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Rice Husk Bio-Chars as Adsorbent for Methylene Blue and Ethinylestradiol from Water

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Abstract: Biobased adsorbents are eco-friendly materials used for water and wastewater treatment and air cleaning. This research work explores the potential use of rice husk chars as a low-cost adsorbent for pollutants from water, such as methylene blue and ethinylestradiol. Rice husk chars are prepared by combustion of rice husks (RH-Char) or pre-treated rice husks (PT-Char). A third char (M-Char) supplied by a local company which uses rice husks as combustion material is also studied. The chars are characterized by field emission scanning electron microscopy (FE-SEM) in conjunction with energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD), and zeta-potential measurements. The three bio-chars are tested as adsorbent for the removal of two wastewater contaminants: methylene blue (MB) and ethinylestradiol (EE2). According to the results, RH-Char and PT-Char present zeta-potential values near −52 mV, whereas M-Char shows a zeta-potential value of −32 mV. Both RH-Char and PTChar are rich in amorphous SiO_2 and M-Char has crystalline SiO_2 (cristobalite). The bio-chars remove MB and EE2 efficiently showing the following results for the adsorption capacity of MB (in $\mu mol\ g^{-1}$): 769.2 (RH-Char), 41.2 (PT-Char), and 31.7 (M-Char). The adsorption capacity values for EE2 (in $\mu mol\ g^{-1}$) are: 33.1 (RH-Char), 19.1 (PT-Char), and 16.9 (M-Char). The information gathered in the present work evidences the potential of rice husks bio-chars for bio-remediation and may in future contribute to the conversion of a side-stream from the rice industry into value-added materials.

Keywords: Rice husk; bio-char; thermal treatment; adsorption; methylene blue; ethinylestradiol

1 Introduction

Rice husks (RH) are the hard-protective coverings of grains of rice and they are removed from rice seeds as a side stream during the milling process. The disposal of RH generates a huge problem for rice industry as

RH represents about 23% of initial rice seed weight. RH are mainly composed by three polymers (cellulose, hemicelluloses and lignin) which could be used as a value-added raw material for different purposes [1,2].

The valorization of this side stream could not only solve the disposal problem but could also reduce the cost of waste treatment and create new commercial opportunities [1]. One possible use for RH valorization is to burn it as fuel for energy and vapor production. When RH are incinerated the ash obtained during the process is called rice husk ash (RHA) which can be used as land filling. In Uruguay, 270000 ton per year of RHA is produced and must be disposed periodically, generating high disposal costs [2].

Other uses for the rice husk have been investigated. Rice husk is used as a fertilizer in agriculture, as an additive for cement and concrete fabrication, and in the production of commodity chemicals. RHA has become a source for the preparation of elementary silicon and silica due to its high silicon content [3]. It is also a source of activated carbon and it is tested as an adsorbent material [4]. Regarding the use of RHA as an adsorbent, previous work efforts are focused on water treatment, due to the large amount of available material and its low cost compared to commercial adsorbents [5,6]. This concept has potential benefits on both water treatment and waste management. However, Bhatnagar and Sillanpää have pointed out that more research is needed to find the practical utility of low-cost adsorbents at a commercial scale [7]. RH and RHA have been evaluated to remove contaminants from water and wastewaters such as dyes, [7,8] antibiotics, [9,10] toxic metals, [11] and nutrients [12].

Considering a further valorization of RH, an alkaline extraction prior thermal degradation has been investigated to separate and purify very valuable products from the husks, adding more value to the production chain of RHA [13]. An alternative is to separate hemicelluloses by organosolv delignification followed by alkaline extraction. The residual solid obtained after this process can also be valorized as an adsorbent by producing a bio-char form this solid. The pre-treatment and production of bio-char could be integrated with energy production, one of the main present uses of rice husks.

Finally, to study and compare the adsorption capacity of different adsorbents, one of the main compounds used is methylene blue [5,6]. Additionally, an interesting group of potential adsorbates is hormones such as estrone, estradiol and ethinylestradiol. These emerging contaminants are found in surface waters and wastewaters [14] at varying concentrations levels of ng L^{-1} [15]. For example, ethinylestradiol is reported in concentrations of 180 ng L^{-1} or 873.8 ng L^{-1} depending on the type of water (surface water or wastewater) and place of origin [16,17]. Several studies associate these hormones with different diseases and pathologies for both humans and wildlife [14,16,18]. Processes for removing hormones from water and wastewaters are reported in literature, including sorption, membrane filtration, liquid-liquid extraction, biological processes and advanced oxidation processes [14,15,19-22].

In this work, different residues from RH and RHA are tested as adsorbents. While other works focus on industrial rice husk char, this one also studies two chars prepared directly from rice husks and compares their performance with the industrial char. A serie of measurements and studies are performed to characterize the bio-chars. Methylene blue (MB) is used as a model adsorbate for comparison purposes and ethinylestradiol (EE2) is tested as a possible hormone to be removed from water.

2 Materials and Methods

2.1 Preparation of Bio-Chars

Rice husks (RH) were kindly supplied by Coopar S.A. (Uruguay) and industrial rice husk char (M-Char) were obtained from Galofer S.A. (Uruguay). Methylene blue (MB) and ethinylestradiol (EE2) were purchased from Sigma-Aldrich (USA) and Urufarma S.A. (Uruguay), respectively. Commercial activated carbon (AC) was produced by Brascarbo Agroindustrial Ltda (Brazil). Rice husk samples were first passed through a 1 mm^2 sieve to remove the small particles, and then grinded using a Fritsch Universal cutting mill pulverisette-19 equipped with a 1 mm trapezoidal perforation sieve cassette V2A.

Two different bio-chars, rice husk char (RH-Char) and pre-treated rice husk char (PT-Char) were prepared from rice husks and pre-treated husks, respectively. The alkaline pre-treatment for the pre-treated rice husk (PT-RH) was performed according to the organosolv delignification treatment followed by hemicellulose extraction with aqueous alkali, as it is described by Hoije et al. [23]. The char samples were prepared in a Heraeus MR 170 furnace (maximum temperature: 1000°C; dimensions: 560 mm × 730 mm × 640 mm; with temperature control adjustment system; W. C. Heraeus GMBH, Hanau, Germany) as follow: 6 g of rice husk or pre-treated rice husk was added to different uncovered crucibles and the crucibles were heated in the furnace, pre-heated at (400 ± 20)°C, for 1 h 20 min. After that, the crucibles were taken out from the furnace, and cooled down in a desiccator. All chars were manually ground and sieved during 5 min at half power in a vibratory sieve shaker (AS 200, Retsch, Germany) and the fraction with a particle size between 50 μm and 160 μm was further used in the experiments. Unless specified, all the values are expressed on oven-dry weight basis.

2.2 Characterization of Solid Particles

2.2.1 Moisture Content

A moisture analyzer MAC 50/NH (Radwag, Poland) was used to obtain the dry content of the rice husk and pre-treated rice husk. A known amount of the solid (1 g) was weighted and placed in the analyzer. The sample was heated up to 105°C until constant weight.

2.2.2 Fixed Solids Content

The fixed solids content of the rice husk and pre-treated rice husk was determined using the Heraeus MR 170 furnace. Temperature was adjusted to (550 ± 20)°C until constant weight.

2.2.3 Methanolysis, Silylation and Gas Chromatography Analysis

The polysaccharide content of RH and PT-RH was determined using methanolysis followed by silylation reaction and gas chromatography analysis. Methanolysis: about 10.0 mg, with 0.1 mg accuracy, of freeze-dried sample in an 8 mL Pyrex screw cap test tube was weighed. Then, 2 mL HCl solution (2 M in anhydrous methanol) was added and the tightly closed tube with the sample was kept in an oven at 105°C during 3 h to ensure a complete methanolysis of the non-cellulosic polysaccharides present in the sample. After that, the tube with the sample was cooling down to ambient temperature and 150 μL of pyridine was added to neutralize the acidic solution. Subsequently, 4 mL of internal standard sorbitol solution (0.1 mg/mL in methanol: water 9:1) was added to the tube and the sample was vortexed. A 750 μL of the resulting liquid phase was transferred to a new Pyrex screw cap test tube and induced upon nitrogen to remove the excess of methanol. The sample was dry further in a Heraeus vacuum oven for about 20 min at 40°C. Silylation: 120 μL–150 μL of pyridine was added to the dry sample obtained before. After shaking the sample with a vortex, 150 μL of hexamethyldisilazane (HMDS) and 70 μL of trimethylchlorosilane (TMCS) were added. After destroying the larger aggregates, which are formed during addition of the silylation reagents, in the ultrasound bath the sample was left to stand overnight. Finally, 100 μL–150 μL of supernatant was transferred to a conical glass vial and injected in the gas chromatograph Gas Chromatography: Temperature program: 100°C to 175°C (ramp: 4°C/min), 175°C to 290°C (ramp: 12°C/min). Injector at 260°C, detector at 290°C. Column: HP-1, 25 m × 0.2 mm × 0.11 μm. The results were analyzed with TotalChrom Navigator software.

2.2.4 Scanning Electron Microscopy (SEM) in Conjunction with Energy Dispersive X-ray Spectroscopy (EDX)

A Leo Gemini 1530 field emission scanning electron microscope with In-Lens detector (LEO Electron Microscopy Ltd., Oberkochen, Germany) was used to perform the analysis. The bio-chars were coated with carbon in Temcarb TB500 sputter coater (Emscope Laboratories, Ashford, UK). Optimum accelerating voltage was 2.70 kV. EDX attachment was directly connected to SEM to carry out the elemental analysis of the same.

2.2.5 X-ray Powder Diffraction (XRD)

A Bruker AXS D8 Discover with a 1-D detector using a Cu Kα X-ray source was used for the XRD measurements. The powder X-ray diffraction (PXRD) patterns of the samples were recorded using Siemens D501 diffractometer with copper K_α radiation (λ = 0.15415 nm). Patterns were recorded in the 2θ ranges of 5°–70° in steps of 0.04° with a counting time per step of 8 s. The chars were analyzed as such by pressing them gently onto a copper sample holder.

2.2.6 Zeta-Potential and Particle Size Measurements

The bio-char suspensions were analyzed in a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK). The solid concentration of all samples was 0.5 mg mL^{-1}. For each sample, the measurements were conducted in triplicate and 7–14 runs were performed for each measurement. The average data was reported after repeated analyses.

2.3 Sorption Assays

The adsorption experiments were carried out at room temperature (21°C ± 1°C) as follow: an amount of the selected bio-char was weighted on a 100 mL Schott Duran® laboratory glass bottle. Subsequently, a known volume of the adsorbate solution was added to the glass bottle containing the bio-char and the final volume of the adsorption solution was adjusted if needed. The flasks were shaken at 200 rpm on an orbital shaker (SKF2050, Lab. companion) during 20 h or 40 h.

2.3.1 Methylene Blue Sorption Assays

An amount of the selected bio-char (10, 20, 40, 60, 80 or 100 mg) was weighted. An exact volume of methylene blue solution (400 µM in 0.60 mM barbital solution, pH 8.5) was added to the glass bottle containing the bio-char (4, 6, 8, 10, 15, 20, 25, 30, 35, 40, 45, 50 or 75 mL depending which bio-char is being tested). The final volume of the solution was adjusted to 50 mL with barbital buffer (0.60 mM, pH 8.5) except when 50 or 75 mL of MB was added. After assays were performed, the final concentration of methylene blue in the solutions was determined by UV spectrophotometry at 664 nm in 1.5 mL polystyrene cuvettes, against barbital buffer (0.60 mM, pH 8.5), using a Shimadzu UV-2600 spectrophotometer.

2.3.2 Ethinylestradiol Hormone Sorption Assays

An amount of the selected bio-char (10, 20, 40, 60, 80 or 100 mg) was weighted. An exact volume of ethinylestradiol solution (7.8 µM in distilled water) was added to the glass bottle containing the bio-char (50 or 75 mL depending which bio-char is being tested). The final concentration of ethinylestradiol in the solutions was determined by high pressure liquid chromatography HPLC (Shimadzu, Japan). EE2 was detected using a fluorescence detector at an excitation wavelength of 280 nm and an emission wavelength of 310 nm. The column was a Phenomenex 5-µm Luna 5u C18 (4.6 mm × 150 mm). The mobile-phase solvent profile was 64.6% distilled water, 35.3% acetonitrile and 0.1% trifluoroacetic acid at a constant flow rate of 1.0 mL/min.

2.3.3 Sorption Isotherms

Two isotherms models, Langmuir and Freundlich, were tested to determine the sorption of methylene blue and ethinylestradiol on RH-Char, PT-Char and M-Char.

The linear form of Langmuir isotherm is given as [24]:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_{max}k_L} + \frac{C_{eq}}{q_{max}} \tag{1}$$

where q_{eq} (µmol/g) is equilibrium capacity of sorption, C_{eq} (µmol/L) is equilibrium concentration of MB or EE2, q_{max} (µmol/g) maximum monolayer sorption capacity, and k_L (L/µmol) is the constant related to affinity and energy binding sites. This model assumes that adsorption takes place onto a homogeneous surface as all sites possess equal affinity for the adsorbate.

The linear form of Freundlich isotherm equation is represented as [24]:

$$\ln\left(q_{eq}\right) = \ln\left(k_F\right) + \frac{1}{n}\ln\left(C_{eq}\right) \tag{2}$$

where q_{eq} (μmol/g) is equilibrium capacity of sorption, C_{eq} (μmol/L) is equilibrium concentration of MB or EE2, k_F is a coefficient which provides an indication of the sorption capacity, and n is a coefficient related to intensity of sorption. The model assumes that adsorption takes place onto a heterogeneous surface.

3 Results and Discussion

3.1 Dry Content, Fixed Solids Content, Non-cellulose Polysaccharide Content of Husks and Yield Percentage

The dry content of RH and PT-RH are 95.1% and 97.1% respectively. The fixed solids content, which are mostly silica, are 19.1% (RH) and 3.7% (PT-RH). This suggests the pre-treatment removes nearly all silica from the rice husks.

Non-cellulosic polysaccharides in samples RH and PT-RH percentage (in dry basis) and composition are shown in Tab. 1. Cellulosic content is estimated by difference considering that volatile solids are composed by cellulosic and non-cellulosic polysaccharides.

The yield percentages of the final prepared biochars from RH and PT-RH are 29.9% (RH-Char) and 18.6% (PT-Char). These values go in line with the lower fix solids content PT-RH has.

Table 1: Non-cellulosic polysaccharides in rice husks and pre-treated rice husks

Sugar monomer	% w/w	
	RH	PT-RH
Arabinose	3.8	5.0
Galactose	1.7	1.9
Galacturonic acid	0.6	0.6
Glucose	4.9	3.4
Glucuronic acid	2.0	0.5
Mannose	0.1	0.1
Rhamnose	0.3	0.3
Xylose	27.9	36.6
Total	41.2	48.4
Cellulosic content	39.7	47.9

RH, rice husks. PT-RH, pre-treated rice husks.

3.2 Structural and Morphological Analysis of Biochars (XRD, SEM and EDX)

The structural analysis of the bio-chars characterized using XRD, SEM and EDX analysis are given in Figs. 1 to 3. The diffractograms from PT and RH- Char display amorphous state of the material. However, with M-Char crystalline peaks are seen at 20.6°, 27.4°, 30.3°, 35.0°, 41.9° (Fig. 1). The EDX analysis reveals the presence of silica in all three materials with the presence of other trace elements (Fig. 3). The

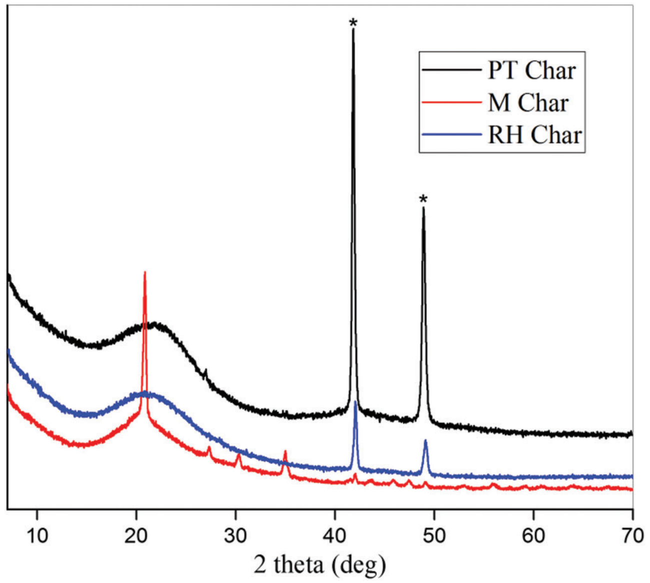

Figure 1: XRD patterns of the bio-chars. (* - To be ignored)

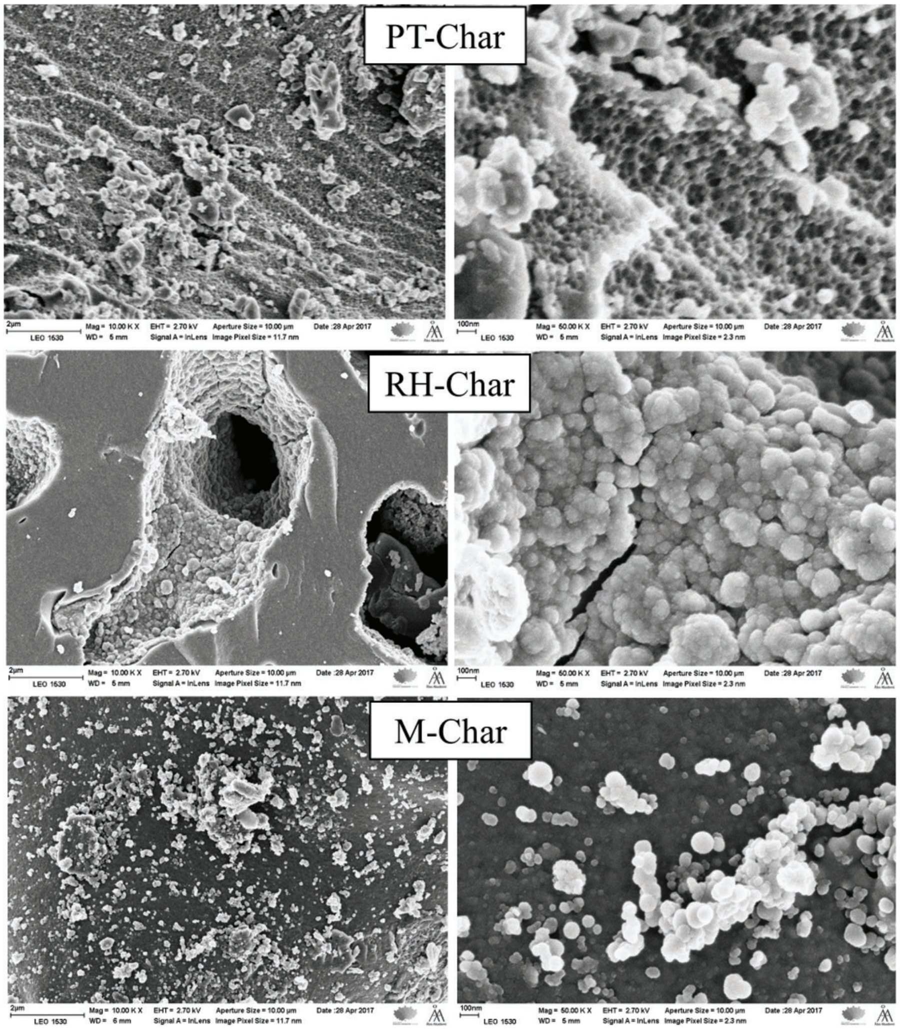

Figure 2: SEM images of the bio-chars

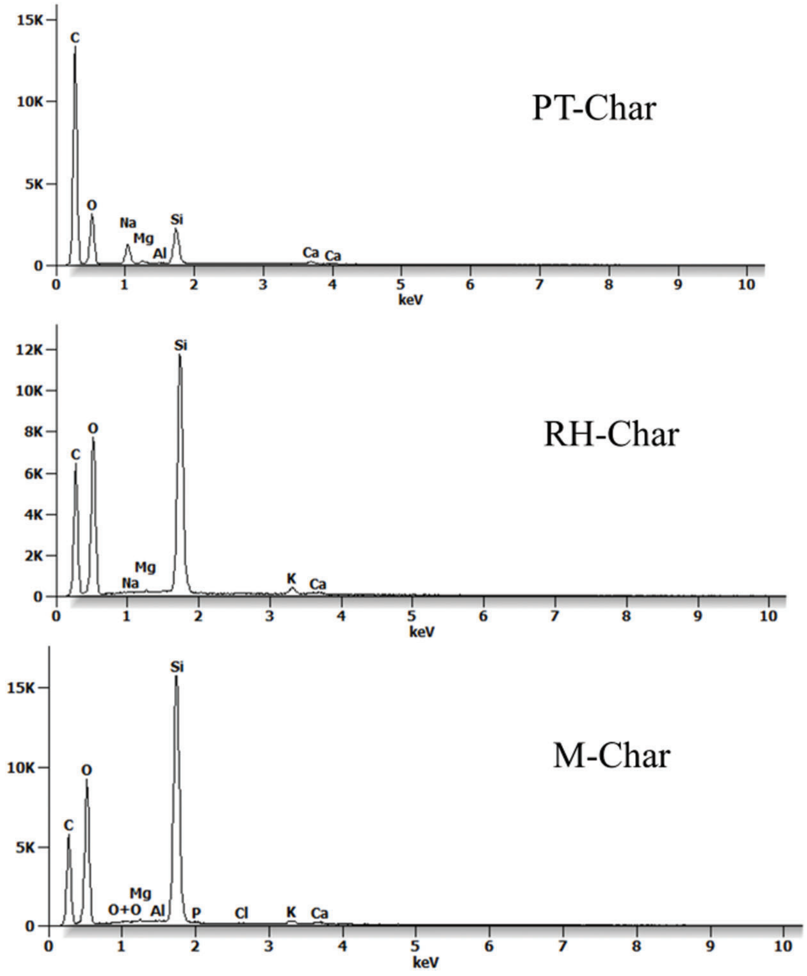

Figure 3: EDX patterns of the bio-chars

morphological feature of the bio-chars shows interesting porous and non-porous observations (Fig. 2). RH-char and M-Char shows particles with spherical structure whereas the PT-Char shows porous structure. Such pores can offer great absorption behavior towards the removal of contaminants from wastewater and other impure water targets.

3.3 *Zeta Potential and Crystallinity of Bio-Chars*

The results of zeta potential obtained for the chars in barbital buffer and distilled water are shown in Tab. 2. It also shows the particle size during the zeta potential measurements and the result of XRD analysis. There seems to be a link between crystallinity and zeta potential as the chars with amorphous silica display higher zeta potential. The different forms of silica the chars present could be explained due to the higher temperature at which M-Char is obtained (more than 1000°C) compared to RH-Char and PT-Char (400°C) The results of zeta potential are similar to those found in literature for amorphous and cristobalite SiO_2 [25,26].

3.4 *Isotherm Analysis*

The sorption assays data for the bio-chars is fitted to Langmuir and Freundlich adsorption models. Tab. 3 presents the correlation coefficients (R^2) of the models. It is found that the Langmuir model fits better the experimental results for both methylene blue and ethinylestradiol. Tab. 4 presents the values of q_{max} and

Table 2: Results of zeta potential, particle size during zeta potential measurements, and X-ray spectroscopy (XRD) of the chars

Sample	Zeta potential (mV)		Particle size (nm)	XRD phases
	Barbital buffer	Distilled water		
RH-Char	−50 ± 4	−52 ± 3	470 ± 30	Amorphous SiO_2
PT-Char	−54 ± 3	−53.4 ± 0,3	640 ± 60	Amorphous SiO_2
M-Char	−32 ± 2	−25.6 ± 0,5	n/d	Cristobalite SiO_2

RH-Char, char prepared with rice husks. PT-Char, char prepared with the pre-treated rice husk.
M-Char, char obtained from a mill in Uruguay.

Table 3: Langmuir and Freundlich isotherms correlation coefficients

	Methylene blue		Ethinylestradiol	
Solid name	Langmuir model R^2	Freundlich model R^2	Langmuir model R^2	Freundlich model R^2
RH-Char	**0.988**	0.881	**0.964**	0.624
PT-Char	**0.995**	0.972	**0.980**	0.912
M-Char	**0.997**	0.625	**0.982**	0.028

Table 4: Langmuir isotherm model parameters

Solid name	Methylene blue		Ethinylestradiol	
	q_{max} (μmol g^{-1})	k_L(L μmol^{-1})	q_{max} (μmol g^{-1})	k_L (L μmol^{-1})
RH-Char	769.2	0.302	33.1	2.349
PT-Char	41.2	0.935	19.1	2.178
M Char	31.7	0.916	16.9	–
AC	349.7	–	122.7	5.9

RH-Char, char prepared with rice husks. PT-Char, char prepared with the pre-treated rice husk.
M-Char, char obtained from a mill in Uruguay; AC, activated carbon.

k_L obtained for the Langmuir isotherm model. Commercial activated carbon (AC) was also tested for comparison and results of Langmuir isotherm fitting are also presented in Tab. 4.

Tabs. 5 and 6 compare the adsorption capacity of different solids in the removal of MB and EE2, respectively, calculated with Langmuir isotherm model. RH-Char presents higher adsorption capacity values than other adsorbents obtained from agroindustry waste materials, but are much lower compared with advanced adsorption materials, creating an opportunity to improve the performance of this bio-char.

3.5 Adsorption Study

The results of the adsorption experiments show that all bio-chars efficiently remove both MB and EE2 from water. However, the behavior of the bio-chars is different with each adsorbate. While PT-Char and M-Char reach similar removal efficiencies for the same initial MB/solid ratio, this is not the case for RH-Char (Fig. 4). According to the results from MB adsorption experiments, the adsorption capacity of the RH-Char is nearly 20 times more than the adsorption capacity showed by PT-Char and M-Char. It is worth mentioning

Table 5: Adsorption capacity 'q_{max}' (μmol g^{-1}) of MB from different adsorbents

Sample	q_{max} (μmol g-1)	Reference
Rice husk	108.8	[27]
Garlic straw	687.2	[28]
Hazelnut shells	206.1	[29]
Coffee husk	241.5	[30]
Activated carbon from oil palm shell	653.7	[31]
Silica nanoparticles	1467.4	[6]
RH-Char	769.2	Present work

Table 6: Adsorption capacity 'q_{max}' (μmol g^{-1}) of EE2 from different adsorbents

Sample	q_{max} (μmol g-1)	Reference
Aliphatic polyamide	83.7	[20]
Reduced graphene oxide magnetic nanocomposite	125.9	[17]
RH-Char	33.1	Present work

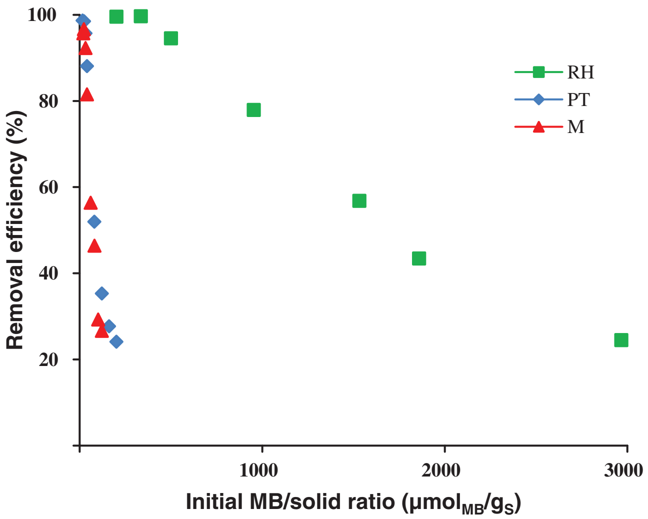

Figure 4: Removal efficiency of MB *vs*. initial MB/solid ratio in the solution

that for RH-Char the adsorption ends after 40 h while during the experiments using PT-Char and M-Char 20 h were enough to reach equilibrium. When EE2 is studied, RH-Char also shows a greater removal efficiency at the same value of initial EE2/solid ratio than the other chars but the difference is not as big as with MB (Fig. 5).

The increase in the apparent adsorption capacity of MB onto RH-Char, compare to the other chars, could be related to the amount of unsatisfied valence on silicon and oxygen in the surface of the char. These

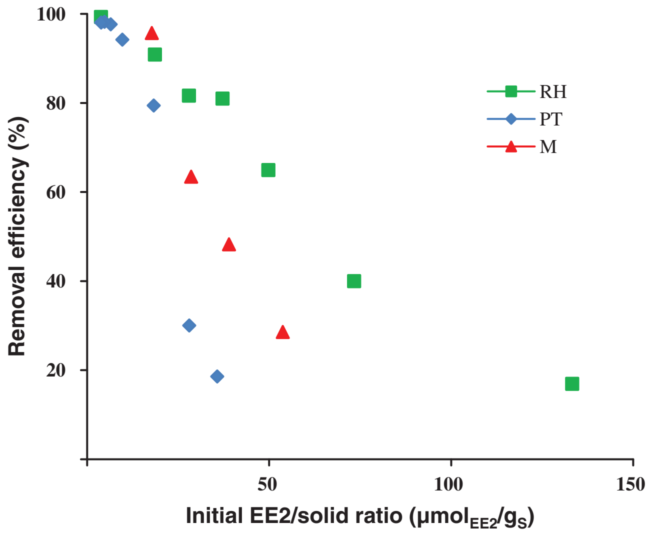

Figure 5: Removal efficiency of EE2 *vs.* initial EE2/solid ratio in the solution

immobilized free radicals react with OH^- and H^+ resulting in the formation of silanol groups $[Si(OH)_n]$, which dissociate in pure water through the following chemical reactions [26]:

$$-SiOH + OH^- \leftrightarrow Si{-}O^- + H_2O \tag{3}$$

$$-SiOH + H^+ \leftrightarrow Si{-}OH^{2+} + H_2O \tag{4}$$

At basic pH, the char presents a negative charged surface, improving the adsorption of positive charged ions/molecules, such as MB [6]. It is suggested that RH-Char presents more silanol groups on its surface than M-Char and PT-Char due to the amorphous SiO_2 found in RH-Char. M-Char is composed by cristobalite SiO_2 and M-Char is mainly a carbonaceous material although XRD reveals the presence of amorphous SiO_2. The results of fixed solids content support this conclusion. On both bio-chars, the amount of silanol groups in the surface would be inferior, explaining the experimental results. This effect could also explain the lower adsorption capacity that the activated carbon presented for the MB. In this case the adsorption was due to the higher surface area and porosity AC has rather than an ionic interaction between the dye molecule and the surface.

The increase in the adsorption capacity of MB due to the silanol groups in the surface of RH-Char is not applied to EE2 as it is a neutral molecule. The results indicate that the interaction between EE2 and the chars is caused by lower interaction forces, with the surface area and porosity of the char having an important role in the adsorption process. This is corroborated by the higher adsorption capacity obtained for the commercial AC.

4 Conclusions

In this work all bio-chars showed an efficient adsorption capacity for both dye (MB) and hormone (EE2), reaching efficiency percentages of more than 90%. After the pre-treatment, PT-Char was still capable of removing MB and EE2, in a similar amount as M-Char, meaning that adsorption could be an opportunity to add value to the rice husk and industrial rice husk char.

RH-Char showed a remarkable efficiency for MB removal compared with PT-Char and M-Char. This might indicate that the positive charge ions/molecules in aqueous solutions with $pH > 7$ are potential candidates to be adsorbed with this bio-char. In the case of EE2, a neutral molecule, all bio-chars would be suitable as adsorbent for a wastewater treatment, although RH-Char would have a slightly better performance. Despite RH-Char showing a lower performance compared with AC when EE2 was adsorbed, rice husk chars are a prominent material with a good potential in wastewater treatment allowing the use and valorization of this agricultural residue. The results show that for all bio-chars and both MB and EE2 Langmuir isotherm model has a better fitting than Freundlich model, giving an idea of the interaction between the molecules and the surface of the chars.

Future work will study the adsorption of MB and EE2 as a function of time, determine the surface area of the bio-chars, and study the effect of different thermal treatments (e.g., pyrolysis) on the adsorption properties of the chars. The use of negative charge ions/molecules such as phosphate in acidic conditions, in which the adsorption capacity of RH-Char is expected to be increased, is an interesting possibility to be evaluated. Finally, an improvement in the adsorption capacity of the bio-chars could be achieved by modification of their surface properties.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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