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TECHNICAL NOTE

Evaluation of the Adsorbent Potential of Biochar obtained by Pyrolysis to remove Emerging Contaminants

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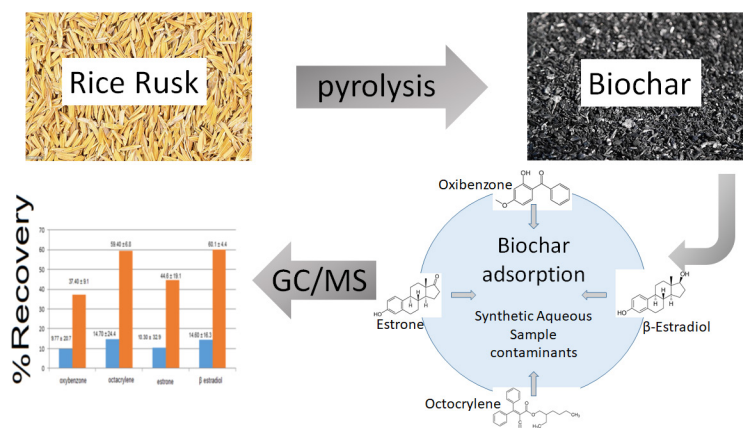Emerging contaminants (EC) can be harmful to human health and the environment, as many of these compounds are persistent, bioaccumulative, toxic and are not regulated. Drugs are part of this group, including hormones (estrone, β-estradiol) and sunscreens (oxybenzone and octocrylene) used in this study. The adsorption capacity of biochar generated from the pyrolysis of rice husks from the region of Pelotas, RS, Brazil was evaluated in this study. The objective was to characterize the biochar and evaluate its adsorbent potential in the removal of hormones and sunscreens. The characterization of biochar was carried out through surface area (BET), Zero charge point (ZPC), X-ray diffraction (XFR), fixed carbon, volatile, and ash. The effectiveness in removing ECs was evaluated by stirring rice husk pyrolysis biochar (RHPB) (0.2 g and 0.5 g) in synthetic aqueous solutions fortified with 10.0 µg L^{-1} of the analytes at 25 °C for 1 hour at 150 rpm. The RHPB was filtered off and the analytes were desorbed with acetone and dichloromethane (DCM) under ultrasound for 30 min. The extract was concentrated, derivatized by silylation, and analyzed by gas chromatography coupled to mass spectrometry (GC-MS). Biochar showed promising removal results, reaching values of 60.1% removal for β-estradiol, 59.4% for estrone, 44.6% for octocrylene and 37.4% for oxybenzone.

Keywords: hormones, sunscreens, rice husks, biochar, adsorption

INTRODUCTION

In recent years, great attention has been paid to the issue of emerging contaminants (EC) and has been addressed in different ways by researchers around the world. Emerging contaminants are chemical substances that are not yet regulated but that are detected in surface and groundwater, soil, air, sediments,

and in aquatic and terrestrial organisms. These substances usually include pharmaceuticals, hormones, personal care products, pesticides, solvents, plasticizers, flame retardants, among others.[1,2]

The types of emerging contaminants can be subdivided, such as the typology of hormones, which may belong to the class of endogenous hormones: estrone, 17β-estradiol, estriol, progesterone, testosterone; or synthetic hormones: mestranol, 17α-ethinylestradiol, diethylstilbestrol, levonorgestrel. Thus, natural and synthetic estrogens are considered endocrine disruptors, therefore, they interfere with the synthesis, secretion, transport, metabolism, binding, action, or elimination of natural hormones in the body, which are responsible for maintaining homeostasis, reproduction, regulation of processes, and of development.[3] Also part of this group of contaminants are chemical sunscreens, such as octocrylene which is often combined with oxybenzone in sunscreens to help increase protection against UV rays and protect the skin from sun damage, on the other hand, oxybenzone and octocrylene are chemical compounds that are toxic to aquatic organisms, including fish, crustaceans, and algae.[4,5] Exposure to these contaminants can cause damage to tissues and organs, as well as reduce the rate of growth and reproduction, and they are bioaccumulative and can pass to humans.

EC could only be detected and quantified recently through the development of new sensitive and more complex analytical techniques, such as gas or liquid chromatography coupled with mass spectrometry (GC-MS and LC-MS). These EC are found in very low concentrations, generally in an aquatic medium, which is of the order of $\mu g\ L^{-1}$ – $ng\ L^{-1}$, however, it may vary, both for more and for less.[3,6] The conventional processes of treatment are not effective for removing these compounds, since they have a stable chemical structure and complex biodegradation, mainly due to the polar nature of many of them. Current conventional treatment technologies applied to effluents generally do not promote significant removal of these contaminants.[1,7]

For the removal of contaminants, the scientific community has studied methods that are effective for the process. According to Ramalho Junior, methodologies are classified as physical-chemical treatments, biological processes, and advanced processes.[8] Some of these methods are costly, making their application unfeasible and directing studies toward methods that are efficient and less costly. In this sense, several options for the treatment of these EC have been discussed, among them, the processes of adsorption and bioadsorption/biodegradation. Activated carbons have hydrophobic characteristics, high surface area, and functional sites on the surface, regenerability, and porous structure, among others, which give them a high adsorptive capacity. However, it is still considered an expensive product, motivating research on the adsorption capacity with low-cost materials, such as lignocellulosic biomass in the form of agro-industrial residues.[7] Among these, biochar is a highly porous material, rich in carbon, may contain oxygenated functional groups, and mineral material.[8] As for organic contaminants, their structure directly determines the types of interaction with biochar. According to Aryee et al., biochar can promote interactions with organic contaminants, such as hydrogen bonds, induced dipole interaction, hydrophilic attractions or ionic attraction, influenced by pH, surface area and chemical groups of biochar.[9]

Rice husk (RH), a by-product of grain processing, is generated in large quantities in the region of Pelotas-RS, causing an environmental problem in disposal, due to its phenol content and silica.[10] Rice husk pyrolysis is considered a promising technique for producing renewable energy and chemicals from agricultural waste.[11] According to Huang and Lo, biochar is a by-product of bio-oil production in yields of 15% and 25%. If bio-oil production becomes widespread, the resulting biochar will be widely available for water and wastewater treatment use.[12]

The novelty of this study lies in the fact that we used an abundant residue, rice husk in the region and in the world, to obtain an adsorbent without additional activation processes. The application of this in the removal of emerging contaminants represents an efficient and low-cost alternative.

The objective of this study was to characterize and evaluate the adsorbent potential of biochar obtained by rice husk pyrolysis (RHPB), in the removal of hormones and sunscreens from water samples considered as emerging contaminants.

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MATERIALS AND METHODS

This study was carried out on the premises of the IFSul-Campus Pelotas, RS, Brazil in the Laboratory of Environmental Contaminants (LACA), and in the Laboratory of Chemical Engineering Processes.

The Biochar used in this work was obtained from (RH), in a stainless-steel reactor installed at the IFSUL-Campus Pelotas, the process was carried out with 100 g of (RH) with 2 mm in diameter, in a fixed bed, with nitrogen at a flow rate of 60 mL min^{-1}, at a temperature of 600 °C, heating rate of 25 °C min^{-1} and residence time of 10 minutes, as performed by Fusinato et al., named in this work rice husk pyrolysis biochar (RHPB).[13]

For the development of the study, the following sunscreens were used: octocrylene, purity ≥ 98.00% HPLC, and oxybenzone, purity ≥ 98.00% GC. As hormones, estrone, purity ≥ 99.00%, and β-estradiol, purity ≥ 98.00% were used. The stock solution of each compound was prepared individually, methanol was used for estrone, purity 99.80% (Synth®), and for the other three analytes, acetonitrile was used, purity 99.98% (Merck®). From the individual stock solutions of each compound, a single solution was prepared, containing the 4 analytes in acetonitrile, where all compounds had a final concentration of 5.0 mg L^{-1}. Working solutions were prepared in dichloromethane, purity 99.99% (Synth®). All solvents used were previously distilled. The standard compounds were all Merck® purchased from Sigma Aldrich Brazil Ltda. Water was purified using a Milli-Q system (Millipore, Bedford, MA, USA). Vetec brand NaOH, Synth brand HCl and NaCl were also used, all with P.A. purity.

Biochar characterization
Immediate analysis

Biochar samples were prepared and analyzed in triplicate, according to the ASTM D1762 standard (ASTM 2007), for analysis of moisture, volatile materials, and ash. Then, the fixed carbon content was mathematically determined, subtracting the moisture content, volatile materials, and ash of the samples from 100, according to Fusinato et al.[13]

X-ray fluorescence (FRX)

Semi-quantitative chemical composition of the inorganic part of the biochar was determined through FRX. The samples were ground, sieved, the loss on fire was removed and analyzed in the Epsilon 1 equipment from the manufacturer Panalytical, in the semi-quantitative Ominion calibration curve, in the following analysis conditions: Ag anode; kV: 50; µA: 100; Filter: Cu-500; Detector: SDD 5; Atmosphere: Air. Performed at the Fossil laboratory at UNISINOS-RS (University of Vale do Rio dos Sinos, RS, Brazil).

X-ray Diffraction (XRD)

The mineralogical characterization of biochar was determined through X-ray Diffraction (XRD) analysis in an X-ray diffractometer model Miniflex 300 (Rigaku) operating at 30 kV and 10 mA, with radiation from the copper Kα line (CuKα → λ = 1.5418 Å) with a sweep speed of 0.03º per second in the 2θ range between 5 and 99.98° at CADEQ Analytical Center of the Federal University of Santa Maria (UFSM), Santa Maria, RS, Brazil. The peaks were identified using the Diffractometer software, and the PDXL (integrated x-ray powder diffraction software).

Brunauer, Emmett, Teller (BET) reviews and Barrett-Joyner-Halenda (BJH)

The methodology applied for the analysis of the specific surface area of the biochar was nitrogen adsorption by the BET method. Pore volume and diameter were determined using the BJH method. The test was carried out in the equipment model Gemini VII 2390ª, in the CIA/FURG laboratory of the Federal University of Rio Grande (FURG), RS, Brazil. The sample was degassed in a vacuum atmosphere at 200 °C for 4 hours.

Zero charge point (PCZ)

For this analysis, 20 mL of 0.1 M NaCl solution was added in a 125 mL Erlenmeyer, with initial pH values (pHi) previously adjusted from 1 to 11 with NaOH and 0.1 M HCl solutions. These values were measured in a pH meter, without contact with the adsorbent. They were then shaken with 0.2 g of the adsorbent (RHPB) in an orbital shaker at 110 rpm and a temperature of 25 °C for 1 hour. The samples were filtered and then the final pH (pHf) of the solutions was measured again in a pH meter. The ΔpH versus pHi graph was performed. The zero-charge potential value is the point where the curve of ΔpH (pHf-pHi) *versus* pHi intersects the x-axis.[14]

Validation of the chromatographic method

Linearity was evaluated by constructing a calibration curve in a range of 0.2 to 2.0 mg L^{-1} obtained by derivatization and dilution of the 5.0 g L^{-1} stock solution of the mixture of standards. Precision studies were determined by calculating the relative standard deviation of the areas obtained from repeating 5 chromatographic analyzes of the 1.0 mg L^{-1} standard. The limits of detection (LOD) and quantification (LOQ) were calculated based on the analysis of the blank signal considering 3 times the standard deviation for LD and 10 times the standard deviation for LQ and divided by the angular coefficient of the analytical curves respectively.[15,16] Blanks were obtained using 100.0 mL of ultrapure water as described in Methodology for recovery of ECs. Accuracy was evaluated through the difference between the value found from the analytical curves and the value considered true (standard 1000 mg L^{-1}) expressed through the relative error. The, ions for quantification used were *m/z*: 285 (oxybenzone); 249 (octacrylene); 342 (estrone); 416 (β estradiol).

Methodology for recovery of ECs

First, a dilute aqueous solution containing 10 µg L^{-1} in 100 mL, was prepared from the fortified synthetic aqueous stock solution, name MIX. A 200 µL aliquot of the MIX was diluted in 100 mL of distilled water in a 100 mL volumetric flask. Then, the BPCA (0.2 g and 0.5 g) was stirred at 25 °C for 1 hour at 150 rpm on an orbital shaking table. The BPCA was separated by filtration and the analytes were desorbed with 10 mL of acetone and 10 mL of dichloromethane (DCM) under ultrasound for 30 min.[17] The extract was percolated in anhydrous sodium sulfate; the volume was reduced in a rotary evaporator. Next, the volume of the standard solution was derivatized, which when diluted to 1.0 mL corresponded to 1.0 mg L^{-1} for each standard, with 40.0 µL of N-trimethylsilyl-N-methyltrifluoroacetamide (MSTFA), at 80 °C in a sand bath for 30 minutes. In the selectivity and matrix effect studies, 100.0 µL of MSTFA and 20.0 µL of pyridine (purity degree ≥ 99.50% - Merck®, Darmstadt, Germany) were used as catalysts for silylation reaction, by 1 hour.[18] Afterwards, the volume was completed with dichloromethane to 1.0 mL and the sample was sent for analysis in GC-MS.

The study was carried out in a gas chromatograph coupled to a mass spectrometer (Model QP2010 ULTRA – SHIMADZU) equipped with an Rtx-5MS column (30.0 m x 0.25 mm d.i. x 0.25 µm – Ohio Valley Specialty Company, Marietta, Ohio, USA). The injection was performed in splitless mode with a purge of 2.0 mL min^{-1} and a carrier gas flow (ultrapure helium) of 1.0 mL min^{-1}. The injector and interface temperature were 280 °C, with an ion source temperature of 200 °C. The oven temperature was programmed in the following sequence: initial temperature of 150 °C maintained for 2 min, increasing 10 ºC min^{-1} until the final temperature of 300 °C, remaining for 15 min. Mass spectra were obtained in SIM mode, through electro-ionization at 70 eV. Furnace programming was based on the studies by Ferreira and Sanches Filho.[18] The data were processed using the GC-MS solution 2.6 software (SHIMADZU, Japan) and the compounds were identified using the NIST-05 library, considering superior similarities at 80%.[19] The recovery calculation was performed considering the standard of 1000 µg L^{-1} as 100% and the value obtained from the analyte corresponds to the % of its recovery.[18,19]

RESULTS AND DISCUSSION
Biochar characterization
Immediate analysis

The results of the immediate analysis of Biochar (RHPB) are Moisture 1.43%, volatile carbon 10.93%, fixed carbon 48.67%, and ash 39.17%, performed in triplicate. Based on the above, we can confirm that the main constituents are, the inorganic material (ash) and the fixed carbon, protagonists in the adsorption process, the results are in agreement with, Fusinato et al., Zangh et al., and Lemos.[13,20,21] The interactions between the adsorbent and the adsorbate are still not completely understood, but in general follow mechanisms involving polar attraction, hydrogen bridges, van der Waals forces, acid-base interactions, and electrostatic attraction, and depend in particular on the properties of the material that will be adsorbed.[12]

X-ray fluorescence (XFR)

The RHPB XFR was used in the work carried out by the group and presented in the article by Fusinato et al.[13] The largest constituent of the sample is SiO_2, corresponding to 71.31%, considering the inorganic part of biochar and discounting the LOI, SiO_2 is equal to 90.79% in weight, confirming that most of the inorganic content of biochar is silica, which has excellent adsorption properties. The result is in line with Ries et al., highlighting the importance of biochar obtained from rice husks having a higher amount of silica and oxygen compared to commercially activated carbons.[22] The result is also in accordance with the values found by Morales et al.[23] According to Kilton, silica is an adsorbent material that presents silanol groups in its structure, which can serve as active sites for the adsorption of aromatic compounds.[24]

X-Ray Diffraction (XRD)

In Figure 1, we can see that the diffractogram shows only the halo of amorphism characteristic of amorphous material, with a centralized peak, located between positions 2θ 15° and 30°, confirming the amorphous nature of biochar. These results are in agreement with Morales et al., and Scapin et al.[23,25]
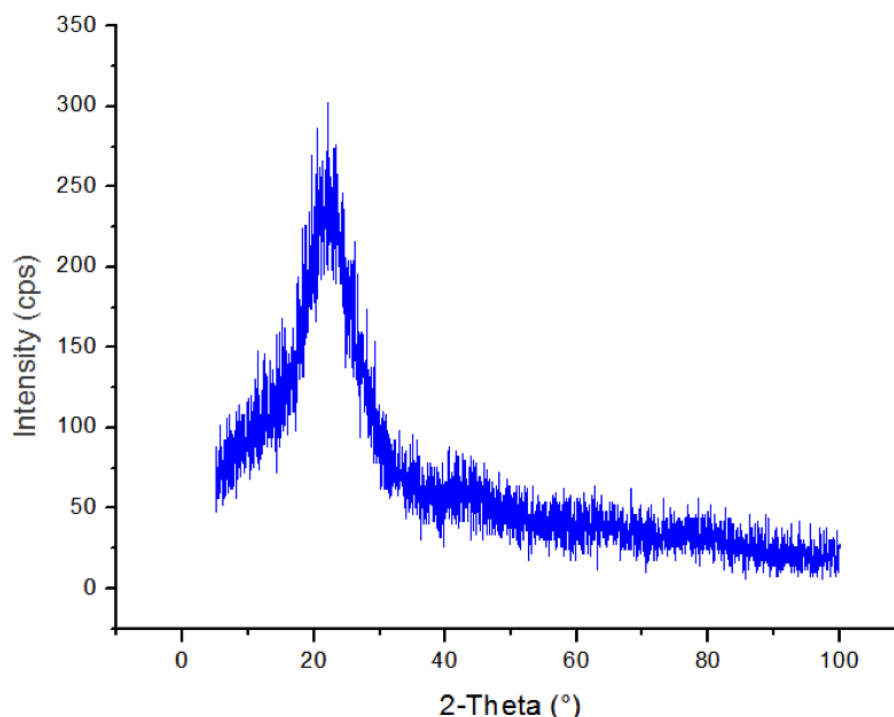

Figure 1. Diffractogram of the RHPB sample.

BET (Brunauer, Emmett, Teller) and BJH (Barrett-Joyner-Halenda)
The nitrogen adsorption-desorption isotherm for the RHPB sample is type IV with hysteresis (according to the IUPAC classification). This indicated the mesoporous nature of the product. Table I shows the results for surface area (BET), total pore volume determined by BJH and pore diameter determined by BJH.

**Table I**. Surface area, total pore volume, pore diameter of sample RHPB

Sample	SBET (m^2 g^{-1})	Vt (cm^3 g^{-1})	DBJH (nm)
RHPB	41.24	0.02	5.69

SBET = surface area by BET calculation, Vt = total pore volume, DBJH = pore diameter by BJH.

The surface area of 41.24 m^2 g^{-1}, this value is in agreement with the result described in the work of Ries et al.,[22] in which the biochar produced by them was also not chemically activated, in contrast to this same work, the surface area of chemically activated commercial carbons was much higher. In the work by Scapin et al.,[25] likewise, biochar without chemical activation has a result similar to that found in this work, and chemically and thermally activated biochars have a much higher surface area. The pore diameter of 5.69 nm confirms the mesoporosity of biochar.

Zero charge point (ZPC)
Figure 2 shows the curves used for the foreign of the ZPC of the RHPB and the value found for pHzpc was 6.3.
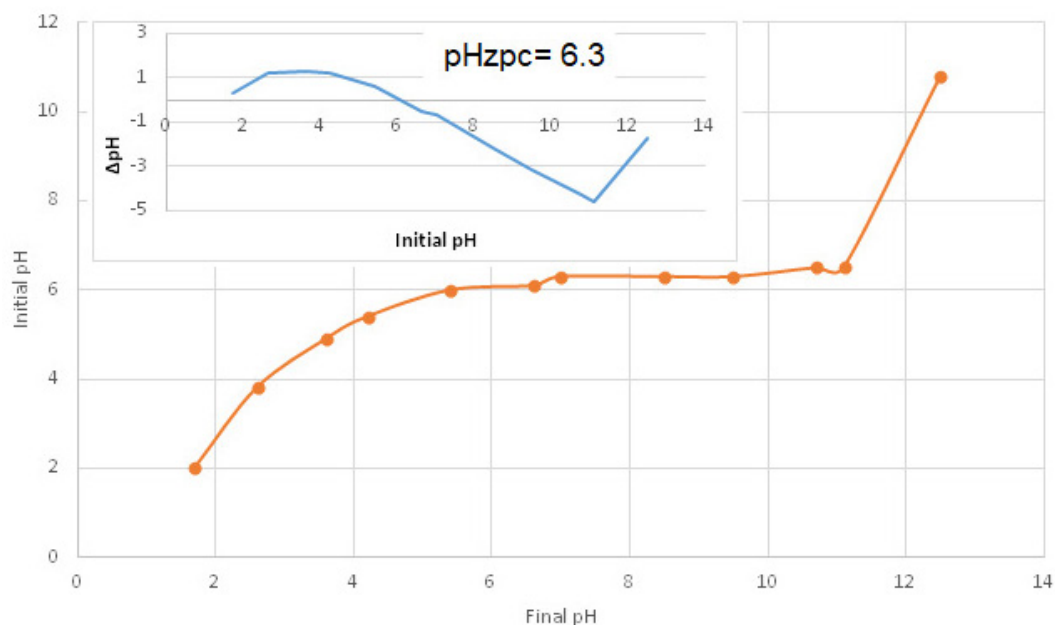
Figure 2. Initial pH *versus* final pH.

The pHpzc is the pH at which the electrical charge density on the surface of an adsorbent is zero, it is an essential criterion used to explain the efficiency of the adsorption process, in pH < pHzpc the surface becomes negatively charged and at pH > pHzpc it becomes negatively charged.[25,26] The pH of the solution indicates how the adsorption process will occur on the surface of the adsorbent, as it determines the chemical speciation of the element in the solution, as well as the surface charge of the adsorbent.[26,27]

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Validation of the chromatographic method

The results for validation of the chromatographic method (the studies of linearity, precision, accuracy, limit of detection and limit of quantification) are presented in Table II.

Table II. Figures of merit for validation of the chromatographic method

Compounds	RT (min)	m/z	Confirmation Ion	Time window (min)	a	b	r	RSD (%)	RE (%)	LOD (µg L⁻¹)	LOQ (µg L⁻¹)
oxibenzone	11.404	285	285; 300	5 - 16	212.22	-16022	0,999	5.0	8.1	0.02	0.08
estrone	16.383	342	257; 342	16 - 27	29.48	-3051	0,996	4.1	8.3	0.47	1.57
octacrylene	16.443	249	249; 361	16 - 27	24.723	-2915	0,998	4.5	6.8	0.53	1.77
β estradiol	16.680	416	285; 416	16 - 27	50.804	-7491	0,996	3.0	9.8	0.23	0.78

a: Angular coefficient; b: linear coeficiente; r: linear correlation coeficiente; RSD: relative standard deviation expressed as a percentage; RE %: relative error expressed as a percentage; LOD: limit of detection; LOQ: limit of quantification.

The chromatographic method behaved linearly for the work range studied with a linear correlation coefficient greater than 0.9 for all analytes.[15,16] Considering the angular coefficient value, the sensitivity was higher for oxybenzone followed by b estradiol due to their higher response factors of the quantitation ions used in the GC-MS.[16]

RSDs lower than 5.0% in RE% lower than 10% indicate a precise and accurate method of analysis according to INMETRO.[15]

Recovery of ECs

Figure 3 shows the results obtained in the recovery of emerging contaminants, the sunscreens: octocrylene, and oxybenzone, and the hormones: estrone, and β-estradiol. As we can see, the adsorption with 0.5 g of RHPB showed much higher gains, demonstrating the effectiveness of the recovery. As the test solutions had an average pH of 5.5, the compounds estradiol estrone and oxybenzone are found in their non-ionized form, which favors the formation of hydrogen bonds with hydroxyl groups in the structure of the RHPB.[27,28] The pH of the solution at low ZPC favors too the attraction of the analytes to the surface of the adsorbent by other mechanisms, compounds with a ring and phenolic group can also establish a π–π type interaction with the aromatic structure of the biochar. Octocrylene which has no ionizable groups or aromatic rings, does not make these types of interactions, the adsorption can be explained by van der Walls forces and induced dipole. The oxybenzone molecule is the smallest and most water soluble, which justifies its greater interaction with the aqueous matrix. The recoveries are in agreement with studies for biochar with the same surface area range.[28]
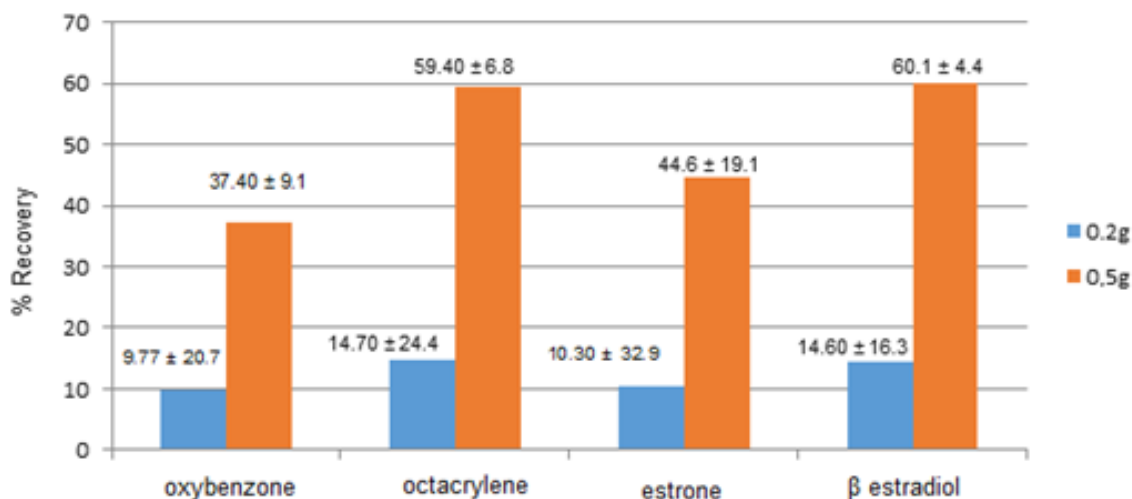
Figure 3. % Environmental Contaminant Recovery ± RSD (relative standard deviation).

CONCLUSIONS

The present study evaluated the adsorbent potential of biochar from rice husk in the removal of emerging contaminants, hormones, and sunscreens in aqueous solutions. Preliminary results already demonstrate that biochar, as it is obtained without any activation, has great adsorption potential, with excellent removal capacity, reaching values of 60.1% removal for β-estradiol, 59.4% for estrone, 44.6% for octocrylene and 37.4% for oxybenzene. The results presented here constitute the first step of promising research. Demonstrating an important application for a material of low-cost, and high-added value from agro-industrial waste that is harmful to the environment.

Conflict of interest

The authors declare that there is no conflict of interest.

Acknowledgements

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