

Meio ambiente

Adsorption study of emerging pollutants by biosorbents derived from different rice harvest residues for large-scale applications

Estudo de adsorção de poluentes emergentes por biosorventes de diferentes resíduos da colheita de arroz para aplicações em larga escala

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ABSTRACT

A large-scale removal of micropollutants from residual waters is an urgent problem to be tackled. In this work, three biomasses from agricultural residues, produced by different processes, were compared in terms of the adsorption efficiency of toxic species in water. The biosorbents used were rice husk ashes (RHA), leached rice husk silica (SRHA), and rice straw ashes (RSA). Two representatives of the most common micropollutants present in the effluent waters, 2-nitrophenol and the pesticide 2,4-dichlorophenoxyacetic acid (2,4-D), were chosen as probing molecules. The biosorbents were characterized by SEM, X-Ray FRX, FT-IR, BET, pHcpz, and hydrophobicity; surface areas of 175.81 m² g⁻¹ (SRHA), 66.11 m² g⁻¹ (RHA) and 42.77 m² g⁻¹ (RSA) were found, together with a microporous morphology. Firstly, the efficiency of removal was evaluated through adsorption isotherms: RHA and SRHA proved to be more efficient, with an adsorption capacity of 29.14 mg g⁻¹ and 23.75 mg g⁻¹ of 2-nitrophenol and 10.82 mg g⁻¹ and 10.55 mg g⁻¹ for 2,4-D. In particular, the removal of more than 90% for both 2-Nitrophenol and 2,4-D stands out as a very promising result. In light of these results, pillow-shaped filters with RHA were fabricated and tested for the first time for 2-Nitrophenol removal on a larger scale. The positive outcome (removal efficiency of 73%) demonstrates the possibility of producing filters based on sustainable and cheap biosorbents that could be implemented industrially to improve water purification as well as to implement the concept of circular economy.

Keywords: Sustainability; Water purification; Water filters

RESUMO

A remoção de micropoluentes em grande escala das águas residuais é um problema urgente a ser resolvido. Neste trabalho foram comparadas três biomassas provenientes de resíduos agrícolas, produzidas por diferentes processos, em termos de eficiência de adsorção de espécies tóxicas em água. Os bio sorventes utilizados foram a cinza de casca de arroz (RHA), a sílica lixiviada da casca de arroz (SRHA) e a cinza de palha de arroz (RSA). Dois representantes dos micropoluentes mais comuns presentes nas águas efluentes, o 2-nitrofenol e o pesticida ácido 2,4-diclorofenoxiacético (2,4-D), foram escolhidos como adsorvatos. Os bio sorventes caracterizaram-se por MEV, Raios X FRX, FT-IR, BET, pH_{czp} e hidrofobicidade, e foram encontradas áreas superficiais de 175,81 m²g⁻¹ (SRHA), 66,11 m²g⁻¹ (RHA) e 42,77 m²g⁻¹ (RSA), além de morfologia microporosa. Primeiramente, avaliou-se a eficiência de remoção através de isotermas de adsorção: RHA e SRHA mostraram-se mais eficientes, com capacidade de adsorção de 29,14 mg g⁻¹ e 23,75 mg g⁻¹ para 2-nitrofenol e 10,82 mg g⁻¹ e 10,55 mg g⁻¹ para 2,4-D. Em particular, a remoção de mais de 90% tanto para o 2-Nitrofenol como para o 2,4-D destaca-se como um resultado muito promissor. À luz desses resultados, filtros em forma de travessieiros com RHA foram fabricados e testados pela primeira vez para remoção de 2-nitrofenol em maior escala. O resultado positivo (eficiência de remoção de 73%) demonstra a possibilidade de produção de filtros baseados em bio sorventes sustentáveis e baratos, que poderiam ser implementados industrialmente para melhorar a purificação da água, bem como para implementar o conceito de economia circular.

Palavras-chave: Sustentável; Purificação de águas; Agrotóxicos

1 INTRODUCTION

In this new century, the world debate on sustainability has gained a lot of strength and it has led to rethink society's development and possible governance structures (Dubey, 2017). As a result, new development strategies have emerged, which comprehend political, economic, social, technological and environmental aspects, guided by the UN's sustainable development goals (ONU,2018). This new paradigm implies the need for profound changes in the current production systems, as well as in the use of essential natural resources (Mc Cormick, 2016).

Access to clean, high-quality water is a basic right. However, river pollution and water reservoirs in general have greatly increased, affecting water public supply and all the aquatic ecosystems (Wang,2021). Nowadays, several organic micropollutants (nitrosamines, organochlorine pesticides, polycyclic aromatic hydrocarbons and phenols, among others) are found in water with ng/L or even

µg/L concentrations, causing a direct link between contaminated water and human health and diseases, especially in developing countries (Xue, 2021). Among these pollutants, two present a very strong impact on the environment, due to its large use: the first is 2-Nitrophenol, the most toxic and carcinogenic member of the nitrophenol family; this molecule is commonly found in electric battery and explosives industries, as well as rubber and dyeing factories (Baysal, 2020). The second pollutant is the herbicide 2,4 dichlorophenoxyacetic acid (2,4-D), the most applied in agriculture in Brazil and worldwide, which also present acute health toxicity (Islam, 2018).

On the other hand, rice is one of the largest commodities produced worldwide: however, the processing of the rice grain leaves high amounts of a by-product, the rice husk (RH) and rice straw (RS), creating a large environmental issue if not exploited. Most of the time, RH and RS are burnt without any rigid control to produce thermal energy: the emissions of VOCs, SO₂, CO, NO₂, and PM10 are also hazardous to human health (Matin, 2023; Njoku, 2021). In addition to that, further residues are generated after calcination, the rice husk ashes (RHA) and rice straw ashes (RSA). Other works demonstrated that RHA can be reused in the manufacture of innovative materials, such as glass (Gonçalves, 2020), ceramic and cement materials (Hossain, 2018) mainly due to its silica composition, and as an adsorbent for water purification (Abaide, 2019; Ahmaruzzaman, 2011).

Adsorption is considered a promising method for removing pollutants from wastewater, particularly as substitution to common purification methods that are inefficient for micropollutants removal (Xue, 2021; Nunes, 2023). To improve the adsorption capacity and promote water purification, various materials such as activated carbon, resins, silica, clays, carbon nanotubes, graphene oxide, have been explored (Salles, 2023; Vargas, 2023; Boayke, 2022, Aragaw, 2021). Several works can also be found in the literature using adsorbents derived from agricultural waste biomasses, due to their wide availability and low economical

value, like sugarcane bagasse, coconut husk, rice husk ashes, rice husk silica and rice straws (Abaide, 2019; Ahmaruzzaman, 2011; Boayke, 2022; Kim, 2008; Thue, 2016). However, in order to achieve very high adsorption capacity, the adsorbents are frequently chemically modified, leading to less green processes, higher costs and difficulties to promote industrial applications.

Thus, the objective of this work was firstly to directly compare three by-products of rice cultivation (RHA, rice husk silica after acid lixiviation (SRHA) and RSA) in terms of adsorption capacity and removal efficiency of 2-Nitrophenol and 2,4-Dichlorophenoxyacetic acid in distilled water. Based on these screening results, the best performing biosorbent was then applied in pillow-shaped filters to simulate water purification on a larger scale, as it could be applied in sedimentation tanks and artesian wells. Overall, this work demonstrated with a practical example that a cost-effective and sustainable solution for water treatment, through a simple process with large scale application in real situations, is at our reach.

2 MATERIALS AND METHODS

2.1 Biosorbent-based Materials

In this work, three agricultural wastes from rice cultivation were used as biosorbent materials: industrial rice husk ash, silica from rice husk ash extracted by acid leaching and rice straw ash.

The rice husk ashes (Figure 1A) was provided by a local industry from RS. According to the information obtained from the company, typically the rice husk is burnt between 700-800°C for 3-6 hours. In this work, this ash will be identified as RHA.

The second biosorbent is the silica extracted from rice husk ashes (Figure 1B) through an acid-leaching process. The rice husk was also provided by the same local company, as harvested. The process was carried as described in (Gonçalves,

2020). Briefly: first, the husk was washed with water to remove impurities such as soil and dust, oven dried and stored in closed bags. For the chemical treatment, 100 g of bark was placed in an acid bath with a 10% solution (mass/mass) of chloric acid (37% v/v). The ratio between the husk mass and the acid solution was kept constant at 1:9 (mass/mass); the suspension was heated at 50 °C for 1 hour. Subsequently, the treated bark was filtered and washed with running water until complete neutralization, being the last washing done with distilled water. The bark was placed in an oven at 100°C for 24 hours to remove moisture and then calcined in a muffle furnace at 800 °C for 5 hours. The samples remained in the muffle until completely cool. In the text, this material will be referred to as SRHA, silica from rice husk ashes.

The last adsorbent material of this work is rice straw ashes (Figure 1C). The rice straws were washed with water to remove impurities such as soil and dust, oven dried, and stored in closed bags. The straws were burned in alumina crucibles placed in a muffle furnace at the combustion temperatures of 600 °C for 5 h, resulting in the ash represented in Figure 1C. After combustion, the ashes underwent an extraction process of oligosaccharides in hot water, as described by Brodeur *et al* (2011). Briefly, the RSA was placed in a pressure-pan for 15 min, after the boiling temperature was reached, and then filtered. This step was applied in order to avoid the leaching of complex sugars in water that absorbed in the same UV-VIS range as the molecules of interest. In the text, this ash will be identified as RSA.

Figure 1 – Production scheme of the three adsorbent materials used in this work: A) Rice husk ashes (RHA), B) silica extracted from rice husk ashes (SRHA) and C) rice straw ashes (RSA)



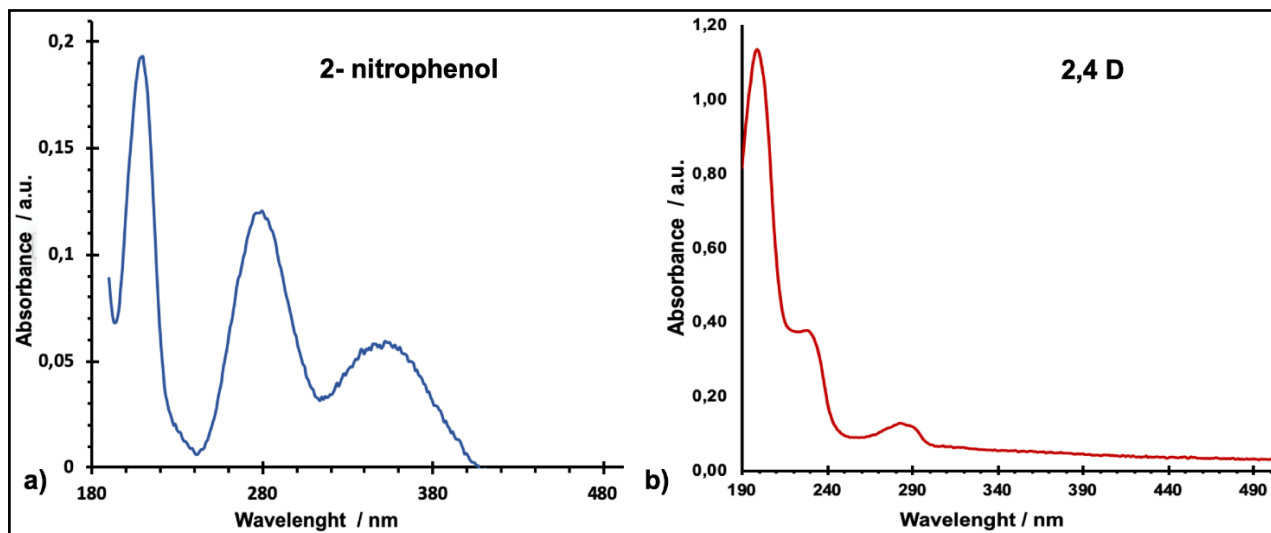
Source: Authors' private collection (October, 2023)

2.2 Pollutant solutions

2-Nitrophenol (Sigma Aldrich) and the 2,4-Dichlorophenoxyacetic acid (2,4-D) also from Sigma-Aldrich (98% purity) were used as testing molecules. For both reagents, 12 solutions were prepared in distilled water with concentrations between 1 and 90 ppm. Natural 2,4-D solution has a pH of about 2,42. In order to removal in a more realistic water body, the solution was stabilized with a phosphate buffer at pH 6.68.

Based on the UV-Vis absorption spectra reported in Figure 2, the peak at 210 nm was chosen as the reference for the calibration curve of 2-Nitrophenol (Figure 2a); on the other hand, the peak at 200 nm was chosen to monitor the concentration changes during the adsorption of 2,4-D (Figure 2b), following Carvalho *et al.* (2021). All the experiments were carried out in triplicates.

Figure 2 – UV-Vis absorbance spectrum of a) 2-nitrophenol and b) 2,4-D. The peak at 210 nm and 200 nm, respectively, were chosen for the adsorption analyses

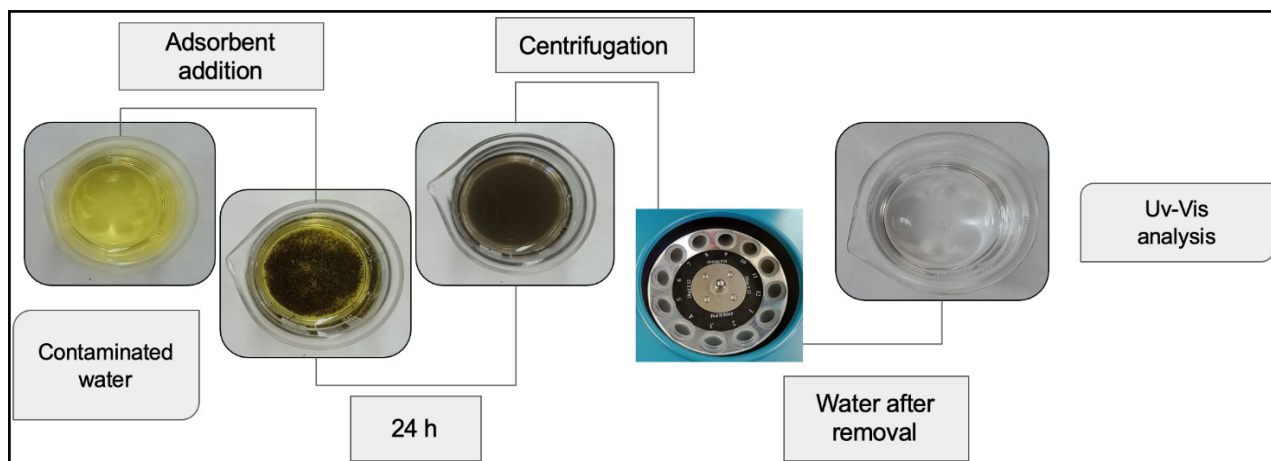


Source: Authors (2022)

2.3 Adsorption Tests

For the adsorption tests, a mass of 0.050 grams of adsorbent was weighed on a precision balance and placed in contact with 20.0 mL of a solution of 2-nitrophenol or 2,4-D. The mixtures were kept under agitation in an orbital shaker at 100 rpm for 24h, so that equilibrium between adsorbent-adsorbate could be reached. For the analysis of the adsorption efficiency, the solution was centrifuged at 3000 rpm, for 10 min, for a total of 4 times. At the end of each centrifugation, the liquid supernatant in the centrifuge tubes was transferred to clean vessels to be centrifuged again. At the end, the remaining solution was analyzed by UV-Vis spectrophotometry to define the final equilibrium concentration of the 2-Nitrophenol and 2,4-D molecules. The scheme in Figure 3 summarizes the method applied in this work.

Figure 3 – Schematic representation of the steps applied in the adsorption tests



Source: Authors (2022)

The adsorption performance (q) was expressed in mg of adsorbate per gram of adsorbent and percentage of molecule removal (%removal), as given in Equation 1 and 2 respectively:

$$q = \frac{(C_o - C_f)}{m} \cdot V \quad (1)$$

$$\%Removal = 100 \cdot \frac{(C_o - C_f)}{C_o} \quad (2)$$

where C_o is the initial adsorbate concentration in contact with the adsorbent (mg L^{-1}); C_f is the concentration of adsorbate after the batch adsorption study (mg L^{-1}); m is the weight of adsorbent (g); and V is the volume of the adsorbate solution (L).

For the proof-of-concept of large-scale application, pillow-shaped filters, 4 cm x 5 cm in size, were fabricated containing 8.0 g of RHA. Tricoline was the fabric chosen after a screening step between 5 others textile; the choice was based on the best compromise between surface wettability, water penetration and best resistance to the leaching of small RHA particles. A cotton thread was used for the sewing. Initial concentrations of 2-nitrophenol at 10, 20 and 60 ppm were prepared in 5L flasks using distilled water without pH adjustment. The filters were placed in contact with the solution for 24hr; a volume of 20mL was retrieved from the flask and analyzed following the same protocol as described before.

2.4 Characterization

The three different adsorbents studied in this work were characterized morphologically by Scanning Electron Microscopy (SEM) (Zeiss, EVO MA10, with EHT: 20.0 kV; current: 2,7 A; magnification: 300x and 5000x); X-rays Diffraction (XDR) on an ULTIMA IV (Rikagu) equipment with Bragg-Brentano geometry. The diffraction pattern was recorded using a $\text{CuK}\alpha$ radiation source, nickel filter, at 40kV and 20mA, with an angular pass of $0,05^\circ$ and 1 s integration time; nitrogen adsorption-desorption analysis by Brunauer-Emmett-Teller (BET) (Quantachrome Instruments, NOVA 4200e) and the pore size distribution was obtained by using the BJH (Barret, Joyner and Halenda) method and DFT (Density Functional Theory). To better understand the surface chemistry and reactivity of the materials, the adsorbents were analyzed by X-ray Fluorescence (FRX) (Panalytical, Epsilon 1, semi-quantitative, $Z > 12$) and by FT- IR by diffuse reflectance (Bomem, MB100 available at LAPMA, UFRGS), before and after the contact with the pollutants, to understand the mechanism of surface adsorption.

The hydrophobicity property or hydrophilicity index (HI) of the biosorbents was obtained as recommended elsewhere (Dos Reis, 2016a; Cunha, 2018). Shortly, 0.3 g of dried biosorbent material was weighed in 10 mL beakers. The samples were exposed to an atmosphere saturated of solvent vapor (n-heptane or water) in Erlenmeyer flasks plugged with a ground glass joint. All beakers containing biosorbent were placed inside the Erlenmeyer flasks in such a way that they were not in contact with the solvent and wall of the Erlenmeyer flask. The experiment was carried out in a temperature-controlled chamber at 25°C . After 24 hours, the materials were removed from the flasks, and the beaker was dried carefully from the outside with clean tissues. The samples were weighed to estimate the weight of water or n-heptane adsorbed. The quantity of vapor adsorbed by the biosorbent is obtained from the weight gain and expressed in g.g^{-1} . The hydrophobic Index (HI) was calculated by the ratio between n-heptane vapor (g.g^{-1}) adsorbed divided by water-vapor (g.g^{-1}) adsorbed (Dos Reis, 2016a; Cunha, 2018).

In this work, the pH of the point of zero charge (pH_{pcz}) was also determined, using the methodology found in (Cunha, 2018). Briefly, an amount of 0.05g of adsorbent was weighed and added to 20mL of aqueous solution with pH ranging from 1.0 to 12. The mixtures were taken to an orbital shaker for 24 hours at 100 RPM to reach equilibrium. After 24 hours, the final pH was measured and the initial pH was plotted versus the difference between the initial and final pH of each solution.

3 RESULTS AND DISCUSSION

3.1 Biosorbent Characterization

The compositions of the three adsorbents were obtained by FRX, and the major constituents are presented in Table 1. As expected, the lixiviated SRHA presents a much higher silica content, almost 90 wt%. When working with silica rich ashes from biomass, a higher amount of silica is normally pursued for better adsorption efficiency due to the presence of the silicate anions, which affects the superficial charges and the resulting surface area (de Oliveira, 2020; Cheah, 2016; Costa *et al*, 2019). On the other hand, several works in the literature also reported that surface presence of alkali elements, after chemical modifications, improved the efficiency of adsorption of different molecules, such as HCl (Usmani, 2022), SO_3 (Adib, 1999), bisphenol and antibiotics (Tang, 2022). The presence of alkali ions locally decreases surface polarity, as they interact with the negatively charged silicate ions. The synergic effect between surface charges (Si-O^-) and less polar domains might be beneficial in the adsorption of organic pollutants with aromatic structures (Tang, 2022). In this sense, pure RHA and RSA presented a lower silica content (72% and 62%, respectively), but also a larger presence of alkali and alkali-hearth elements, which could still improve the overall adsorption capacity. The presence of phosphorous, detected here as its P_2O_5 , was reported to not affect the adsorbing capacity of biomasses (Tang, 2022).

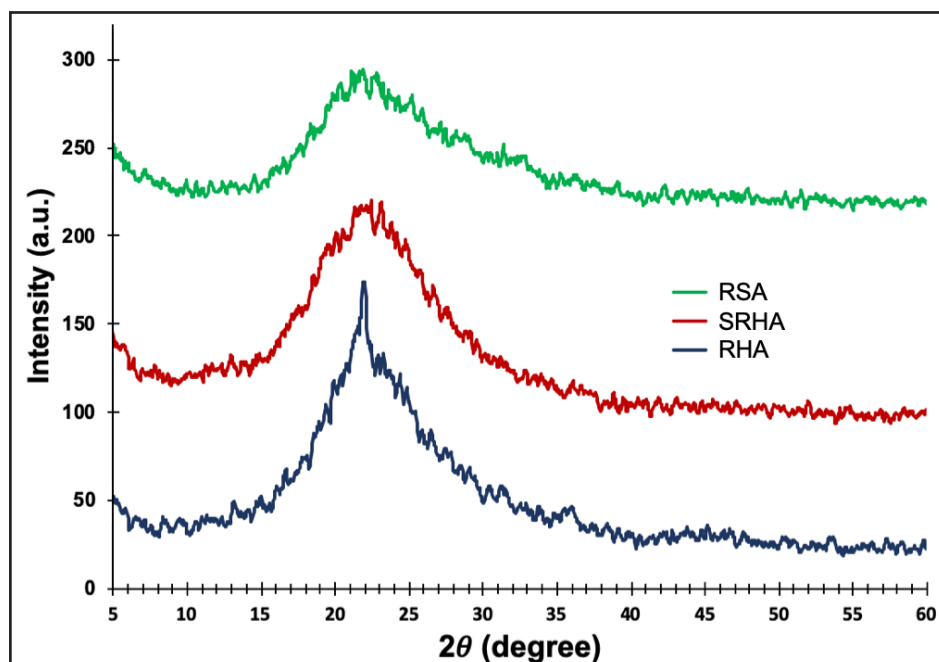
Table 1 – Principal composition of the three adsorbents materials used in this study, in wt%

Material	SiO ₂	K ₂ O	MgO	SO ₃	P ₂ O ₅	CaO
RHA	72.707	2.367	1.472	0.262	1.070	0.882
SRHA	89.454	0.026	3.941	0.193	0.501	0.270
RSA	62.543	3.663	1.626	0.709	1.678	4.023

Source: Authors (2022)

The three biosorbents produced are amorphous, as it can be seen by the XRD results presented in Figure 4. Particularly, the RHA (blue line) obtained from the local rice industry presents a small peak centered at 21.8°, suggesting that a small quantity of silica is its crystalline form (tridymite phase, JCPDS 18-1170). This might occur when the calcination process is not well controlled, as in this case, and the temperature reaches above 850 °C (Saceda, 2011).

Figure 4 – XRD diffractogram of RSA (green line), SRHA (red line), and RHA (blue line).



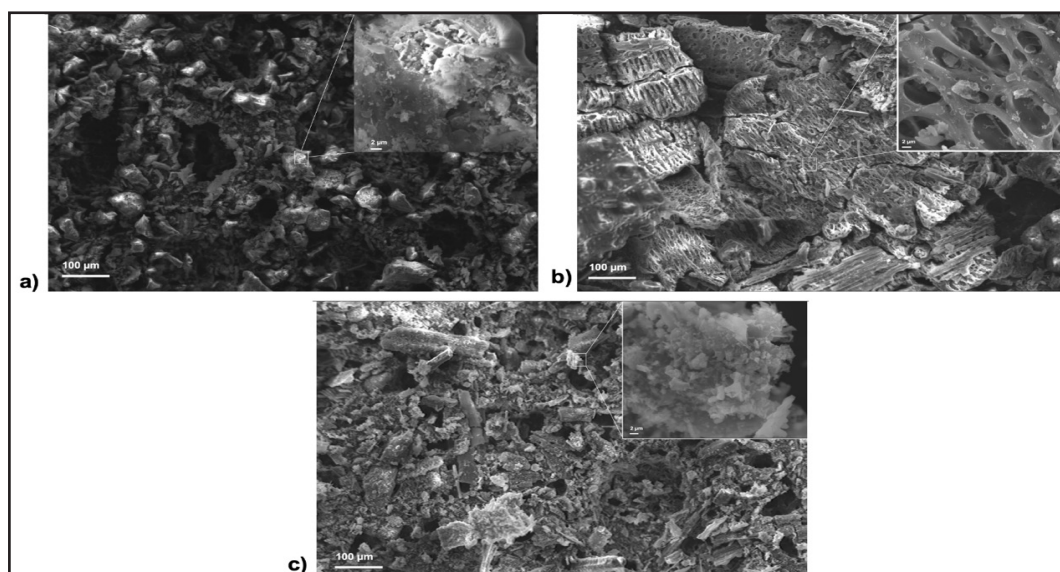
Source: Authors (2022)

In Figure 5 the SEM images with 2000x magnification of a) SRHA, b) RHA and c) RSA are reported. Different structures and particle sizes can be clearly noticed. Particularly, in

the RSA and even more in the RHA, it is possible to see some cellulose-derived content, as reflected by the rigid and elongated structures, although as loose layers, enhancing porosity (Andreola,2020). The lixiviated silica presents overall a more flocculated aspect, due to the formation of silica grains, which tend to agglomerate (Dhaneswara, 2020).

The morphology of the material is extremely important for the adsorption process: the more surface area and pore volume, the higher the chances for mass transfer and surface interaction of the adsorbate. In Table 2, a summary of the nitrogen adsorption (BET) characterization is reported. As already found in the literature, chemical lixiviation of RHA increases surface area and pore diameter, in comparison to pure RHA (KIM, 2008; Daffalla, 2020). Here, SRHA presents almost 3 times the surface area of RHA, and more than 4 times in comparison with RSA. Regarding the pore diameter, again, it was found that the SRHA presents a double average size in respect to RHA, and it shows a 50% increase in respect to RSA. At last, in terms of average pore volume, RHA and RSA present a similar value of $0.0530 \text{ cm}^3 \text{ g}^{-1}$, while the SRHA presents a larger value of almost 30%, being $0.0690 \text{ cm}^3 \text{ g}^{-1}$.

Figure 5 – SEM micrograph of the a) SRHA, b) RHA and c) RSA as prepared at 300X magnification. The details in the inset were taken at 5000X magnification. EHT: 20.0 kV. Current: 2,7 A



Source: Authors (2022)

Table 2 – Principal characterization of the BET and HK method analysis

Material	RHA	SRHA	RSA
Surface Area	66.11 m ² /g	175.81 m ² /g	42.77 m ² /g
Average Pore Diameter	9.687 Å	18.14 Å	11.56 Å
Average pore Volume	0.0529 cm ³ /g	0.0689 cm ³ /g	0.0528 cm ³ /g

Source: Authors (2022)

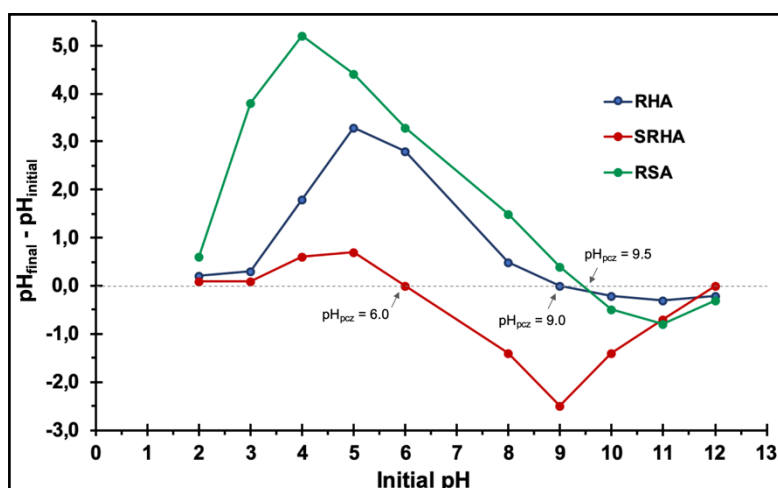
The values of surface area and average pore diameter for RHA are higher than what already reported in the literature for controlled calcination (Abaide, 2019; Daffalla, 2020), probably due to the lower calcination temperatures used in those works. When compared to industrial calcinated RHA, the morphological characteristics are very similar (Ahmaruzzaman, 2011). The extracted silica also presents comparable characteristic with what was reported by (Dhaneswara, 2020). Although, they combined an alkali and acid lixiviation treatment, so the method presented in this work is simpler and more efficient. Abaide *et al.* reported lower values of surface areas and pore volume for rice RSA (Abaide, 2019); however, (Sun, 2022) reported a specific surface area and total pore volume of carbonized rice straw of 113.58 cm³g⁻¹ and 0.062 cm³g⁻¹, respectively, with the mean pore diameter of 4.22 nm (Sun, 2022): the much larger surface area might be due to the carbonization process, carried out at 500 °C under limited oxygen conditions. Overall, the three adsorbents present themselves as microporous materials with optimal morphology for adsorption processes.

At last, in order to fully understand the adsorption process, the adsorbents materials were characterized by other two very important parameters: the hydrophobic index (HI) and the surface pH of zero charge (pH_{zpc}). The result for the HI were found to be 0.936 ± 0.010; 0.828 ± 0.056 and 1.492 ± 0.061 for RHA, SRHA and RSA respectively. All the values are quite different from one another; nevertheless, RHA and SRHA materials clearly show hydrophilic properties, while the RSA sample shows a more hydrophobic behavior. It is possible to relate the Si-O content with the HI: in fact,

the sample with higher SiO₂-content (SRHA and RHA in Table 1) and rich in silanol group (Si-OH) and oxygen groups (see pH_{pzc} in Fig 6) can more easily form hydrogen-bonds and presents a more polar surface. On the other hands, the RSA sample, in which the oligosaccharides were extracted and the Si-O content is lower, it will tend to adsorb more n-heptane (less polar surface) rather than water.

Figure 6 reports the results of the pH of point of zero charge analysis. The pH_{pzc} indicated the pH at which the positive and negative charges on the surface of the material are balanced. For RHA, this occurs at pH of 9.0; for SRHA at pH = 6.0 and for RSA at pH = 9.5. Overall, it is possible to infer that the SRHA biosorbent presented a more acid behavior, probably due to the larger number of Si-OH groups present.

Figure 6 – pH of surface point of zero charge for RHA (blue), SRHA (red) and RSA (green)



Source: Authors (2022)

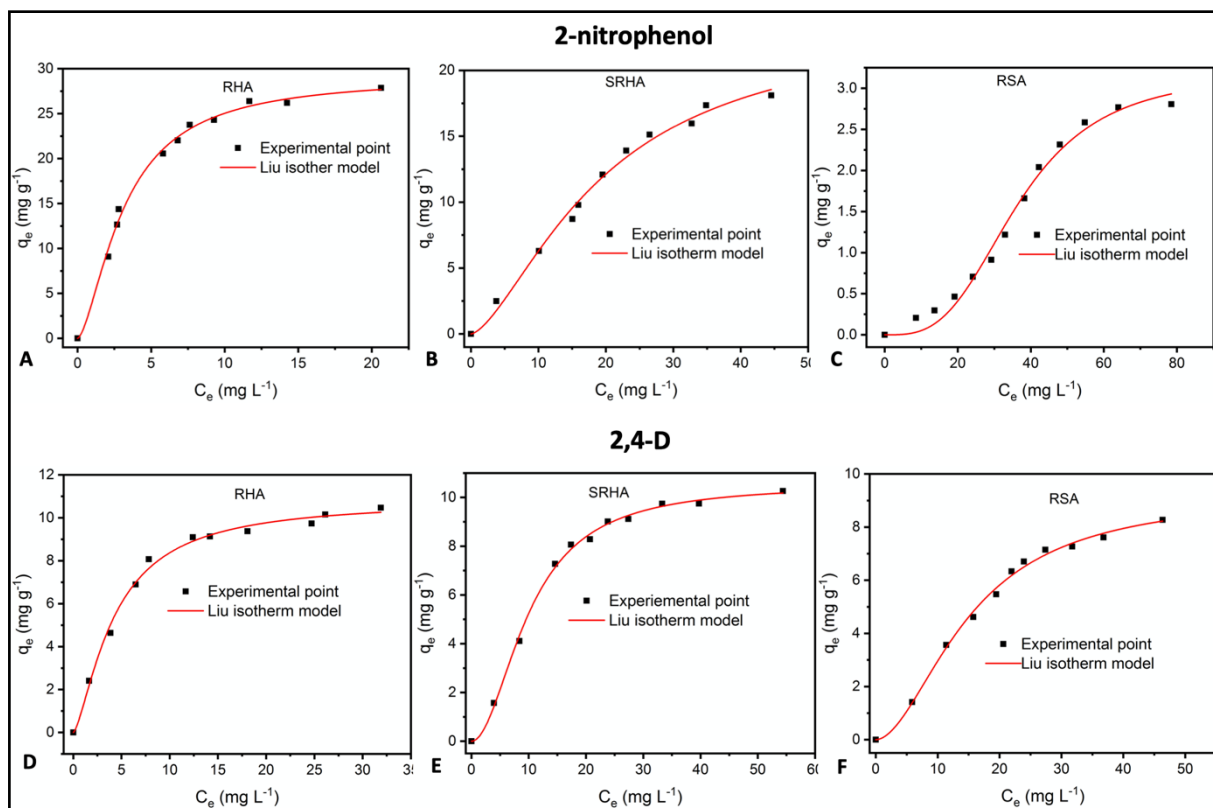
3.3 Adsorption Analysis and Surface Interaction:

Obtaining the isotherm curves and parameters is a necessary step to obtain a better understanding of the adsorption phenomenon, as well as to accurately plan a design for real scale applications.

The adsorption results were plotted as q_e vs C_e as reported in Figure 7 for the adsorption of 2-nitrophenol (Fig 7A, B and C) and 2,4-D (Fig 7D, E and F) on RHA, SRHA and RSA biosorbents from aqueous media at 25°C temperature. In general, the adsorbed

quantity (q_e) increased as the concentration of the 2-nitrophenol or 2,4-D adsorbates also increased, till reaching the equilibrium. This can be explained by the fact that when the initial concentration increases, more molecules are available to be adsorbed onto the biosorbents active sites. In addition, the diffusion of the adsorbates in solution and to the adsorption sites at high concentrations is much higher than at lower concentrations (Thue, 2013). In fact, as the concentration of the adsorbates increases, the resistance to the mass transfer of 2-nitrophenol and 2,4-D adsorbates between the solid and aqueous phase is reduced (Thue, 2013).

Figure 7 – Liu isotherm curve of the adsorption of 2-nitrophenol (A, B and C) and 2,4-D (D, E and F) on RHA, SRHA and RSA biosorbents from aqueous media at temperature 25°C



Source: Authors (2023)

Table 3 shows Liu isotherm parameters for the adsorption of 2-nitrophenol and 2,4-D on RHA, SRHA and RSA biosorbents. Liu isotherm was the best suitable isotherm model for the three adsorbents, compared to Langmuir and Sips (not shown). The Liu

model exhibited values of R^2 adjusted closer to 1.00 and lower values of SD for almost all the biosorbents, inferring that the values of sorption capacity calculated by the nonlinear isotherm model are closer to the sorption capacity obtained experimentally (Lima, 2021; Caicedo, 2020). Moreover, the Liu model infers that the adsorbents present active sites with different energies, which implies the existence of preferred interaction sites, as well as the possibility to have more than a monolayer-type of interaction. Considering the biosorbent compositions and surface functional groups, as described in Section 3.1, the assumption of having different energy sites is coherent (Lima, 2015).

Table 3 – Liu isotherm parameters for the adsorption of 2-nitrophenol and 2,4-dichlorophenoxyacetic acid (2,4-D) on rice husk ash (RHA), leached rice husk silica (SRHA) and rice straw ash (RSA) materials. Adsorbent dosage of 2.5 g L⁻¹

2-Nitrophenol			
Liu isotherm model	RHA	SRHA	RSA
Q_{\max} (mg g ⁻¹)	29.13	23.75	3.193
K_g (L mg ⁻¹)	0.3159	0.05140	0.02734
η_L	1.573	1.536	3.167
R^2_{adj}	0.9943	0.9916	0.9869
SD (mg g ⁻¹)	0.9674	2.439	0.1938
2,4-D			
Q_{\max} (mg g ⁻¹)	10.82	10.55	9.252
K_g (L mg ⁻¹)	0.2345	0.0994	0.06646
η_L	1.441	1.972	1.849
R^2_{adj}	0.9935	0.9976	0.9956
SD (mg g ⁻¹)	0.32215	0.1817	0.37861

Source: Authors (2022)

Besides, it is possible to observe that the adsorption quantity (Q_{\max}) of 2-nitrophenol and 2,4-D adsorbates onto the three biosorbents are different. The maximum adsorption (Q_{\max}) values achieved were 29.13 and 10.82 mg g⁻¹, respectively, for 2-nitrophenol and 2,4-D adsorbates, at 25°C for the RHA biosorbent. Leached rice husk silica (SRHA) material presented almost a similar result for the removal of 2-nitrophenol and 2,4-D adsorbates. In the literature, a wide range of adsorption

capacity, from 1-15 mg g⁻¹ to 200 mg g⁻¹, can be found for similar biosorbent materials (Ahmaruzzaman, 2011; Brodeur, 2011; Wasilewska, 2021; Deokar & Mandavgane, 2015). Most of the time, higher adsorption capacities are associated with material that underwent chemical activation and several preparation steps. When comparing with more simple-step preparations, the biosorbents presented in this work performed well: Andrade *et al.* (2020), for example, found an adsorption capacity of 6.61 mg g⁻¹ for the removal of oxytetracycline on RHA, while Costa *et al.* (2019) demonstrated a 11.83 mg g⁻¹ maximum of adsorption for Remazol Red. For the removal of 2,4-D, Deokar and Mandavgane (2015) found a maximum capacity much lower of 1,43 mg g⁻¹ for RHA at lower pH. Even if higher, the efficiency presented in this work is not optimal: as reported by Arefieva *et al.* (2020), microporous-type materials demonstrated less adsorption than mesoporous biosorbents.

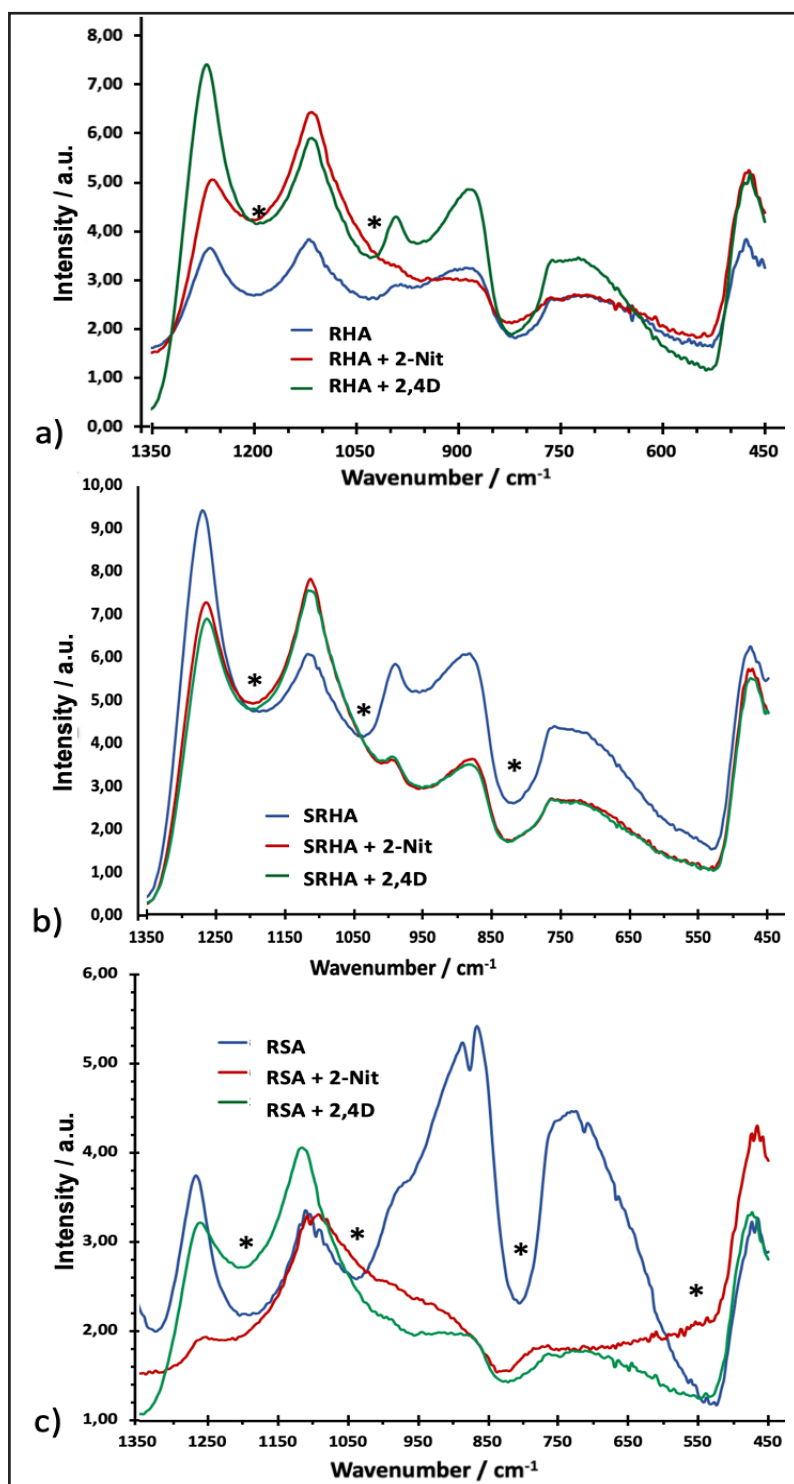
Last, RSA was the least efficient, particularly when compared for the adsorption of 2-nitrophenol. The lower adsorption capacities are due mainly to the different surface properties of the biosorbent.

In order to understand surface reactivity and to predict a possible adsorption mechanism, the three adsorbent materials were also characterized by Infrared Spectroscopy before and after adsorption. The spectra for the RHA (Figure 8a), SRHA (Figure 8b) and RSA (Figure 8c) were collected in the range between 450-1350 cm⁻¹; the major peak changes are also reported in Table 3. In details, the spectra before the adsorption are represented with blue lines; the spectra after the adsorption of 2-Nitrophenol are represented by red lines and the 2,4-D adsorption by green lines. The stars highlight the main differences found between the spectra.

Overall, the spectra of pure materials correspond to what is already reported in the literature for RHA and silica extracted from RHA (Abadi, 2014; Wang, 2019). Particularly, the band at 530 cm⁻¹ can be related to the Si-H stretch, while the band at 805-830 cm⁻¹ and the band at 1040 cm⁻¹ can be associated with the Si-O-Si asymmetric and symmetric stretching vibration, respectively. This characteristic is typical for

amorphous silica, as demonstrated in Figure 4. The band centered at 1200 cm^{-1} is related to the stretching of residual alcohol from the surface Si-OH (Wang,2019).

Figure 8 – FT-IR spectra a) RHA, b) SRHA and c) RSA before and after the pollutant removal. Blue line: pure adsorbent material; red line: after the adsorption of 2-nitrophenol;



Source: Authors (2022)

Table 4 – Most important stretching/bending wavenumber variations after the adsorption process

Material		Wavenumber (cm ⁻¹)			
Vibrational mode:		Si-O-Si assym stretching	Si-O-Si sym stretching	Si-OH stretching	Si-H stretching
RHA	pure	821	1032	1201	
	2-Nitrophenol	833	-	1205	
	2,4-D	827	1028	1198	
SRHA	pure	827	1027	1199	
	2-Nitrophenol	829	1016	1204	
	2,4-D	829	1016	1207	
RSA	pure	806	1043	1191	532
	2-Nitrophenol	825	-	1211	532
	2,4-D	828	-	1205	-

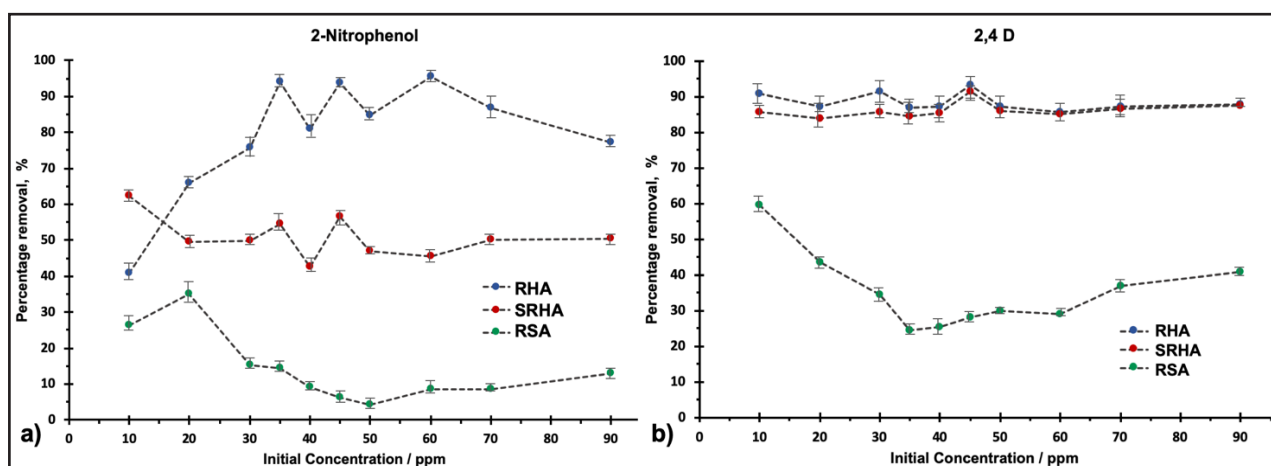
Source: Authors (2022)

As it can be seen from Table 4, after the adsorption process, both the Si-O-Si stretching bands shifted to higher wavenumbers, as well as the band of the alcoholic group; particularly, the symmetric stretching of the Si-O-Si bonds was suppressed completely in the case of RSA. These modifications of the environment of the silica tetrahedral network and the C-O present on the surface do confirm molecule adsorption, as reported by (Daffalla, 2020); the fact that the Si-H was unaffected by the presence of the positively charged 2-nitrophenol also confirms that electrostatic interaction mainly through the negative group is the main adsorption mechanism, as found elsewhere (Abaide, 2019; Alinnor & Nwachukwu, 2011; Andrade *et al*, 2020, Daffalla 2010). It was not possible to identify any appearance of the aromatic band due to the presence of the adsorbates, probably due to the low concentration (< 70 ppm).

The performance of the adsorbents was also evaluated by removal percentage at different initial concentrations (Eq. 2), as it can be seen in Figure 9. The values plotted are the average of three separated adsorption tests; the calculated errors from standard deviations were always found to be less than 8%. Particularly, Figure 9a reports the value of removal% for 2-Nitrophenol, while Figure 9b shows the efficiency

for the adsorption of 2,4-D. The adsorbent RHA is represented with blue circles, the silica SRHA with red circles and RSA with green circles.

Figure 9 – Percentage removal for a) 2-Nitrophenol and b) 2,4-D, using RHA (blue), SRHA (red) and RSA (green) as adsorbent materials



Source: Authors (2022)

In details, it is possible to notice that RHA showed an extremely good efficiency: above 80% of removal was found for both molecules, mostly independent of the initial concentrations. A maximum of 95% and 93% was achieved for 2-nitrophenol and 2,4-D, respectively. SRHA demonstrated a different behavior: in the case of 2-nitrophenol, a medium removal efficiency, about 50%, was retrieved; on the other hand, the silica demonstrated a very high removal of 2,4-D, above 85% for all concentrations. At last, in the case of RSA as adsorbent material, for both molecules the removal efficiency was not found to be very high, being mainly lower than 20% for 2-Nitrophenol and 40% on average for 2,4-D.

SRHA was expected to present a better performance overall, for the high silica content and the good textural properties ($SBET = 175.81 \text{ m}^2/\text{g}$ and $V = 0.0689 \text{ cm}^3/\text{g}$); however, in the case of 2-nitrophenol, the lower adsorption efficiency might be due to unfavorable surface charges interactions. The 2-Nitrophenol solution presented a pH of 5.5, which is lower than the pH_{pcz} of SRHA. This means that the surface is slightly positively charged, creating electrostatic repulsion with the positive nitro

group of 2-Nitrophenol. For the case of RHA and RSA, the chemical composition and the morphology differences are minimal and should behave similarly as adsorbates. Therefore, the lower adsorption efficiency presented by RSA can only be explained by surface chemistry interactions. As reported by (Dos Reis, 2016b), it is the synergy of the silanol, alcohol/carbonyl and hydrogen donors group present on the surface that promote adsorption. In this case, as demonstrated by the HI results, the oligosaccharide extraction modified the RSA surface such that the presence of the phenol group, major building block of both adsorbates in this work, was compromised.

Values with more than 90% of removal efficiency or more were already reported in the literature for phenols with unmodified RHA or other biomasses (Ahmaruzzaman, 2011; Wasilewska, 2021; Deokar & Mandavgane, 2015). Again, the adsorbate that presented greater performances than this work normally required more preparation steps or chemical activation, which might limit their practical use in large batches. Here, an industrial calcinated biomass was employed, with the purpose of idealizing a future large-scale industrial application.

In addition, in the case of 2,4-D, the efficiency reported was also found to be very high. In the literature, Deokar and Mandavgane2015 found a removal of 54% with an initial concentration of 50 ppm (Deokar& Mandavgane, 2015). Arefieva *et al.* (2015) reported a removal efficiency between 23-35% for the three adsorbents used here, RHA, RSHA and RSA. However, the most important aspect is that, normally, the best adsorption efficiencies of 2,4-D solutions are found at low pH, (Mandal *et al.*, 2019; Khan, 2021), between 2 and 3. This condition does not reflect what it is found in common water effluents; therefore, our results are very interesting for real water purification applications. Overall, it is important to highlight that, in general, the efficiency of removal is not very dependent on the initial concentration, as reported in other works (Mandal, 2019). This means that the adsorbents will behave similarly in different situations, being more robust.

3.4 Large-scale Evaluation

Based on the previously presented results, pillow-shaped filters were produced with RHA, as this adsorbent presented almost the same efficiency as SRHA, without requiring the chemical extraction step. The removal efficiency of 2-nitrophenol in water to evaluate. As shown in Table 5, the maximum efficiency obtain was of 73, almost 20% then what found in the lab-scale experiment. Particularly, all the efficiency encountered at different initial concentration of the pollutant are between 12 and 20% less than what found before (Figure 9). In this case, it can be assumed that mass transfer of the adsorbate molecules through the fabric can have a great impact on the access to the reactive surface of the adsorbent. Still, the results are very promising and demonstrate that is possible to create a cheap and easy-to-use pillow-shaped filter that can be applied on a large-scale in water sedimentation tanks.

Table 5 – Adsorption efficiency of large-scale tests with RHA in a pillow-shape filter

InitialConcentration	Removal Efficiency (%)
10 ppm	29.62
20 ppm	55,85
60 ppm	73,03



Source: Authors (2022)

In the future, experiments evaluating the adsorption efficiency of RHA in more complex matrices, like synthetic effluents, will be carried out. Moreover, evaluation about the possibility of reuse of the filter are already taking place.

Overall, it was shown in this work that agricultural waste biomasses can be applied as sustainable adsorbent materials, with important applications in water effluent purification.

4 CONCLUSIONS

In this work the comparison in terms of adsorption of three different types of rice agricultural waste were presented. Industrial rice husk, rice husk silica and rice straw ashes, were tested as adsorbents for the removal of 2-nitrophenol and the herbicide 2,4-D. The adsorption capacity for 2-nitrophenol were found to be 29.13 mg g⁻¹, 23.75 mg g⁻¹ and 3.193 mg g⁻¹, for RHA, SRHA and RSA, respectively. The values are in good accordance with the literature for unmodified agricultural biomasses. Overall, the values of adsorption efficiency found were also extremely high, particularly, being above 90% for both micropollutants in the case of RHA as adsorbent. Based on the results obtained, large-scale adsorption tests were also carried out using pillow-shaped filters containing RHA. The removal of 2-nitrophenol was evaluated at three initial concentrations and found up to 20% less than the analytical scale efficiency, proving that mass transfer through the fabric might be a limiting factor. Still, the results found are very interesting, demonstrating with a cheap and simple preparation processes that can be applied very easily on a large scale to tackle water pollution, demonstrating that it is possible to produce sustainable, ready-to-use and cheap filters for water purification.

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