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Assessment of the adsorption capacity of biochar samples obtained from agricultural biomasses

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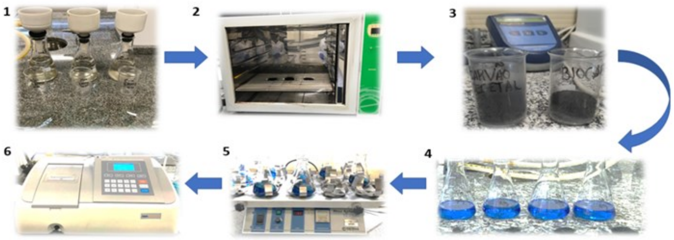

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Abstract: The study consists of adsorption tests on two samples of biochar, obtained from rice husk and coconut fiber biochar biomass, as well as a sample of charcarbon, both prepared under different conditions: macerated and non-macerated; impregnation with and without HCl and H_3PO_4; and washing or not with deionized water after impregnation. The test was performed in duplicate, for 30 min, with masses of 0.5 g; 0.3 g; 0.1 g; and 0.05 g, and an initial methylene blue concentration of 0.01 g·L^{-1}. The study was carried out with the objective of identifying, in the analyzed samples, the material with the greatest adsorption capacity of methylene blue dye, comparing the data with commercial activated carbon. The results identified removal above 70 % in both types of biochars, suggesting the feasibility of application as an adsorbent material to remove organic contaminants. The sample that most closely resembled the removal percentage of commercial activated carbon (98.84 %) was that of biochar obtained from coconut fibers, with 91.71 %. Thus, the research showed promise in studying the application and valorization of biochars, produced from agro-industrial waste, in adsorption processes.

Keywords: Rice husk, coconut fiber, removal, methylene blue, contaminants.

Introduction

Adsorption is a mass transfer process, which studies the ability of some solids to concentrate certain substances on their surface, which allows the separation of other components. In recent decades, adsorption has become one of the most popular methods for physico-chemical treatments of contaminated waters to remove organic and inorganic pollutants [1].

The use of biochar, produced from the pyrolysis of biomass, as an adsorbent material contributes to the biogenic cycle of the carbon in biomass, as well as provides the recovery of "agroindustrial waste" [2]. In some cases, before the use of biochar, activation processes are carried out to increase porosity and surface area. The selection of the chemical activating agent is an important step in controlling the performance and applicability of carbon, activated by acidic or basic compounds. Phosphoric acid (H_3PO_4), zinc chloride ($ZnCl_2$), potassium carbonate (K_2CO_3), potassium hydroxide (KOH), and hydrochloric acid (HCl) are some examples of activators applied [3].

To test the adsorption and degradation of contaminants, as well as the activation of biochar, dyes are commonly used as simulators of pollutants. Thus, methylene blue dye is a water-soluble organic compound, with a molar mass of 319.85 g mol^{-1} and molecular formula $C_{16}H_{18}C_1N_3S$ [4], which, among its many applications, can be used in adsorption tests.

Rosa et al. (2019) used zinc chloride and iron chloride to impregnate samples of rice husks and sugarcane bagasse, to test the removal of methylene blue dye. The pyrolysis process to obtain the biochar and test with the methylene blue dye was carried out after the impregnation process. The best removal concentration obtained by the authors was 99.8 %, in a solution of 100 mg L^{-1} of methylene blue, 100 mg of sugarcane bagasse biochar with zinc chloride, in a time of 180 minutes the amount of adsorbed dye was 99.8 % [5].

Teixeira (2020) tested the removal of methylene blue dye through coconut fiber biochar impregnated with H_3PO_4 with concentrations of 20 % and 85 %. Removal was 99.9 % after 180 minutes, in 1 g of biochar. The samples were previously crushed to an average particle size of 1 to 3 mm and the biochar was obtained through pyrolysis in an argon atmosphere [6]. The author used to wash the material with deionized water after impregnation to eliminate excess acid, but there is no description of the amount of water used.

Impregnation before the pyrolysis process results in better results, however, in quartz reactors, the use of samples containing alkaline materials or hydrofluoric and phosphoric acids can trigger devitrification processes, capable of damaging the material [7].

In some studies, biochars are tested for methylene blue dye removal without the impregnation process. Silva et al. (2016) used sugarcane bagasse biochar without impregnation and obtained 80 % removal, using 50 mg of the adsorbent at an initial concentration of 100 mgL^{-1} [8]. In this context, this work aims to test two types of biochar, obtained from different biomasses, as well as charcarbon, under different preparation conditions in order to identify the condition for the maximum removal of the methylene blue dye.

Experimental Section

The experiment was carried out with four different samples:

a) Sample of biochar, produced through pyrolysis of rice husk biomass;
b) Sample of biochar, produced through pyrolysis of coconut fiber biomass;
c) Charcarbon;
d) Sample of commercial activated carbon.

Biochar production

Two types of biochar were studied, one produced from rice husk biomass and the other from coconut fiber biomass. The thermochemical transformation of biomass (rice husk and coconut fiber) into biochar was carried out through carbonization in a horizontal quartz reactor in a two-part muffle furnace, in an inert atmosphere, N_2 with a fixed flow rate, Sanchis brand, which reaches a maximum temperature of 1200 °C and power of 6 kW (Table 1).

Table 1. Effective reactor operating conditions during carbonization.

Parameter/Unity	Value
Temperature (°C)	550
Heating rate (°C min^{-1})	10
Heating ramp (min)	55
Immersion time (min)	30
Residence time (min)	85
Nitrogen flow rate (L min^{-1})	0.2

Source: references [9,10,11,12]

Immersion time is the time that the biomass or sample remains in reaction after reaching the pyrolysis temperature. The residence time is the total residence time of the sample during the carbonization process from the moment the oven is turned on with the sample positioned under an N_2 gas atmosphere.

Impregnation of biochar with the use of acids

The selection of impregnation methodologies, either in basic or acidic media, was based on a literature review. The acid impregnation method was chosen because it is a method in which impregnation can be carried out after pyrolysis and not necessarily during pyrolysis. Post-pyrolysis impregnation, in addition to facilitating the process, prevents possible damage to the reactor. Impregnation with acids and subsequent removal test with methylene blue was also used by other authors such as Teixeira (2020) [6] and Fierro et al. (2010) [15].

The activation of biochar was tested by impregnating acids after the pyrolysis process. Phosphoric acid (H_3PO_4) 85 % (m/v); H_3PO_4 72.5 % (v/v); and hydrochloric acid (HCl) 5 % (v/v) were used. After impregnation, some samples underwent abundant washing until the pH increased (nearby neutral pH). In others, the washing was performed with 250 mL of deionized water, without pH increase. The acids H_3PO_4 [10] and HCl [13] were chosen because they are activation agents that can be used separately from the pyrolysis process.

Both were performed in order to compare the removal results in the two conditions. Impregnation with 5 % HCl (v/v) was performed in the sample-to-acid ratio of 1:10 (m/v) for 24 h, in which 2.0 g of sample was used for 20 ml of hydrochloric acid. Then, some samples were filtered (with the aid of vacuum pump and black band filter paper) and dried in an oven at 110 °C for 3 h [13]. The impregnation with H_3PO_4 lasted 24 h. One gram (1.0 g) of sample and 40 ml of H_3PO_4 were used. Then, vacuum filtration was performed, and the solid material was washed abundantly with deionized water at room temperature to eliminate excess acid. After washing, the samples were placed in an oven at 50 ºC for 12 h [14].

Commercial activated carbon

The commercial activated carbon, used as a basis for comparison in the adsorption of samples, was obtained from the Synth brand. The methylene blue removal test with the sample was carried out as marketed, in powder form.

Adsorption test with methylene blue

The sample preparation conditions before the methylene blue adsorption test are shown in Table 2. Tests were carried out on macerated and non-macerated samples; samples impregnated with H_3PO_4 72.5 % (v/v), H_3PO_4 85 % (m/v), HCl (v/v) and without washing with deionized water; and samples impregnated with HCl, after filtering with deionized water and pH measurements. The adsorption test was performed in 30 min, with an initial concentration of methylene blue of 0.01 g L^{-1} and in sample masses of 0.50 g; 0.30 g; 0.10 g, and 0.05 g. The absorbance was measured in a UV Spectrophometer – 1600 at a wavelength of 665 nm [10].

Statistical analysis

To analyze the yield results obtained, Analysis of Variance (ANOVA) was applied. And to identify significant inequalities within each treatment found in the ANOVA, the Tukey test was used with a 95 % confidence interval, considering statistical differences P ≤ 0.05).

Table 2. Conditions of the samples prepared for the adsorption test.

N°	Samples	Pretreatment
1	Rice husk biochar	No maceration or impregnation
2	Rice husk biochar	No maceration and impregnated with H_3PO_4 72.5% (v/v)
3	Rice husk biochar	No maceration and impregnated with H_3PO_4 85% (m/v)
4	Rice husk biochar	No maceration and impregnated with HCl 5% (v/v)
5	Rice husk biochar	Macerated and not impregnated
6	Rice husk biochar	Macerated and impregnated with HCl 5% (v/v)
7	Rice husk biochar	Macerated and impregnated with HCl 5% (v/v) washing until pH 5
8	Rice husk biochar	Macerated and impregnated with HCl 5% (v/v) washing until pH 7.26
9	Charcarbon	Macerated and not impregnated
10	Charcarbon	Macerated and impregnated with HCl 5% (v/v)
11	Charcarbon	Macerated and impregnated with HCl 5% (v/v) washing until pH 5
12	Charcarbon	Macerated and impregnated with HCl 5% (v/v) washing until pH 5.95
13	Coconut fiber biochar	Macerated and not impregnated
14	Coconut fiber biochar	Macerated and impregnated with HCl 5% (v/v)
15	Commercial activated carbon	as received (powder)

Results and Discussion

The results obtained in the methylene blue removal tests are shown in Table 3. The results of the two-factor ANOVA with replication can be seen in Table 4 and the Tukey test in Table 5.

Using the ANOVA test, it can be concluded that there are significant variations (F value> critical F value; P ≤ 0.05) between: a) the types of treatments, b) among the masses, and c) in the interactions between treatments and masses.

Adsorption test - – biochar sample from rice husks

The results show that, after carbonization, the impregnation carried out with H_3PO_4 and HCl does not increase the percentage of adsorption of the samples when compared to biochar samples without impregnation. To illustrate, the 0.5 g adsorbent sample without maceration and without impregnation showed 23.54 % removal, and in the same sample impregnated with H_3PO_4 85 % (m/v), the result was 1.58 % and with H_3PO_4 impregnation 72.5 % (v/v) was 15.95 % and the sample impregnated with HCl 5 % (v/v) was 18.00 %.

The significant difference is in the size of the particles. Samples which were prepared previously with maceration for particle size reduction showed higher adsorption percentages than samples that did not undergo preparation. The 0.5 g adsorbent sample without maceration and without impregnation showed 23.54 % removal, and in the same sample macerated and without impregnation 75.92 %. The reduced particle size favors the availability of surface active sites, contributing to a better performance of the adsorption capacity [14].

The increase in percentages after washing the sample suggests that the longer the wash, the greater the adsorption of the sample. As an example, the sample with an adsorbent mass of 0.5 g impregnated with 5 % HCl and without washing had a result of 29.17 %, while the same sample with washing until reaching pH 5 presented a result of 52.58 % and, in sample washed until reaching pH 7.26, the result was 56.41 %. However, this practice generates an excessive volume of liquid effluent containing acid, which makes the procedure unfeasible from an environmental and economic point of view.

As for the adsorbent mass, the sample that showed the highest percentage of removal was those with 0.5 g, which was macerated and without impregnation, with 75.92 %.

Adsorption test – charcarbon sample

The behavior of charcarbon samples with 0.5 g and 0.3 g were very similar to those of biochar. The highest percentages were in the macerated and not impregnated samples (76.41 % and 64.74 %, respectively). When comparing with the samples of 0.5 g of adsorbents macerated and impregnated with HCl (39.61 %; 64.06 %; and 60.23 %), the samples with 0.3 g of adsorbent showed similar results, which were 31.74 %; 62.72 %; and 49.93 %, respectively, of removal in the samples.

In the samples with 0.10 g and 0.05 g, the behavior was different; the removal in the samples impregnated with HCl and washed with deionized water until the pH increased was higher than in the biochar samples without impregnation.

As for the adsorbent mass, the sample that showed the highest percentage of removal was the one with 0.5 g, which was macerated and without impregnation, with 76.41 %.

Adsorption test – coconut fiber biochar sample

The highest removal percentages were in samples macerated and without impregnation: 91.71 % (sample with 0.5 g), 85.31 % (sample with 0.3 g), 58.29 % (sample with 0.1 g), and 50.32 % (sample with 0.05 g). As in the adsorption tests with rice husk biochar and charcarbon, samples with HCl

Table 3. Results of the means and standard deviation of the 14 treatments, of the rice husk biochar, coconut fiber biochar and charcarbon samples.

		0.5		0.3		0.1		0.5	
		Removal (%)		Removal (%)		Removal (%)		Removal (%)	
N°	Samples	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.
1	No maceration or impregnation	23.54	0.08	16.99	1.62	12.62	7.11	12.94	2.01
2	No maceration and impregnated with H_3PO_4 72.5 % (v/v)	15.95	0.08	14.20	0.15	8.71	0.50	11.28	1.82
3	No maceration and impregnated with H_3PO_4 85 % (m/v)	11.58	6.41	10.73	2.36	8.85	2.55	6.28	3.32
4	No maceration and impregnated with HCl 5 % (v/v)	18.00	2.59	12.94	2.63	9.50	0.85	9.83	3.55
5	Macerated and not impregnated	75.92	6.22	50.40	5.45	20.13	2.43	13.57	2.59
6	Macerated and impregnated with HCl 5 % (v/v)	29.17	1.08	22.78	4.25	9.50	0.85	9.83	3.55
7	Macerated and impregnated with HCl 5 % (v/v) washing until pH 5	52.58	4.29	50.10	3.32	42.07	3.48	41.00	0.27
8	Macerated and impregnated with HCl 5 % (v/v) washing until pH 7.26	56.41	1.12	48.27	0.81	44.61	2.05	44.03	0.39
9	Macerated and not impregnated	76.41	15.57	64.74	18.00	41.44	18.12	31.77	19.90
10	Macerated and impregnated with HCl 5 % (v/v)	74.96	3.25	55.48	6.30	26.28	1.78	18.60	6.22
11	Macerated and impregnated with HCl 5 % (v/v) washing until pH 5	64.06	12.71	62.72	5.56	50.67	6.76	33.60	20.01
12	Macerated and impregnated with HCl 5 % (v/v) washing until pH 5.95	60.23	2.51	49.93	2.09	44.55	2.51	46.93	2.70
13	Macerated and not impregnated	91.71	1.20	85.31	2.28	58.29	1.00	50.32	0.62
14	Macerated and impregnated with HCl 5 % (v/v)	74.96	3.25	55.48	6.30	26.28	1.78	18.60	6.22
15	Without impregnation	98.84	3.32	100.23	0.81	101.21	0.11	100.86	1.08

*S.D. Standard deviation

Table 4. ANOVA: double factor with repetition of the 14 treatments, samples of rice husk biochar, coconut fiber biochar and charcarbon.

Source of variation	Sum of Squares	Degrees of freedom	Medium square	Value-F	Value-P	F critical
Sample	15242.92	7	2177.56	222.33	2.80079×10^{-25}	2.3127
Columns	3030.76	3	1010.25	103.15	1.5622×10^{-16}	2.9011
Interactions	3262.40	21	155.35	15.86	1.77951×10^{-11}	1.8957
Inside	313.42	32	9.79			
Total	21849.49	63				

impregnation did not show higher removal percentages when compared to samples without impregnation.

The samples of biochar produced from coconut fiber were not tested for adsorption after impregnation of H_3PO_4 because, after impregnation, during the drying process, they would stick to the used paper (Figure 1). To avoid generating a larger amount of liquid effluent, the samples were not tested regarding washing with deionized water to increase pH.

Adsorption test – commercial activates coal

The test with the commercial activated carbon sample served as the basis for validating the removal analysis with the methylene blue dye. The results, as expected, showed a removal percentage of approximately 100 %. Results found above 100 % may be related to rounding in the equipment's absorbance reading.

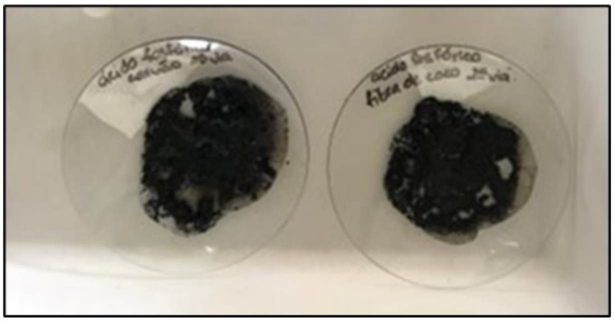

Figure 1. Image of the coconut fibers biochar samples after impregnation with H_3PO_4 and drying process.

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Table 5. Results of the Tukey test on samples of rice husk biochar, coconut fiber biochar and charcarbon, in the 14 treatments.

0.5 Adsorbent mass (g)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1st sample	23.49	15.89	16.11	16.17	80.31	29.94	49.55	55.62	65.40	77.25	73.05	58.46	92.55	77.25
2nd sample	23.60	16.00	7.04	19.83	71.52	28.41	55.62	57.20	87.42	72.66	55.07	62.01	90.86	72.66
Average	*23.54 Ac*	*15.95 Bc*	*11.58 Cc*	*18.00 Dc*	*75.92 Ea*	*29.17 Gc*	*52.58 Hb*	*56.41 Jb*	*76.41 La*	*74.96 Na*	*64.06 Pb*	*60.23 Sb*	*91.71 Ta*	*74.96Va*
0.3 Adsorbent mass (g)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1st sample	18.13	14.09	12.40	11.09	54.25	25.78	47.75	47.69	52.01	59.93	58.79	51.41	83.70	59.93
2nd sample	15.84	14.31	9.06	14.80	46.55	19.77	52.45	48.84	77.47	51.03	66.65	48.46	86.92	51.03
Average	*16.99 Af*	*14.20 Bf*	*10.73 Cf*	*12.94 Df*	*50.40 Fe*	*22.78 Gf*	*50.10 Ie*	*48.27 Je*	*64.74 Ld*	*55.48 Ne*	*62.72 Pe*	*49.93 Se*	*85.31 Td*	*55.48 Ve*
0.1 Adsorbent mass (g)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1st sample	17.64	8.35	10.65	10.10	21.85	10.10	39.61	46.06	28.63	27.53	45.89	46.33	57.58	27.53
2nd sample	7.59	9.06	7.04	8.90	18.41	8.90	44.53	43.16	54.25	25.02	55.45	42.78	59.00	25.02
Average	*12.62 Ai*	*8.71 Bi*	*8.85 Ci*	*9.50 Di*	*20.13 Fh*	*9.50 Gi*	*42.07 Ig*	*44.61 Jg*	*41.44 Mg*	*26.28 Oh*	*50.67 Pg*	*44.55 Sg*	*58.29 Ug*	*26.28 Xh*
0.05 Adsorbent mass (g)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1st sample	14.36	12.56	8.63	12.34	11.74	12.34	40.81	44.31	17.70	23.00	19.45	45.02	50.75	23.00
2nd sample	11.52	9.99	3.93	7.32	15.40	7.32	41.19	43.76	45.84	14.20	47.75	48.84	49.88	14.20
Average	*12.94 Al*	*11.28 Bl*	*6.28 Cl*	*9.83 Dl*	*13.57 Fl*	*9.83 Gi*	*41.00 Ij*	*44.03 Jj*	*31.77 Mj*	*18.60 Ol*	*33.60 Rj*	*46.93 Sj*	*50.32U j*	*18.60 Xl*

* Same lowercase letters, treatments with similar means; capital letters equal masses with similar averages.

Conclusion

Based on the results presented, it can be concluded that impregnation with hydrochloric acid and phosphoric acid, in the studied samples, with the aim of activating the samples and increasing contaminant removal, did not present better results than untreated samples. Regarding the comparison of the samples with commercial activated carbon, the biochar sample obtained from coconut fibers was the most similar. The two types of biochar, as well as charcarbon, showed removal percentages above 70 % (in samples with a mass of 0.5 g), suggesting the feasibility of application as an adsorbent material to remove contaminants.

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Authors Contribution

D. M. Souza: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing, and Data curation; M. M. Souza: Investigation, Methodology; F. C. Pereira: Methodology, Validation; B. K. Severo: Methodology, Original draft; F. A. Brehm: Resources, Supervision and Writing – review & editing; Carlos Alberto Mendes Moraes: Project administration, Funding acquisition, Resources, Writing – review & editing, Conceptualization and supervision. All authors have approved the final version of the manuscript.

Conflicts of Interest

The authors have declare no conflicts of interest.

References

[1] NASCIMENTO, Ronaldo Ferreira; et al. Adsorção [livro eletrônico]: aspectos teóricos e aplicações ambientais. 2.ed. , Fortaleza: Imprensa Universitária, 2020. 4749 Kb : il. color; PDF (Estudos da Pós-Graduação).

[2] D. M. Souza, K. C. Lima, G. Kappler, R. C. E. Modolo, F. A. Brehm, C. A. M. Moraes. Comparison between the properties of two biochar, aiming application in agricultural soil. In: V Workshop de Tecnologias Limpas e III Jornada de Tecnologias Limpas, 2022, Plataforma online. http://www.tecnologiaslimpas.ufba.br/, 2022.

[3] Z. Heidarinejad, M. H. Dehghani, M. Heidari, G. Javedan, I. Ali ,M. Sillanpää. Methods for preparation and activation of activated carbon: a review. *Environ Chem Lett,* vol. 18, pp. 393-415, 2020. DOI:10.1007/s10311-019-00955-0;

[4] G. B. Vieira. Uso de nanopartículas de ferro zero-valente na remediação de solos contaminados: degradação redutiva do azul de metileno. Dissertação (mestrado) - Universidade Federal de Santa Catarina, Centro Tecnológico. Programa

de Pós-Graduação em Engenharia Química. Santa Catarina, 2014.

[5] I. A. Rosa, M. C. M. Rodrigues, S.F. Paulo. Remoção de azul de metileno em biocarvões de casca de arroz e de bagaço de cana-de-açucar. *Sustentare*, vol. 3(1), pp. 64-74, 2019. DOI: 10.5892/st.v3i1.5742.

[6] J. L. Teixeira. Obtenção e caracterização de carvão ativado a partir da casca de coco verde. Dissertação (Mestrado) Programa de Pós-graduação em Engenharia de Minas, Metalúrgica e de Materiais. Universidade Federal do Rio Grande do Sul. Porto Alegre, 2020.

[7] Heliosquartz. Propriedades do quartzo. [s.d..] Disponível em https://www.heliosquartz.com/prodotti/propriedades-do-quartzo/?lang=pt-br. Acesso em: 03 julho de 2024.

[8] M. C. M. da Silva, R. R. P. Souza, L. A. Soares, M. M. S e Silva, C. P. de Souza, M. M. L. Duarte, A. L. Lopes-Moriyama. Adsorção de azul de metileno sobre carvão ativado obtido a partir do bagaço de cana-deaçúcar. XXI Congresso Brasileiro de Engenharia Química e XVI Encontro Brasileiro sobre o Ensino de Engenharia Química. Fortaleza, 2016.

[9] D. M. Souza, C. A. M. Moraes, R. C. E. Modolo. Propriedades da casca de arroz in natura e carbonizada em aterro industrial para valorização agrícola. In: VII Escola de combustão – VII Edc, 2019. Unifei, UNESP e INPE. São Paulo, 2019.

[10] K. Genyr. Valorização de agrorresíduos por meio da pirólise na produção de biochar. Tese do Programa de Pós-Graduação em Engenharia Civil da Universidade do Vale do Rio dos Sinos – UNISINOS. Maio de 2021.

[11] K. C Lima, D. M. Souza, G. Kappler, R. C. E. Modolo, C. A. M. Moraes. In natura and carbonized coconut fiber characterization from pyrolysis process. *Mix Sustentável* Florianópolis, vol. 8(4), pp. 27-38, 2022. DOI: 10.29183/2447-3073.mix2022.v8.n4.27-38.

[12] D. M. Souza, R. C. E. Modolo, Santos, E. C. A. dos Santos, J. L. da Silva, F. A. Sachetti, G. Kappler, F. A. Brehm, C. A. M. Moraes. Evaluation of the properties of biochar obtained from rice husk for its application in agricultural soils. *Revista AIDIS de ingeniería y ciencias ambientales: Investigación, desarrollo y práctica*, vol. 16 (2), pp. 398–417, 2023. DOI: 10.22201/ iingen.0718378xe.2023.16.2.82391.

[13] F. Hanum, O. Bani and L.I. Wirani. Characterization of Activated Carbon from Rice Husk by HCl Activation and Its Application for Lead (Pb) Removal in Car Battery Wastewater. *IOP Conf. Ser.: Mater. Sci. Eng.*, vol. 180, pp. 012151, 2017. DOI: 10.1088/1757-899X/180/1/012151.

[14] W. Hajjaji, R. C. Pullar, J. A. Labrincha, F. Rocha. Aqueous Acid Orange 7 dye removal by clay and red mud mixes. *Appl. Clay Sci.*, vol. 126, pp. 197-206, 2016. DOI: 10.1016/j.clay.2016.03.016.

[15] V. Fierro, G. Muñiz, A. Basta. Rice straw as precursor of activated carbons: activation with ortho-phosphoric acid. *J. Hazard. Mater.*, vol. 181, pp. 27–34, 2010. DOI: 10.1016/ j.jhazm at.2010.04.062.