ketone, aldehyde or carboxyl groups. However, this band is not so evident on hydrochar (the carboxylic acid groups are thus not so predominant in this biosorbent).

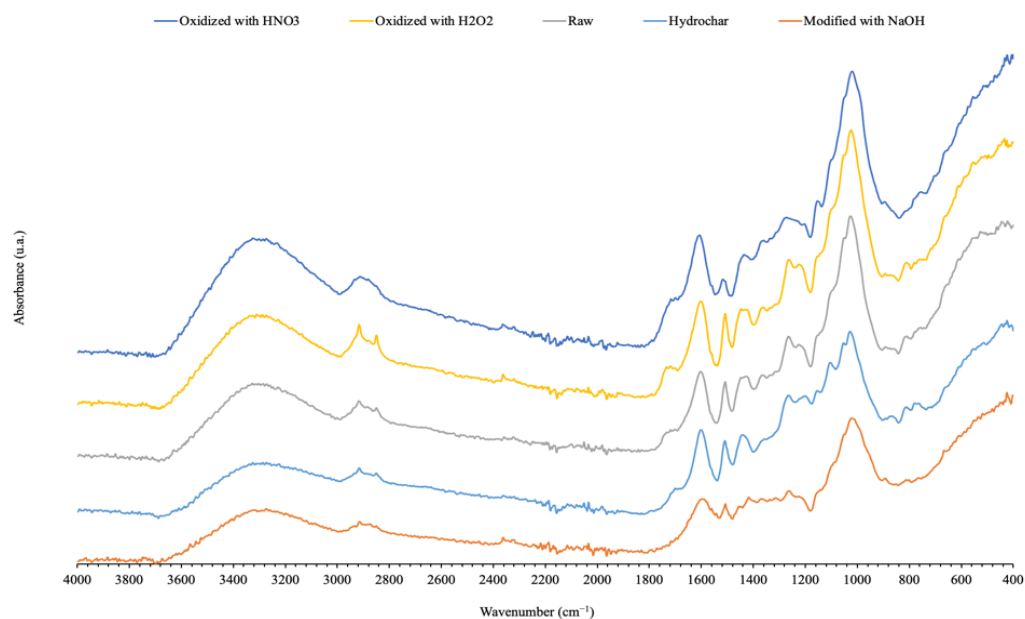


Figure 1. ATR-FTIR spectra of raw pine and modified biosorbents.

SEM has been used as a primary tool to characterize the surface morphology and the essential physical properties of the adsorbents, such as porosity and structure. Figure 2

shows a radial view of a ray of *Pinus pinaster* bark constituted of small pits. Pine bark presents a very low specific surface area (<4 m²/g [17]).

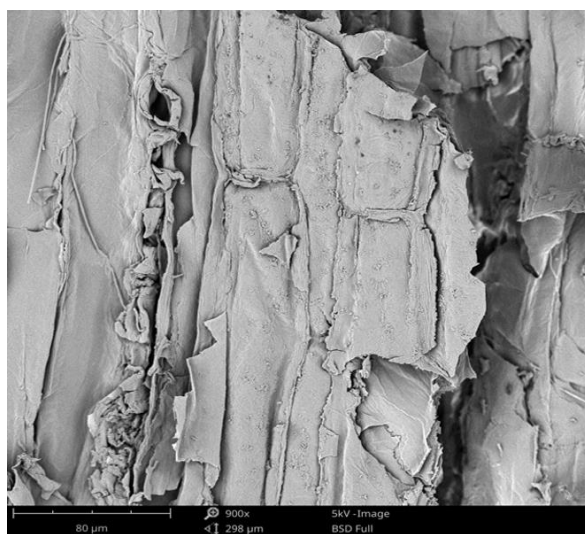


Figure 2. SEM micrographs of pine bark.

3.2. Modified Biosorbents Performance

Figure 3 shows the maximum adsorption capacity of selected biosorbents. The adsorbed amount of FLX was similar apart from the type of sorbent. The electrostatic attraction between the positively charged FLX molecules and the negatively charged biosorbent surface (except the alkali-modified one) promotes the adsorption of this analyte. On the alkali-modified biosorbent, the sorbate repulsion did not have a relevant impact on the adsorption mechanism. This less important electrostatic repulsion is due to a small difference between solution pH and the p*H*_{ZPC} value, which produces a not-so-intense positive charge on the biosorbent surface [20].

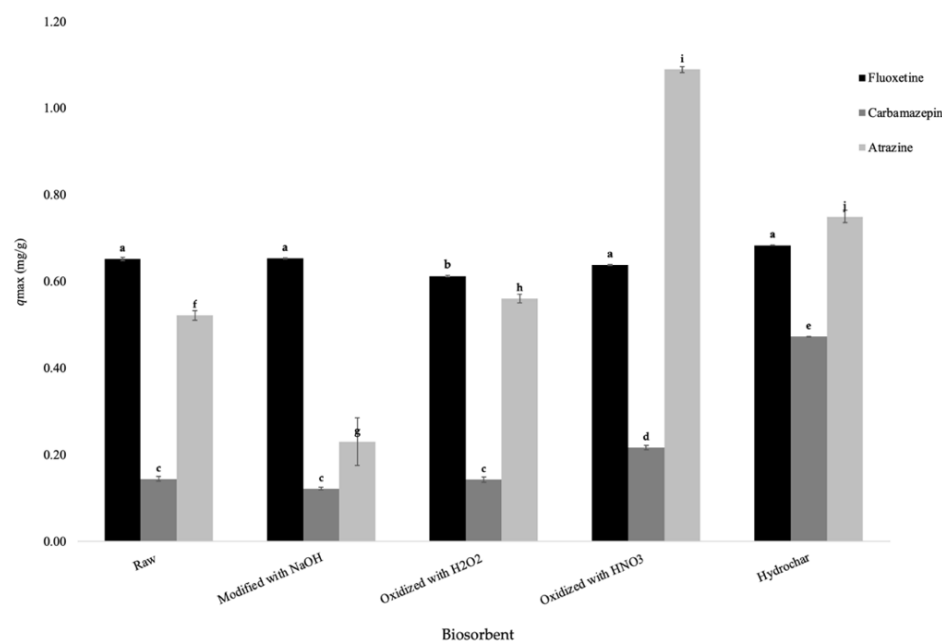


Figure 3. Maximum adsorption capacity of FLX, CRB and ATZ by different biosorbents. Experimental conditions: C = 5 mg/L each, biosorbent dose 10 g/L. Different letters show significant differences (*p* < 0.05) between biosorbents against raw pine performance for the same pollutant using the Dunnett’s test for multiple comparison. FLX (a,b), CRB (c–e) and ATZ (f,j).

The modification of pine with NaOH decreased the capacity for CRB and ATZ adsorption, compared to the raw material. These results can be explained by the hydrophilicity of CRB and ATZ molecules and the very weak attraction forces assumed by CRB and ATZ neutral charges and the positive charge of the surface.

An acid treatment induces a negative charge on the surface, promoting the adsorption of positively charged analytes. The biosorbent treated with HNO₃ was more efficient than the one with H₂O₂ due to the lowest p*H*_{ZPC} value that promoted stronger electrostatic attraction between the negative biosorbent surface and the sorbate molecules. An increment in adsorption capacity of 52.07% for ATZ and 6.95% for CRB was reported with the HNO₃ treated biosorbent.

The majority of the CRB molecules are neutral along with pH. Thus, even though the surface of biosorbents changes, their adsorption ability toward neutral molecules will remain low, due to a very weak electrostatic attraction between sorbate and biosorbent. The results indicate that pine hydrochar shows a high adsorption capacity for all pollutants. The maximum increase was obtained for CRB (69.46%), followed by ATZ and FLX at 30.39% and 4.58%, respectively. This can be correlated with the abundant functional groups on hydrochar surface, confirmed by the FTIR measurements.

3.3. Air-Lift Reactor Performance

To evaluate the behavior of the waste biosorbent obtained from *Pinus pinaster* biomass waste in an upgrade adsorption system, a discontinuous experimental assay was performed using a preupscale air-lift reactor. The air-lift system has several advantages, such as stable fluid motion due to separation of upward and downward flows and a high efficiency of suspending particles due to the fast fluid flow [21]. To the best of the authors' knowledge, this is the first study in this kind of reactor using pine bark for the adsorption of FLX, CRB and ATZ.

The results obtained from the assay in the air-lift reactor are shown in Figure 4. The sorbent reached saturation in FLX after approximately 6 h, while it saturated in CRB in 124 h and in ATZ in 144 h. The adsorption capacity of FLX, CRB and ATZ in this system at equilibrium was 0.462, 0.275 and 0.447 mg/g, respectively. The results support the effectiveness of FLX, CRB and ATZ adsorption under dynamic (flow) conditions. The air-lift reactor represents thus a viable upscale rehabilitation design to treat water contaminated with pharmaceuticals and pesticides.

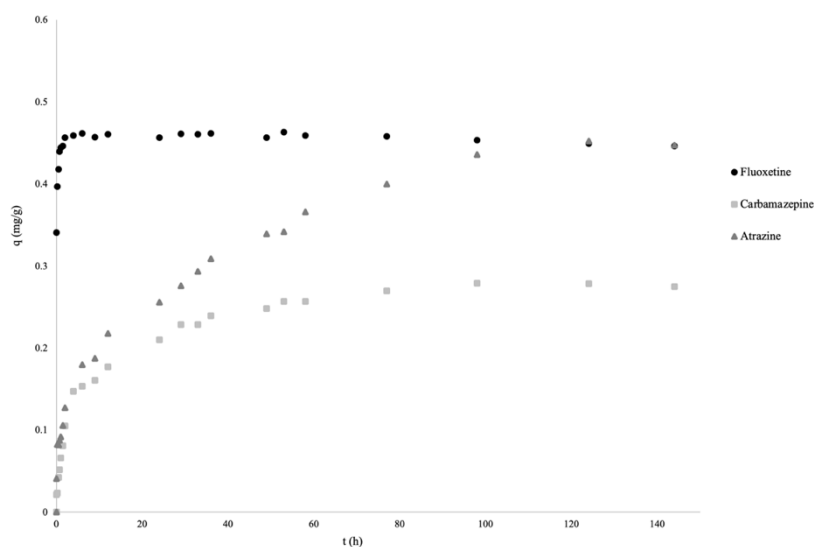


Figure 4. Adsorption of FLX, CRB and ATZ along time using an air-lift reactor. Experimental conditions: C = 5 mg/L of each pollutant, biosorbent dose 15 g/L, air flow 2 L/min.

4. Conclusions

The present work displays pine bark as a promising biosorbent for the removal of active pharmaceutical ingredients and pesticides from aqueous solutions. The sequence of adsorption efficiency for targeted pollutants onto raw pine was as follows: FLX > ATZ > CRB. Chemically and thermally modified pine biosorbents were investigated to compare adsorption capacities, based on surface accessibility and affinity to adsorbates. Pine modified with HNO₃ revealed to be the best biosorbent in terms of overall pollutant removal (1.95 mg/g). The adsorption of FLX, CRB and ATZ by the raw biomass was also evaluated under dynamic (flow) conditions in a prepilot air-lift type reactor. The results allow to confirm the effectiveness and viability of the system to treat contaminated water for upscale purposes. Waste biosorbents may be successfully applied and be cost-effective for the removal of emerging pollutants from water. With the exploitation of forest wastes for adsorption applications, an environmental protection technology is promoted by pollution mitigation and waste valorization.

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