REVISTA MATÉRIA V.27 N.01

ISSN 1517-7076 artigos e13142, 2022

Chemical treatment of sugarcane bagasse and its influence on glyphosate adsorption

Tratamento químico de bagaço de cana-de-açúcar e sua influência na adsorção de glifosato

Williene Faria da Penha Bezerra[1], Guilherme Dognani[1], Laura Neves de Alencar[1], Marcela Prado Silva Parizi[2], Rosane Freire Boina[3], Flávio Camargo Cabrera[4], Aldo Eloízo Job[1]

[1]Universidade Estadual Paulista "Júlio de Mesquita Filho", Departamento de Física, R. Roberto Simonsen, 305, CEP: 19060-900, São Paulo, Presidente Prudente, Brasil.
[2]Universidade Estadual Paulista "Júlio de Mesquita Filho" - Campus Experimental de Rosana, Departamento de Engenharia de Energia, Av. dos Barrageiros, 1881, CEP: 19274-000, São Paulo, Rosana, Brasil.
[3]Universidade Estadual Paulista "Júlio de Mesquita Filho", Departamento de Química e Bioquímica, R. Roberto Simonsen, 305. CEP: 19060-900, São Paulo, Presidente Prudente, Brasil.
[4]Universidade Estadual de Maringá, UEM - Campus de Umuarama, Departamento de Meio Ambiente, Av. Ângelo Moreira da Fonseca, 1800, CEP: 87506-370, Paraná, Umuarama, Brasil.
e-mail: williene_eng@hotmail.com, dognani.g@gmail.com, laura_ndea@hotmail.com, aldo.job@unesp.br, marcela.prado@unesp.br, rosane.freire@unesp.br, flavioccabrera@yahoo.com.br

ABSTRACT

Due to the production rates of sugarcane, nowadays, the sugarcane bagasse stemming in the sugar and alcohol industry is the agro-industrial waste produced in greater volume throughout in Brazil. In 2019, about 192 million tons of this waste were generated. The use of this waste has been the aim of researches around the world, with emphasis on applications that aim to meet the prerogatives of the concept of circular economy. Within this scenario, sugarcane bagasse (SB) was treated in an alkaline medium, forming an adsorbent material, SB_{NaOH}. The effects of chemical treatment were evaluated for surface properties and for glyphosate removal in an aqueous medium. The adsorptive phenomenon was studied through isotherm tests. The results obtained were fitted to classical models of Langmuir, Freundlich and Dubinin-Radushkevich. The characterization indicated that the chemical treatment promoted an important change in the surface of the residue, increasing the surface area. SB and SB_{NAOH} had a feasible behavior as adsorbent and good performance in the removal of the herbicide, presenting values greater than 65% of under all working conditions. The theoretical adsorption saturation governed by Dubinin-Radushkevich (q_S) was in the order of 8.988 mg/g (R^2=0.988) for SB at 120 minutes of contact and maximum adsorption capacity by Langmuir (Q_{max}) was 13.720 mg/g (R^2=0.984) for SB_{NaOH} at 40 minutes of contact. The process was governed by the exchange or sharing of electrons. The adsorbate is distributed heterogeneously on the SB surface, justifying the presence of active sites with greater ionic strength, and homogeneously on the SB_{NaOH} surface (monolayer). In general, the treated sugarcane bagasse, coming from an agro-industrial residue, proved to be an alternative and promising biosorbent for the removal of glyphosate from aqueous systems, thus generating a new application of this residue.

Keywords: Biosorbent, Agro-industrial waste, Adsorption, Herbicide, Alkaline treatment.

RESUMO

Em virtude dos índices de produção da cana-de-açúcar, o bagaço proveniente do processamento da cana na indústria sucroalcooleira é hoje o resíduo agroindustrial produzido em maior volume no Brasil. Em 2019 foram gerados cerca de 192 milhões de toneladas deste resíduo. A utilização deste resíduo tem sido alvo de pesquisas em todo o mundo, com destaque às aplicações que visam atender as prerrogativas do conceito de economia circular. Dentro desse cenário, o bagaço de cana-de açúcar (SB) foi tratado em meio alcalino, formando um material adsorvente, SB_{NaOH}. Os efeitos do tratamento químico foram avaliados quanto a proprie-

Autor Responsável: Williene Faria da Penha Bezerra Data de envio: 11/02/2021 Data de aceite: 19/09/2021

10.1590/S1517-707620220001.1342

dades de superfície e quanto a remoção do herbicida glifosato em meio aquoso. O fenômeno adsortivo foi estudado por meio de ensaios de isotermas. Os resultados obtidos foram ajustados aos modelos clássicos de Langmuir, Freundlich e Dubinin-Radushkevich, onde cada material adsorvente se encaixou em um modelo diferente. A caracterização indicou que o tratamento químico promoveu alteração importante na superfície do resíduo, ampliando a área superficial. SB e o SB_{NaOH} tiveram um comportamento favorável como adsorvente e boa performance na remoção do herbicida, apresentando valores maiores que 65% de em todas as condições de trabalho. A saturação teórica de adsorção regida por Dubinin-Radushkevich (q_S) foi na ordem de 8,988 mg/g (R^2=0,988) para o SB aos 120 minutos de contato e capacidade máxima encontrada por Langmuir ($Q_{máx}$) foi de 13,720 mg/g (R^2=0,984) para o SB_{NaOH} aos 40 minutos de contato. O processo foi governado por troca ou partilha de elétrons. O adsorvato se distribui de forma heterogênea na superfície SB, justificando a presença sítios ativos com maior força iônica, e homogeneamente sobre a superfície (monocamada) de SB_{NaOH}. Em geral, o bagaço de cana tratado, provindo de um resíduo agroindustrial, se mostrou um biosorvente alternativo e promissor para remoção de glifosato de sistemas aquosos, gerando assim uma nova aplicação deste resíduo.
Palavras-chave: Biosorvente, Resíduos agroindustriais, Adsorção, Herbicida, Tratamento alcalino.

1. INTRODUCTION

The world population has been growing in an alarming number. According to the United Nations (UN) in 2024 the total number of people will be superior to 8 billion, and in 2050, more than 9 billion; those numbers show an increase of 13.16% from 2012 to 2024 and 34.90% from 2012 to 2050 [1]. With the population growth, the demand for food, has been increasing and consequently the increase of world agricultural production. The intensive utilization of pesticides, fertilizers and genetic development of seeds, among other factors contributed to increase the world agricultural production [2]. Among the compounds that are more used in the agricultural field can highlight the herbicides, because eliminate plants that will compete with planted crops for nutrients [3]. Glyphosate (N-(phosphonomethyl)glycine) is the most widely used herbicide on earth with properties of a non-selective, systemic and emerging herbicide which its most important function is to control the growth of weeds and grasses [4].

Its application in large areas of cultivation and possible excessive use makes the glyphosate appear more between researches. Although it is considered non-toxic in the last few years it is preoccupying the whole world because of its direct and indirect possible effects on health [5]. The effect to the human body from this herbicide had been demonstrated in a temporary study (2001 to 2015) in adults who live in the northeast of Germany which showed the concentrations of glyphosate on its limit and beyond quantification limit in these people´s urine [6]. MARTÍNEZ *et al.* [7] reported alterations in neurotransmitters in mice brain after exposure to glyphosate. Meanwhile in zebrafish the glyphosate caused alteration in morphological and behavioral parameters [8]. Furthermore, the contamination in the air, soil and water for excessive use of pesticides become a constant concern in last years [9].

Due to high mobility of water bodies, it becomes the main concern since even when the herbicide is applied to the soil in large quantities, the contaminating residues are leached into groundwater sources [10]. This possibility of contaminants leaching makes the water available to the human, animal and plant population even more scarce. Unfortunately, about 1.2 billion people in the world do not have safe, potable and affordable water for their use, due their own activities including extensive use of pesticides, herbicides and, fertilizers [11].

Once this contaminant reaches water bodies removal and remediation pathways such as coagulation [12], membrane filtration [13] and advanced oxidative processes (AOPs) [14, 15], are being studied. Among these, the adsorption process seems to be the most promising removal pathways of this contaminant [16, 17]. Because of the large amount produced, being non-toxic and low cost, agricultural residues such as fruit [18, 19], sawdust [20], rice husks [21], coconut fibers [22, 23] and sugarcane bagasse [24- 26], show as an alternative to this adsorption process.

Recently, the bagasse from the processing of the sugar-alcohol industry is the agricultural residue produced in a large volume in Brazil because of the high production of sugarcane (*Saccharum officinarum*) in the country. In 2019/2020 season were produced 642.7 tons of million of sugarcane [27]. The quantities of sugarcane bagasse (SB) from this activity corresponds around 30% of the total cane crushed in the industry, generating large amount of residues [28]. Being a lignocellulosic material in the form of biomass plant the sugarcane bagasse is constituted specially of cellulose ($C_5H_{10}O_5$), hemicellulose ($C_5H_8O_4$) and lignin ($C_7H_{10}O_3$) [29, 30]. Cellulose is rich in hydroxyl which allows the molecule to go through countless of chemical modifications making it interesting to the production of new materials and with different applications [31].

In function of the quantity produced, physical and chemical characteristics, such as environment and low cost the sugarcane bagasse has been studied in several areas including animal nutrition [32], construction [33] and biocomposites [34]. Its versatility allows to be used as a biosorbent in the removal of water contaminants including dyes [35, 36], metal ions [37], medicines [38] and pesticides [39]. Furthermore, researchers about biochar production from waste has demonstrated the removal of caffeine [40], oxytetracycline [41] and copper [42] an easier adsorption even though assigned process and consequently obtaining costs in the adsorbent. CUBA *et al.* [43] used sugarcane bagasse in the biochar production to remove glyphosate demonstrating that the use of sugarcane bagasse as raw material to produce charcoal chemically activated shows that it is favorable to the formulation removal based on glyphosate.

Based on the above considerations, its notorious the relevance of waste used from clean source in the adsorption process for the water decontamination. Because of the low number of studies in relations to adsorption of pesticides in the sugarcane bagasse its potential to generate new materials and the exacerbated in the use of glyphosate in agriculture. The present study aims use the sugarcane bagasse treated and untreated as adsorbent material to glyphosate removal.

2. MATERIALS AND METHODS

Commercial active Roundup® Original DI herbicide glyphosate (N-(phosphonomethyl) glycine) was used for this study obtained in the local market. The sugarcane bagasse was donated from Usina Alto Alegre S/A sugar-alcohol industry located in Santo Inácio-Paraná- Brazil. Sodium hydroxide (99% purity; NaOH; Synth), Ninhydrin (99% purity; $C_9H_6O_4$; Chemical Dynamics) and sodium molybdate (99% purity; $Na_2MoO_4.2H_2O$; Synth). All chemicals were used as received.

2.1 Sugarcane bagasse fibers processing and treatment

For the removal of impurities in the sugarcane bagasse it was washed in running water during 48 hours and later on washed in deionized water. The fibers were dried in an oven at 60 °C for 72 h until the mass stabilized. Finally, the fibers were micronized and sieved to obtain particles between 0.15 and 0.11 mm (100 and 140 mesh). This process resulted in the sugarcane bagasse (SB).

The chemical treatment of the sugarcane bagasse fibers was carried out with the main purpose of removing the lignin and increasing cellulose access. For this procedure it used sodium hydroxide solution, 10% w/v (NaOH) and 50 g of sugarcane bagasse according to the methodology described by SANCHEZ *et al.* [44]. Briefly, the waste was immersed in alkaline solution under agitation for 24 hours in room temperature (25ºC±2ºC). After this time, the fibers were removed from the solution and washed with deionized water until its pH neutralization. The resulting of the bagasse was dried in the oven for 5 hours at 100 ° C. The treated bagasse is called SB_{NaOH}.

2.2 Characterization

The determination of the point of zero charge (pH_{pzc}) was based on GIACOMNI *et al.* [45], which it kept in contact 0.1 g of adsorbent with 10 mL of the aqueous solutions of 100 mg L^{-1} of glyphosate with 11 different initial pH conditions (1 to 11). The pH_{pzc} of the samples were obtained when calculating the average between the final points of pH tended the same value.

The specific surface area was determined by Brunauer-Emmett-Teller (BET) analyses, using ASAP 2020 (196 ºC - 0 ºC), and pore volume and diameter were calculated using the Barrett-Johner-Halenda method (BJH). The morphology of fibers was determined using Scanning Electron Microscopy (SEM), the images were obtained in a Carls Zeiss microscope EVO-LS 15 model.

2.3 Herbicide Solution and Analysis

Using the methodology proposed by TZASKOS *et al.*[46] calibration curve was prepared from a stock solution of 100 mg L^{-1} of glyphosate. A volume of 1.5 mL of glyphosate solution with aliquots ranging from 0.5 to 10 mg L^{-1} were transferred to glass vials and 1.5 mL of 5% ninhydrin and 1.5 mL of 5% of sodium molybdate were added to each of the vials. The vials were sealed and kept in a water bath in a temperature of 85-95° C for 12 minutes. Then the samples were cooled to room temperature (25ºC±2ºC) and were quantitatively transferred to volumetric flasks and added 8 mL of MilliQ water. Then the reading was performed by Spectrophotometer-1800, SHIMADZU spectrophotometer at 570 nm.

From this data was constructed a calibration curve with the absorbance as a function of glyphosate concentration in the range from 0.5 to 10 mg L^{-1}. For the baseline of the instrument 1,5 mL of ninhydrin and sodium molybdate solution was used, to a total volume of 4,5 mL. The coefficient od determination (Rsquared) was 0.99589.

2.4 Adsorption tests

The pH study of adsorption tests was performed in which the value between the pH range analyzed those results in a larger glyphosate removal. To evaluate this effect the pH solution was adjusted in nine different conditions (2.0 to 10.0) with hydrochloric acid solution and/or NaOH at 0.5 M.

The kinetics adsorption studies were performed through the contact of 0.1g of the adsorbent to 10 mL of contaminated solution (glyphosate concentration of 100 mg L^{-1}) added in glass vials and agitated by a mechanical stirrer at room temperature (25ºC±2ºC) and a gap of 10 min to 24 hours and pH 5 and 9 to the SB and SB_{NaOH}, respectively. After the adsorption time the adsorbents were separated from the aqueous solutions by centrifugation at 4000 rpm for 30 min and so the supernatant was collected. Sequentially, the remain amount of glyphosate was analyzed with the quoted procedure before (item 2.3). All experiments were conducted in triplicates.

The amount of glyphosate adsorbed at equilibrium (q_e) was calculated by Equation (1).

$$q_e = \frac{(C_0 - C_f)\, V}{m} \tag{1}$$

Where: q_e (mg g^{-1}) is the adsorption capacity at the equilibrium; C_0 (mg L^{-1}) corresponding the initial concentration of glyphosate in the solution, C_f (mg L^{-1}) the concentration of glyphosate at equilibrium, V (L) is the volume of the glyphosate solution and m (g) is the mass of the sugarcane bagasse.

2.5 Adsorption isotherms

For the adsorption of isotherm studies were utilized fixed amounts of adsorbents were used, 0.1 g for 10 mL of contaminated solution. The concentrations range were 5 - 10 - 20 - 30 - 40 - 50 - 60 - 80 and 100 mg L^{-1}, time of 2 hours at pH 6 to SB and 40 min at pH 9 to SB_{NaOH}. The glyphosate adsorption capacity (q_e) was calculated by Equation 1 and the removal percentage calculated by Equation 2.

$$\%\ \text{Removal} = \left[\frac{C_0 - C_F}{C_0}\right] * 100 \tag{2}$$

In order to describe the interactive behavior between the glyphosate and sugarcane bagasse, were calculated the adsorption balance through nonlinear models by LANGMUIR, FREUNDLICH [47] and DUBININ-RADUSHKEVICH [48], according with the Equation (3), (4) and (5), respectively.

$$q_e = Q_{max} * K_l * C_e / [1 + (K_l * C_e)] \tag{3}$$

$$q_e = K_f \,.\, C_e^{1/n} \tag{4}$$

$$q_e = (q_s)\,.\exp(-K_{ad}\varepsilon^2) \tag{5}$$

Where: q_e (mg g-^{1}); is the amount of glyphosate adsorbed at equilibrium on the sugarcane bagasse; Q_{max} (g.mg^{-1}) is the amount of glyphosate adsorbed at saturation; K_l (L g^{-1}) is the Langmuir adsorption equilibrium that represents surface affinity; C_e (mg L^{-1}) is the concentration of glyphosate in the liquid phase at equilibrium; K_f (mg g^{-1}); n is an empirical parameter (dimensionless) of Freundlich model, where n provides an indication whether the isotherm is favorable or unfavorable. For D-R isotherm, q_s indicate the theoretical isotherm saturation capacity (mg/g), K_{ad} is the constant related to the adsorption energy (mol^2 kJ^{-2}), and ε is the Dubinin–Radushkevich isotherm constant.

3. RESULTS AND DISCUSSION

The chemical treatment of the sugarcane bagasse surface with alkaline solution of sodium hydroxide it was possible the majority remove of lignin and the increased exposure to cellulose in consequent increase of roughness and surface area of material. This was observed by PAIVA *et al.* [34] when those treated sugarcane bagasse with alkaline solution for composites production. The treatment of sugarcane bagasse with sodium hydroxide caused swelling in the fibers, increasing the interior surface of the cellulose causing the decrease of crystallinity that is necessary for the lignin breakdown [49] explain the significant increase of the surface area and pore volume of the fibers treated as shown in Table 1.

Table 1: BET and BJH surface parameters of raw sugarcane bagasse (SB) and treated (SB_{NaOH}).

Samples	Surface Area ($m^2\ g^{-1}$)	Pore Volume ($cm^3\ g^{-1}$)	Pore Size (Ǎ)
SB	0.114	0.0018	620.3297
SB_{NaOH}	0.411	0.0021	205.0075

It can be observed that a variation in the results of the surface area SB (0.114 $m^2\ g^{-1}$) in the present study and one reported by MOUBARIK & NABIL [50] (0.487 $m^2\ g^{-1}$). This variation between the value of literature and this work can be considered not significant once these fibers properties can slightly vary because of the production factors, such as: planting conditions, seasonality factors, irrigation volumes like the way the plant is harvested.

The samples morphology was analyzed by SEM. The Figure 1 shows SB (a - b) and SB_{NaOH} (c-d). The SB images shows an ordered uniform and smooth structure which is associated with the presence of amorphous constituents such as lignin and hemicellulose, as well as wax and extracts as reported by LI *et al.* [51]. While in the SB_{NaOH} images the fibrils were exposed due to the effect of lignin removal that causes the fibrillation process indicating the disorganization in the cellulose structure, confirming the increase of roughness and structure surface area (Table 1) result corroborated by AGUIAR and LUCENA [52]. However, the alkaline treatment promotes the release of new active sites thus allowing a better interaction between the bagasse and the contaminant.

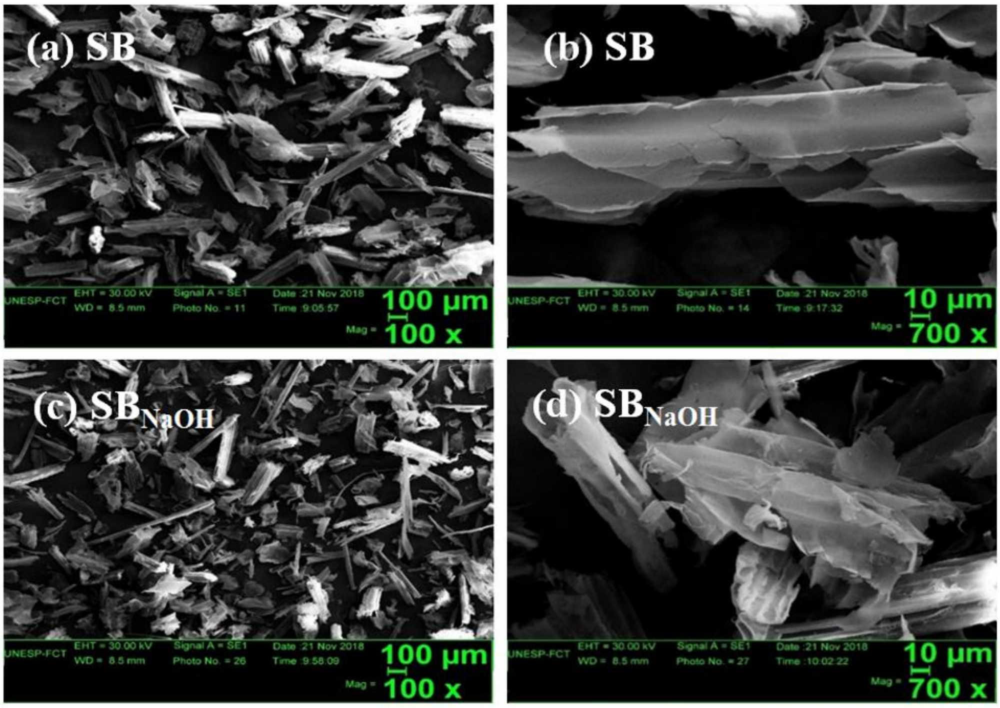

Figure 1. Scanning electron microscopy images of SB (a) 100 X; b) 700 X; and SB_{NaOH} (c) 100 X; (d) 700 X.

Using the plot of final pH *vs* initial pH for the SB and SB_{NaOH}, it is possible evaluate the stabilization trend at a given pH, regardless of the initial conditions, which we call pH_{PZC}. The investigation in the adsorption efficiency of glyphosate in different pH`s such as the determination of the point of zero charge (pH_{PZC}) the adsorbents is justified because the adsorption process is dependent on the pH which affects the surface charge ionization level and adsorbate species [45]. According Figure 2 the point of zero charge (pH_{PZC}) was obtained at pH 6.36 and pH 9.12, for SB and $SB_{NaOH,}$ respectively.

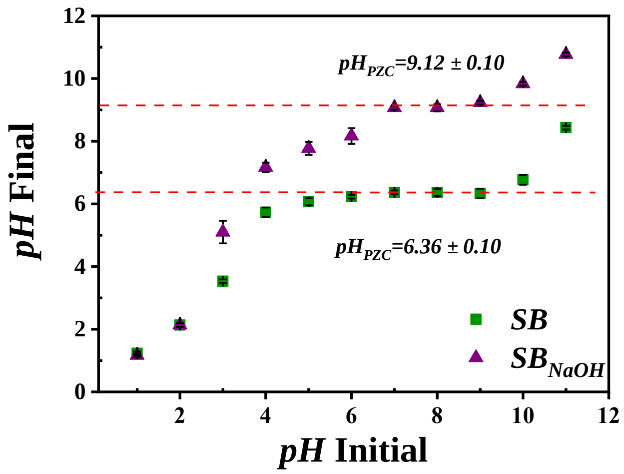

Figure 2. pH at the point of zero charge (pH_{pzc}) of SB and SB_{NaOH}.

The adsorption study of the pH indicates what value between the analyzed pH range which results in greater glyphosate removal. According to pH_{PZC}, for SB_{NaOH} the optimum adsorption pH would be higher than for SB adsorbent reaching more active sites for adsorption. As observed in Figure 3 the pH value which showed a greater SB removal was the pH 5 approximately 67% while for SB_{NaOH} was the pH 9 with 86%.

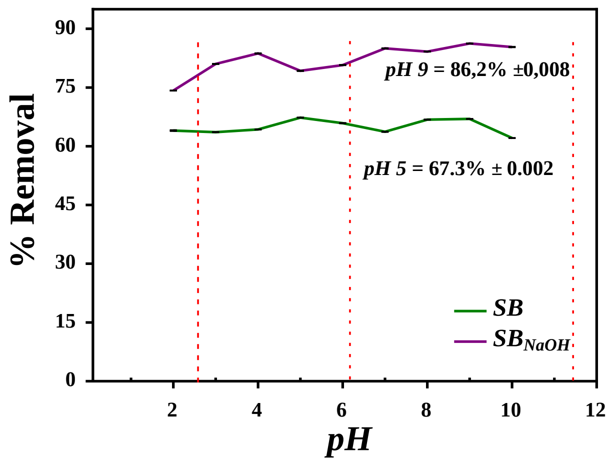

Figure 3. Glyphosate removal percentage as a function of effect pH on the adsorption and dissociation onto SB and SB_{NAOH}.

Glyphosate belongs to the phosphonated amino acids group and like the precursor glycine can be separated in two charges being one positive in the amino group and one negative in the phosphonate group [53]. In a pH < 2.6 the glyphosate shows a positive liquid charge, in a pH = 2.6 the glyphosate is neutral and the negative charges increase with pH > 2.6 [54]. MAYAKADUWA *et al.* [53] and ESSANDOH *et al.* [55] reported that when the pH_{pzc} is lower than the pH of the solution the adsorbent surface will be negatively charged while when the pH_{PZC} is higher than the pH of the solution the adsorbent surface tends to be positively charged.

For the SB the pH_{PZC} is greater than the pH solution and the glyphosate molecule in the values of pH 5 (Figure 3) has a prevalence of negative charges, value similar to that used by CUBA *et al.* [43] therefore in this case the removal occurs with the interaction of positive biosorbent charges and negative charges of glyphosate phosphonate group. For SB_{NaOH} the pH_{PZC} value is equal to the pH solution indicating the adsorbent matrix surface has the same amount of positive and negative charges being this way the adsorption occurs by a ligand exchange between the sugarcane bagasse hydroxyl treated with sodium hydroxide and glyphosate phosphonic portion of P-O- group similar reported by PICCOLO *et al.* [56].

The percentual kinetic study of glyphosate removal in function to time was performed taking in consideration the pH values. Analyzing Figure 4 it is established that the kinetics process was fast for both adsorbents in 40 minutes happens 81.4% of removal to SB_{NaOH} while for the SB has showed a percentage of removal of 77.2% in the first two hours and the maximum removal of 77.9% in 24 hours.

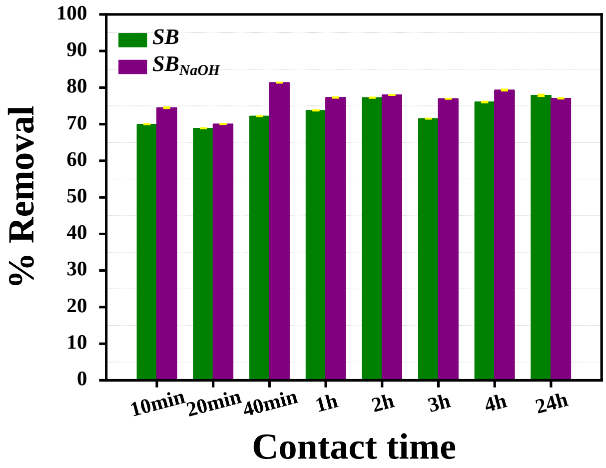

Figure 4. % Glyphosate removal in function of adsorption time on SB and SB_{NAOH} (concentration of of 100 mg L^{-1}).

Observing the data can be noted a reduction in the glyphosate removal percentage after obtaining the maximum samples removal. Such fact can be explained because the bagasse has initially various empty places which were progressively filled until an equilibrium point was reached. When the amount of adsorption glyphosate increased like forces of repulsion between adsorbed molecules made more difficult the adsorption on the rest sites, reducing consequently the adsorption rate making it possible the desorption phenomenon that can occur in the biosorbent surface [54].

The results in the application of nonlinear models of Langmuir, Freundlich and Dubinin-Radushkevich in the obtained experimental data are shown in Figure 5 (A and B), that shows glyphosate adsorbed at equilibrium (qe) as function of concentration of glyphosate in the liquid phase at equilibrium (Ce). The values of the calculated parameters are shown in Table 2.

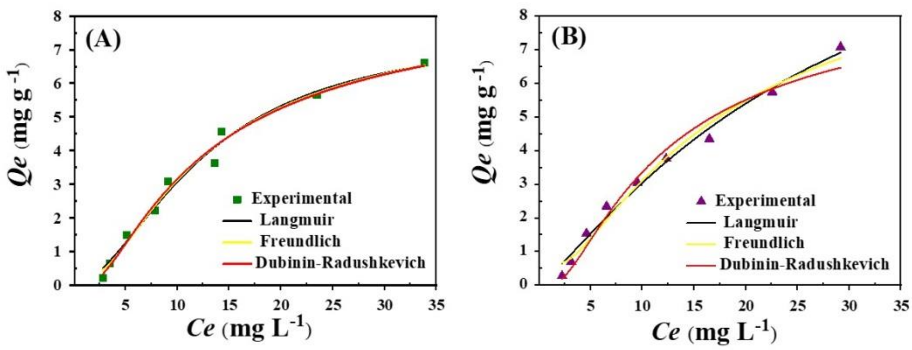

Figure 5. Experimental and predicted adsorption isotherms for glyphosate for the Langmuir, Freundlich and Dubinin-Radushkevich non-linear models for (A) SB and (B) SB_{NAOH}.

It is important to note that all isotherm models applied in that work had satisfactory behavior for both adsorbent materials, with similar adjustments for tested models when consider R^2. However, even with similar coefficient of determination, each type of adsorbent present better fits for different model.

Table 2. Freundlich and Langmuir isotherm parameters for glyphosate removal using SB and SB_{NaOH}.

	Langmuir				**Freundlich**				**Dubinin-Radushkevich**		
Adsorbent	**Q_{max} (mg/g)**	**K_L (L/mg)**	**R_L**	**R^2**	**n**	**1/n**	**K_F (mg/g)**	**R^2**	**q_s (mg/g)**	**K_{ad} (mol^2/kJ^2)**	**R^2**
SB	7.628	0.011	0.759	0.981	13.259	0.075	8.353	0.982	8.988	11.013	0.988
SB_{NaOH}	13.720	0.018	0.767	0.984	9.391	0.107	11.174	0.975	9.266	10.683	0.973

The sugarcane bagasse adsorbent (SB) was adjusted for both models, the high R^2 values (Langmuir and Freundlich) and the n value (Freundlich) which was showed in Table 2 is greater than 1 indicating that the adsorption is favorable a result confirmed by K_L and the 1/N value is 0.075. NASCIMENTO *et al.* [47] explained the as higher the n value is lower the 1/n value will be implying in a greater interaction between the glyphosate and the sugarcane bagasse. However, the Dubinin-Raduchkevich (D-R) fitted slightly better for those fibers. The D–R isotherm model was developed to account for the effect of the porous structure assuming that the adsorption process was related to micropore volume on the adsorbent walls [57]. Which is in accordance with the SEM discussion, where the SB has amorphous part in its structure.

When analyzing the coefficients of determination (R^2), the treated sugarcane bagasse (SB_{NaOH}) showed better fit in Langmuir isotherm, where the herbicide molecules are adsorbed in monolayer. That result corroborate with the experiments of ABREU *et al.* [58] with sugarcane biochar for the adsorption of Cadmium (Cd), and CARVALHO *et al.* [59] who studied orange peel biochar for tetracycline removal. Analyzing the SB_{NaOH} for the Langmuir model was noticed that the maximum adsorbed amount in the experiment (Table 2) was 13.720 $mg.g^{-1}$ while the R_L factor (separation factor at 100 $mg.L^{-1}$) was 0.767 mgL^{-1} indicating that adsorption was favorable ($0 < R_L < 1$) that is the adsorbate prefer the solid phase than the liquid [47]. The fit in Langmuir model proposed that adsorption occurs by covering the monolayer of glyphosate molecules above surface of SB_{NaOH} that is each site is responsible by adsorption of only one molecule cannot to occurs additional adsorption [60], further assuming that the adsorption takes with active sites of the adsorbent with equal affinity for the adsorbate in which interferences in the adsorption of neighboring sites are disregarded [59].

4. CONCLUSIONS

The use of sugarcane bagasse (SB) and chemically treated sugarcane (SB_{NaOH}) showed as favorable to the glyphosate removal in the studied conditions being with pH 5 for SB and pH 9 for SB_{NaOH} at room temperature. SB adsorbent showed removal efficiency of 77% (q_S 8.988 mg g^{-1}) occurred in 2 hours with an adsorption plateau, fitting to all tested models (Langmuir, Freundlich and Dubinin-Radushkevich) with showed a similar coefficient of determination. However, the Dubinin-Radushkevich fitted better for those fibers due their amorphous and porous structure of lignin and hemicellulose compounds.

The SB_{NaOH} showed a similar behavior, with small difference between the R^2. This adsorbent present fast adsorption with 81% of removal in 40 min and maximum capacity of adsorption of 13.720 mg g^{-1} (Q_{max}). In this case it occurred adjust for the Langmuir model, therefore the adsorption occurs by covering the monolayers of glyphosate molecules over the surface bagasse.

All factors involved in the study showed that the alkaline treatment in sugarcane bagasse and final glyphosate adsorption fulfill the proposed objective providing biosorbent with capacity of maximum removal higher than untreated material as well a smaller taken time for adsorption.

As shown in previous literature - mentioned in this work - the alkaline treatment for natural fibers has been shown to be very efficient and viable for different applications. In this case it was no different, the treatment proved to be efficient in improving the adsorbent material for herbicide removal. As it is a cheap alkaline, easy to handle, and with small amount of waste, this type of treatment has been feasible in terms of cost/benefit.

Therefore, presenting a possibility alkaline treatment to increase efficiency in the lignocellulosic fibers such as aqueous solutions decontamination agents. Hence, the perspectives for this material and its future application in the industry are very favorable, however more evaluations such as the effect of temperature and recyclability must be carried out.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support from "Coordenação de Aperfeiçoamento de Pessoal de Nível Superior" (CAPES - Brazil) - Finance Code 001 and "Conselho Nacional de Desenvolvimento Científico e Tecnológico" (CNPq). The authors also thank "LabMMEV- FCT/UNESP" by microscopy images.

6. BIBLIOGRAPHY

[1] United Nations, Department of Economic and Social Affairs Population Dynamics, 2019, *Revision of World Population Prospects*, Available in: https://population.un.org/wpp2019/. Accessed November 10 of 2020.

[2] CARVALHO, F.P., "Pesticides, environment, and food safety", *Pesticides, Environment, and Food Safety*, v. 6, n.2, pp. 48-60, 2017.

[3] ZHAN, H., FENG, Y., FAN, X., *et al*., "Recent advances in glyphosate biodegradation", *Applied Microbiology and Biotechnology*, v. 102, n. 12, pp. 5033–5043, 2018.

[4] SILVA, A.S., FERNANDES, F.C.B., TOGNOLLI, J.O., *et al*., "A simple and green analytical method for determination of glyphosate in commercial formulations and water by diffuse reflectance spectroscopy", *Spectrochimica Acta Part A.*, v. 79, n. 5, pp. 1881– 1885, 2011.

[5] AMARANTE JÚNIOR, O.P., SANTOS, T.C.R., "Glyphosate: properties, toxicity, use and legislation", *Química Nova*, v. 25, n.4, pp. 589-593, 2002.

[6] CONRAD, A., SCHROTER-KERMANI, C., HOPPE, H.W., *et al.*, "Glyphosate in German adults – Time trend (2001 to 2015) of human exposure to a widely used herbicide". *International Journal of Hygiene and Environmental Health*, v. 220, n. 1, pp. 8-16, Jan. 2017.

[7] MARTÍNEZ, M.A., ARES, I., RODRÍGUEZ, J.L., *et al.*, "Neurotransmitter changes in rat brain regions following glyphosate exposure". *Environmental Research*, v. 161, pp. 212–219, 2018.

[8] BRIDI, D., ALTENHOFEN, S., GONZALEZ, J.B., *et al.*, "Glyphosate and Roundup® alter morphology and behavior in zebrafish", *Toxicology*, v. 392, n. 32–39, 2017.

[9] VAN BRUGGEN, A.H.C., HE, M.M., SHIN, K., *et al.*, "Environmental and health effects of the herbicide glyphosate", *Science of the Total Environment*, v. 616–617, pp. 255–268, 2018.

[10] DYNIA, J.F. "Nitrate Retention and Leaching in Variable Charge Soils of a watershed in São Paulo State, Brazil", *Commun. Soil Sci. Plant Anal*., v. 31, n. 5-6, pp. 777-791, 2000.

[11] MITIKU, A.A. "A Review on Water Pollution: Causes, Effects and Treatment methods", *Int. J. Pharm. Sci. Rev. Res.*, v. 60, n. 2, pp. 94-101, 2020.

[12] BONGIOVANI, M.C., KONRADT-MORAES, L.C., BERGAMASCO, R., *et al.*, "The benefits of using natural coagulants to obtain potable water", *Acta Scientiarum Technology*, v. 32, n. 2, pp. 167-170, 2010.

[13] YUAN, J., DUAN, J., SAINT, C.P., *et al.*, "Removal of glyphosate and aminomethylphosphonic acid from synthetic water by nanofiltration", *Environmental Technology*, v. 19, n. 11, pp. 1384 – 1392, 2017.

[14] MATAMOROS, V., SALA, L., SALVADÓ, V., "Evaluation of a biologically-based filtration water reclamation plant for removing emerging contaminants: A pilot plant study", *Bioresource Technology*, v. 104, pp. 243-249, 2012.

[15] SERNA-GALVIS, E.A., SILVA-AGREDO, J., GIRALDO, A.L., *et al*., "Comparison of route, mechanism and extent of treatment for the degradation of β-lactam antibiotic by TiO2 photocatalysis, sonochemistry, electrochemistry and the photo-Fenton system", *Chemical Engineering Journal*, v. 284, pp. 953–962, 2016.

[16] HERATH, I., KUMARATHILAKA, P., AL-WABEL, M.I., *et al.*, "Mechanistic modeling of glyphosate interaction with rice husk derived engineered biochar", *Microporous and Mesoporous Materials*, v. 225, n. 280-288, 2016.

[17] RODRIGUEZ-NARVAEZ, O.M., PERALTA-HERNANDEZ, J.M., GOONETILLEKE, A., BANDALA, E.R., "Treatment technologies for emerging contaminants in water: A review", *Chemical Engineering Journal*, v. 323, pp. 361-380, 2017.

[18] GUIZA S. "Biosorption of heavy metal from aqueous solution using cellulosic waste orange peel", *Ecological Engineering*, v. 99, pp. 134–140, 2017.

[19] LEANDRO-SILVA, E., PIPI, A.R.F., MAGDALENA, A.G., *et al.*, "Aplicação dos modelos de Langmuir e Freundlich no estudo da casca de banana como bioadsorvente de cobre (II) em meio aquoso". *Revista Matéria*, v.25, n.2, 2020.

[20] NJIMOU, J.R., MĂICĂNEANU, A., INDOLEAN, C., *et al.*, "Removal of Cd(II) from synthetic wastewater by alginate–Ayous wood sawdust (Triplochiton scleroxylon) composite material", *Environmental Technology*, v. 37, n. 11, pp. 1369–1381, 2016.

[21] VITHANAGE, M., MAYAKADUWA, S.S., HERATH, I., *et al.* "Kinetics, thermodynamics and mechanistic studies of carbofuran removal using biochars from tea waste and rice husks", *Chemosphere*, v. 150, pp. 781-789, 2016.

[22] HENR, Y.K.K., JAROSŁAW, C., WITOLD, Z., "Peat and coconut fiber as biofilters for chromium adsorption from contaminated wastewaters", *Environmental Science and Pollution Research,* v. 23, pp. 527–534, 2016.

[23] MERCI, A., REZENDE, M.I., CONSTANTINO, L.V., *et al.* "Evaluation of different factors in the removal of remazol brilliant blue from aqueous solutions by adsorption in sugarcane and green coconut fibers". *Revista Matéria*, v.24, n.3, 2019.

[24] XING, Y., LIU, D., ZHANG, L. "Enhanced adsorption of Methylene Blue by EDTAD-modified sugarcane bagasse and photocatalytic regeneration of the adsorbent". *Desalination*, v. 259, n. 1-3, pp. 187–19, 2010.

[25] FIDELES, R.A., TEODORO, F.S., XAVIER, A.L.P., *et al.*, "Trimellitated sugarcane bagasse: A versatile adsorbent for removal of cationic dyes from aqueous solution. Part II: Batch and continuous adsorption in a bicomponent system", *Journal of Colloid and Interface Science*, v. 552, pp. 752-763, 2019.

[26] XAVIER, C.S.F., CRISPINIANO, F.F., NASCIMENTO, K.K.R., *et al*., "Secagem e avaliação do bagaço de cana-de-açúcar como adsorvente de corantes têxteis presentes em soluções aquosas", *Revista Matéria*, v.26, n.1, 2021.

[27] CONAB (2020) - Companhia Nacional de Abastecimento, "Monitoring of the Brazilian sugarcane season", *Fourth survey - 2019/2020 Season*, Brazilia, v. 6, n. 4, pp. 1-58, April 2020, Available in: http://www.conab.gov.br. Accessed May 10 of 2020.

[28] SILVA, D.C., MELO, C.A., SOARES JUNIOR, F.H., *et al*., "Effect of the reaction medium on the immobilization of nutrients in hydrochars Obtained using sugarcane industry residues", *Bioresource Technology*, v. 237, pp. 213-221, 2017.

[29] GOUVEIA, E.R., NASCIMENTO, R.T., SOUTO-MAIOR, A.M., "Validation of methodology for the chemical characterization of sugar cane bagasse", *Química Nova*, v. 32, n. 6, pp. 1500-1503, 2009.

[30] FERREIRA, V.F., ROCHA, D.R., "Potentiality and opportunity in the chemistry of sucrose and other sugars", *Química Nova*, v. 32, n. 3, pp. 623-638, 2009.

[31] FERREIRA, B.C.S., GIL, L.F., GURGEL, L.V.A., *et al.* "Obtaining a New Carboxylated Derivative of Microcrystalline Cellulose: An Easy and Solvent-Free Synthesise", *Revista Virtual de Química*, v. 9, n. 1, pp. 431-451, 2017.

[32] GUNUN, N., WANAPAT, M., GUNUN, P., *et al.,* "Effect of treating sugarcane bagasse with urea and calcium hydroxide on feed intake, digestibility, and rumen fermentation in beef cattle", *Tropical Animal Health and Production*, v. 48, pp. 1123-1128, 2016.

[33] CASTRO, T.R., MARTINS, C.H. "Evaluation of the addition of sugarcane bagasse ashes in mixed mortars", *Ambiente Construído*, v. 16, n. 3, pp. 137-151, 2016.

[34] PAIVA, F.F.G., DE MARIA, V.P.K., TORRES, G.B., *et al*., "Sugarcane bagasse fiber as semi-reinforcement filler in natural rubber composite sandals", *Journal of Material Cycles and Waste Management*, v. 2, n. 2, pp. 326-335, 2019.

[35] TAHIR, H., SULTAN, M., AKHTAR, N., *et al*., "Application of natural and modified sugar cane bagasse for the removal of dye from aqueous solution", *Journal of Saudi Chemical Society*, v. 20, n. 1, pp. 115-121, 2016.

[36] UTOMO, H.D., PHOON, R.Y.N., SHEN, Z., *et al*., "Removal of Methylene Blue Using Chemically Modified Sugarcane Bagasse", *Natural Resources*, v. 6, n. 4, pp. 209-220, 2015.

[37] MANH, K.N., MINH, T.H., THI, T.P., *et al.* "Performance Comparison of Chemically Modified Sugarcane Bagasse for Removing Cd(II) in Water Environment", *Journal of Renewable Materials*, v. 7, n. 5, pp. 414-427, 2019.

[38] CARVALHO, R.S., ARGUELHO, M.L.P.M., FACCIOLI, G.G., *et al.* "Use of orange bagasse biocarbon for the removal of tetracycline in wastewater", *Revista Matéria*, v.24, n.3, 2019.

[39] TOLEDO-JALDIN, H.P., SÁNCHEZ-MENDIETA, V., BLANCO-FLORES, A., *et al.*, "Low-cost sugarcane bagasse and peanut shell magnetic-composites applied in the removal of carbofuran and iprodione pesticides", *Environmental Science and Pollution Research*, v. 27, pp. 7872–7885, 2020.

[40] ANASTOPOULOS, I., KATSOUROMALLI, A., PASHALIDIS, I., "Oxidized biochar obtained from pine needles as a novel adsorbent to remove caffeine from aqueous solutions", *Journal of Molecular Liquids*, v. 304, pp. 11266, 2020.

[41] ZHANG, M., MENG, J., LIU, Q., *et al*., "Corn stover–derived biochar for efficient adsorption of oxytetracycline from wastewater", *Journal of Materials Research*, v. 34, n. 17, pp. 3050-3060, 2019.

[42] SAMARAWEERA, H., PITTMAN JR, C.U., THIRUMALAI, R.V.K.G., *et. al*., "Characterization of graphene/pine wood biochar hybrids: Potential to remove aqueous Cu^{2+}", *Environmental Research*, v. 192, pp. 110283, 2021.

[43] CUBA, R.M.F., GUIMARÃES, M.S., TERÁN, F.J.C., "Production of biochar from sugarcane bagasse to remove glyphosate (commercial formulation) in aqueous medium", In: *1° South American Congress on Solid Waste and Sustainability*, Gramado, Rio Grande do Sul, Brazil, 12 – 14 June 2018.
[44] SANCHEZ, E.M.S., CAVANI, C.S., LEAL, C.V., *et al.*, "Unsaturated polyester resin composite with sugar cane bagasse: influence of treatment on the fibers properties", *Polímeros*, v. 20, n. 3, pp. 194–200, 2010.
[45] GIACOMNI, F., MENEGAZZO, M.A.B., SILVA, M.G., *et al.*, "Point of zero charge of protein fibers, an important characteristic for dyeing", *Revista Matéria*, v. 22, n. 2, 2017.
[46] TZASKOS, D.F., MARCOVICZ, C., DIAS, N.M.P., *et al.* "Development of sampling for quantification of glyphosate in natural waters", *Agricultural Sciences*, v. 36, n. 4, pp. 399-405, 2012.
[47] NASCIMENTO, R.F., LIMA, A.C.A., VIDAL, C.B., *et al.*, "Adsorption - Theoretical and Environmental Aspects", *Postgraduate Studies Collection* - Universidade Federal do Ceará – UFC; 2014.
[48] FOO, K.Y., HAMEED, B.H. "Insights into the modeling of adsorption isotherm systems", *Chemical Engineering Journal*, v. 156, n. 1, pp. 2–10, 2010.
[49] ALVIRA, P., TOMÁS-PEJÓ, E., BALLESTEROS, M., *et al.* "Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review", *Bioresource Technology*, v. 101, n. 13, pp. 4851-486, 2010.
[50] MOUBARIK, A., GRIMI, N., "Valorization of olive stone and sugar cane bagasse by-products as biosorbents for the removal of cadmium from aqueous solution", *Food Research International*, v. 73, pp. 169-175, 2015.
[51] LI, X., TABIL, L.G., PANIGRAHI, S., "Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review". *Journal of Polymers and the Environment*, v. 15, pp. 25-33, 2007.
[52] AGUIAR, C.M., LUCENA, S.L., "Cellulases production by Aspergillus niger and cellulase deactivation kinetic", *Acta Scientiarum Technology*, v. 33, n.4, pp. 385-391, 2011.
[53] MAYAKADUWA, S.S., KUMARATHILAKA, P., HERATH, I., "Equilibrium and kinetic mechanisms of woody biochar on aqueous glyphosate removal", *Chemosphere*, v. 144, pp. 2516-2521, 2016.
[54] CARNEIRO, R.T.A., TAKETA, T.B., NETO, R.J.G., *et al.*, "Removal of glyphosate herbicide from water using biopolymer membranes", *Journal of Environmental Management*, v. 151, pp. 353-360, 2015.
[55] ESSANDOH, M., KUNWAR, B., PITTIMAN, J.R.C.U., *et al.*, "Sorptive removal of salicylic acid and ibuprofen from aqueous solutions using pine wood fast pyrolysis biochar", *Chemical Engineering Journal*, v. 265, pp. 219-227, 2015.
[56] PICCOLO, A., CELANO, G., PIETRAMELLARA, G. "Adsorption of the herbicide glyphosate on a metal-humic acid complex", *Science of The Total Environment*, v. 123-124, pp. 77-82, 1992.
[57] HU, Q., ZHANG, Z. "Application of Dubinin–Radushkevich isotherm model at the solid/solution interface: A theoretical analysis", *Journal of Molecular Liquids*, v. 277, n. 1, pp. 646-648, 2019.
[58] ABREU, M.B., ANDRADE, J.R., TURBIANI, F.R.B., *et al., "*Aplicação de carvão ativado de bagaço de cana-de-açúcar na adsorção de Cd (II) e Cu(II)". In: Congresso Brasileiro de Sistemas Particulados – ENEMP, Universidade Federal de São Carlos, São Carlos, SP, 2015.
[59] CARVALHO, R.S., ARGUELHO, M.L.P.M., FACCIOLI, G.G., *et al*., "Utilização do biocarvão de bagaço de laranja na remoção de tetraciclina em água residuária", *Revista Matéria*, v.26, n.2, 2021.
[60] BANERJEE, S., CHATTOPADHYAYA, M.C., "Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by product", *Arabian Journal of Chemistry*, v. 10, n. 2, pp. S1629-S1638, 2017.

ORCID

Williene Faria da Penha Bezerra	https://orcid.org/0000-0003-2662-9774
Guilherme Dognani	https://orcid.org/0000-0002-6794-8440
Laura Neves de Alencar	https://orcid.org/0000-0002-9008-381X
Marcela Prado Silva Parizi	https://orcid.org/0000-0002-4159-8016
Rosane Freire Boina	https://orcid.org/0000-0002-9903-5902
Flávio Camargo Cabrera	https://orcid.org/0000-0001-7924-7089
Aldo Eloízo Job	https://orcid.org/0000-0002-1979-8257