

## Alternative treatments to improve the potential of rice husk as adsorbent for methylene blue

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### ABSTRACT

Alternative treatments, such as, NaOH, ultrasound assisted (UA) and supercritical CO<sub>2</sub> (SCO<sub>2</sub>), were performed to improve the potential of rice husk as adsorbent to remove methylene blue (MB) from aqueous media. All the treatments improved the surface characteristics of rice husk, exposing its organic fraction and/or providing more adsorption sites. The Langmuir and Hill models were able to explain the MB adsorption for all adsorbents in all studied temperatures. The experimental and modeled parameters demonstrated that the MB adsorption was favored by the temperature increase and by the use of NaOH-rice husk. The maximum adsorption capacities for the MB solutions (ranging from 10 to 100 mg L<sup>-1</sup>), estimated from the Langmuir model at 328 K, were in the following order: NaOH rice-husk (65.0 mg g<sup>-1</sup>) > UA-rice husk (58.7 mg g<sup>-1</sup>) > SCO<sub>2</sub>-rice husk (56.4 mg g<sup>-1</sup>) > raw rice husk (52.2 mg g<sup>-1</sup>). The adsorption was a spontaneous, favorable and endothermic process. In general, this work demonstrated that NaOH, UA and SCO<sub>2</sub> treatments are alternatives to improve the potential of rice husk as adsorbent.

**Key words** | adsorption, methylene blue, rice husk, surface modification

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### INTRODUCTION

Nowadays, the presence of synthetic dyes in effluents has become one of the major concerns to the scientific community. It is well known that the reduction of light penetration and photosynthetic activity, toxicity, mutagenicity and carcinogenicity can be effects caused by the incorrect discharge of the dye-containing effluents into the environment (Gupta & Suhas 2009). Adsorption is a commonly used technique for removal of dyes, due its low cost, low energy requirements, high efficiency, simplicity of implementation and operation (Dotto *et al.* 2015a).

One problem of the adsorption process is related to the adsorbent. Generally, activated carbon is the main choice; nonetheless, the high cost is a major drawback (Weng *et al.* 2009). One way to reduce the costs is the use of waste materials, especially from agro-industrial sources, due their low cost and high availability (Ali 2012; Weber *et al.* 2014; Wang *et al.* 2016; Silva *et al.* 2016). Rice husk fit well in the concept of low-cost adsorbents, due its high annual generation and presence of organic compounds (Soltani *et al.* 2015). However, its low surface area and non-functionalized/accessible sites prejudice its efficiency (Thakur 2014). With

the objective of improving the adsorbent performance, alternative surface modifications can be implemented, increasing the surface area and providing new accessible sites.

For this purpose, some modifications were performed on the rice husk surface, including acid or alkaline treatments. The treatment with NaOH, for example, can attack the cellulose chains, generating new accessible sites (Soltani *et al.* 2015). Other modifications such as ultrasound assisted (UA) and supercritical CO<sub>2</sub> (SCO<sub>2</sub>) have been used as viable methods for surface modification of organic materials. It was concluded that these technologies can provide new adsorption sites and an additional porosity (Dotto *et al.* 2015b).

In this work, rice husk was modified with NaOH, UA and SCO<sub>2</sub> treatments, in order to improve its adsorption potential regarding the methylene blue (MB) dye. All adsorbents (raw and treated rice husks) were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). For all materials, experimental equilibrium curves were constructed at different temperatures (from 298 to 328 K). Langmuir and Hill models were used to interpret

the equilibrium curves. Also, thermodynamic parameters, such as standard Gibbs free energy change ( $\Delta G^0$ ), standard enthalpy change ( $\Delta H^0$ ) and standard entropy change ( $\Delta S^0$ ) were estimated.

## MATERIALS AND METHODS

### Obtainment and treatments of rice husk

Raw rice husk was obtained from a local processing industry (Santa Maria RS, Brazil). First, rice husk was washed several times with distilled water, for cleaning and removing any undesirable particles. After, it was dried at 313 K for 24 h and stored for further use. Rice husk was used without milling, with particle size of 5 mm.

**Sodium hydroxide treatment:** a sodium hydroxide solution (700 mL and 2.5 mol L<sup>-1</sup>) was poured into a beaker with 20 g of raw rice husk. The suspension was agitated for 2 h and the rice husk was removed. The NaOH treated rice husk was washed with distilled water until neutral pH was achieved, and oven dried for 24 h at 313 K. This adsorbent was named NaOH-rice husk.

**UA treatment:** for the UA treatment, 20 g of raw rice husk were mixed with 700 L of distilled water. Then the mixture was treated by an ultrasonic processor (UP400S, Hielscher, Germany) of 400 W equipped with a titanium sonotrode for 2 h. The treatment was performed with cycle of 1 and amplitude of 90% at 313 K. The ultrasound treated rice husk (UA-rice husk) was dried at 313 K for 24 h and stored for further experiments.

**SCO<sub>2</sub> treatment:** initially, 20 g of rice husk were put in a sealed jacketed stainless steel 304 reactor at 313 K (the temperature was controlled by a thermostat bath). The CO<sub>2</sub> (White Martins, 99.5%) was pumped and pressurized by a high pressure syringe pump (500D, Teledyne Isco, USA). When CO<sub>2</sub> reached 20 MPa, it was fed into the reactor; then rice husk was exposed to the treatment for 2 h. Finally the reactor was depressurized and the supercritical treated rice husk (SCO<sub>2</sub>-rice husk) was collected and stored.

All the abovementioned treatments and their conditions were determined by preliminary tests and literature (Soltani *et al.* 2015; Dotto *et al.* 2015a, 2015b). The treatments were performed in replicate ( $n = 3$ ).

### Characterization techniques

Raw rice husk and the respective modifications (NaOH-rice husk, UA-rice husk and SCO<sub>2</sub>-rice husk) were characterized

by FT-IR, XRD, SEM and EDS. FT-IR (Shimadzu, Prestige 21, Japan) was carried out in the range of 500–3,500 cm<sup>-1</sup> to identify the functional groups and the changes caused by the treatments (Silverstein *et al.* 2007). XRD (Rigaku, Miniflex 300, Japan) was performed to verify the possible alterations in the amorphous/crystalline structure of the samples (Waseda *et al.* 2011). SEM and EDS were performed (Tescan, Vega3 SB, Czech Republic) to visualize the surface and composition of the samples (Goldstein *et al.* 2003).

### Adsorption assays

Methylene blue (color index 52015, molar weight of 319.8 g mol<sup>-1</sup>,  $\lambda_{\max} = 664$  nm, solubility of 43.6 g L<sup>-1</sup> at 25 °C) was purchased from Vetec, Brazil. All other reagents utilized were of analytical grade, purchased from Sigma-Aldrich. To ensure the experimental accuracy, reproducibility and reliability of the collected data, the adsorption experiments were performed in triplicate; blanks were run in parallel and all dye solutions were stored in glass flasks, which were cleaned by soaking in HNO<sub>3</sub> (1.5 mol L<sup>-1</sup>) for 24 h.

The equilibrium experiments were carried out in a thermostated agitator (Marconi, Ma 093 Brazil) at 298, 308, 318 and 328 K. Each adsorbent (5.0 g L<sup>-1</sup>) was put in contact with MB solutions (initial concentration ranging from 10 to 100 mg L<sup>-1</sup> and pH of 11.0), which were agitated at 150 rpm until equilibrium (all the experiments attained equilibrium within 6 hours). The pH value was selected on the basis of preliminary tests varying the pH from 1 to 12. All experimental conditions were determined by previous experiments. The remaining MB concentration in liquid phase was determined using a spectrophotometer (Shimadzu, UV mini 1240, Japan). The equilibrium adsorption capacity ( $q_e$ ) was determined by:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where  $C_0$  is the initial MB concentration in liquid phase (mg L<sup>-1</sup>),  $C_e$  is the equilibrium MB concentration in liquid phase (mg L<sup>-1</sup>),  $m$  is the amount of adsorbent (g) and  $V$  is the volume of solution (L).

### Langmuir model

The Langmuir model considers that the adsorption occurs in a monolayer, where the binding sites have equal affinity and

energy (Langmuir 1918):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where  $q_m$  is the maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium MB concentration in liquid phase ( $\text{mg L}^{-1}$ ) and  $K_L$  is the Langmuir constant ( $\text{L mg}^{-1}$ ).

### Hill model

The Hill model is a physical statistical approach developed by Ben Lamine research group. It is known that the Langmuir model assumes that a pore of the adsorbent accepts one molecule. In contrast, the Hill model represents the general case and assumes that a pore contains  $n$  molecules, where  $n$  is an adjustable parameter variable as a function of temperature. It is important to know approximately the number of molecules per site or per pore. This information represents one of the advantages of the Hill model. Returning now to the Langmuir model, if this model assumes one molecule per site or per pore, it is necessary that the molecule interacts with an inclined position on the adsorbent surface. The Hill model describes in general two anchorage types (parallel and non-parallel) based on the values of the number of molecules per site. The second advantage of the Hill model is that it takes into consideration that a variable number  $c$  of molecules per unit volume are adsorbed onto  $N_M$  receptor sites located on a unit mass of adsorbent (Khalfaoui et al. 2003):

$$N_a = \frac{nN_M}{1 + (C_{1/2}/c)^n} \quad (3)$$

where  $n$  is the number of adsorbed molecule(s) per site,  $N_M$  is the receptor sites density,  $N_a$  is the number of adsorbed molecule(s),  $c$  is the MB equilibrium concentration ( $\text{mg L}^{-1}$ ) and  $C_{1/2}$  is the concentration at half saturation. To calculate the adsorbed quantity at saturation, it is necessary to calculate the model limit if the concentration tends to infinity:

$$\lim_{c \rightarrow \infty} \left( \frac{nN_M}{1 + (C_{1/2}/c)^n} \right) = nN_M \quad (4)$$

The stoichiometric coefficient  $n$  is related to the anchorage number  $n'$ :

$$n' = \frac{1}{n} \quad (5)$$

The  $n'$  parameter describes how the molecule tends to be positioned in relation to the adsorbent surface. If  $n' > 1$ , the molecules are in parallel with the surface and, if  $n' < 1$ , the molecules are inclined to the surface. For a solid-liquid adsorption system the concentration at half saturation can be related to the molar adsorption energy:

$$C_{1/2} = c_s e^{-\Delta E^a/RT} \quad (6)$$

where  $c_s$  is the solubility of the adsorbate,  $\Delta E^a$  ( $\text{kJ mol}^{-1}$ ) is molar adsorption energy,  $T$  is the temperature (K), and  $R$  is the universal gas constant ( $8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ ).

### Thermodynamic parameters

The thermodynamic parameters ( $\Delta S^0$ ,  $\Delta H^0$ ,  $\Delta G^0$ ) were estimated according to the Gibbs and Van't Hoff equations (Anastopoulos & Kyzas 2016):

$$\Delta G^0 = -RT \ln(\rho K_e) \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

where  $\Delta G^0$  is the standard Gibbs free energy change ( $\text{kJ mol}^{-1}$ ),  $\Delta H^0$  is the standard enthalpy change ( $\text{kJ mol}^{-1}$ ),  $\Delta S^0$  is the standard entropy change ( $\text{kJ mol}^{-1} \text{ K}^{-1}$ ),  $K_e$  is the equilibrium constant ( $\text{L g}^{-1}$ ),  $T$  is the temperature (K),  $R$  is the universal gas constant ( $8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ ) and  $\rho$  is the solution density ( $\text{g L}^{-1}$ ).

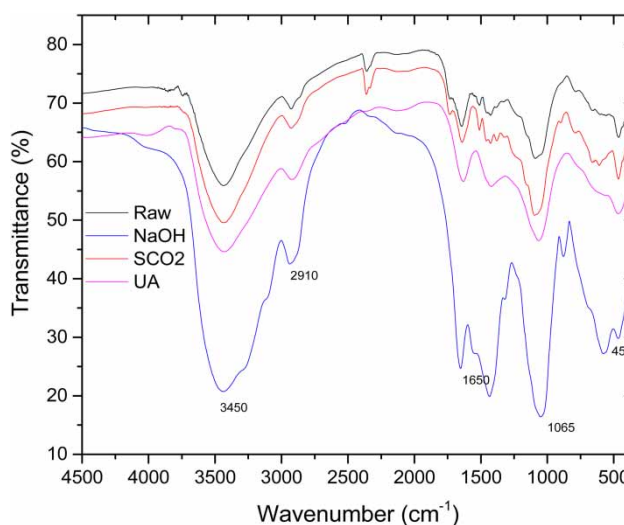


Figure 1 | FT-IR spectrum of the raw rice husk (—), NaOH-rice husk (—), UA-rice husk (—) and SCO<sub>2</sub>-rice husk (—).

## Parameters estimation

The equilibrium and thermodynamic parameters were determined by the fit of the models with the experimental data through nonlinear regression. The estimation was based on the minimization of the least squares function using the quasi-Newton method. The calculations were performed using the Statistic 9.1 software (Statsoft, USA). The fit quality was evaluated by the coefficient of determination ( $R^2$ ) and average relative error ( $ARE$ ) (Dotto *et al.* 2013):

$$R^2 = \left( \frac{\sum_i^n (q_{i,\text{exp}} - \bar{q}_{i,\text{exp}})^2 - \sum_i^n (q_{i,\text{exp}} - q_{i,\text{model}})^2}{\sum_i^n (q_{i,\text{exp}} - \bar{q}_{i,\text{exp}})^2} \right) \quad (9)$$

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{i,\text{model}} - q_{i,\text{exp}}}{q_{i,\text{exp}}} \right| \quad (10)$$

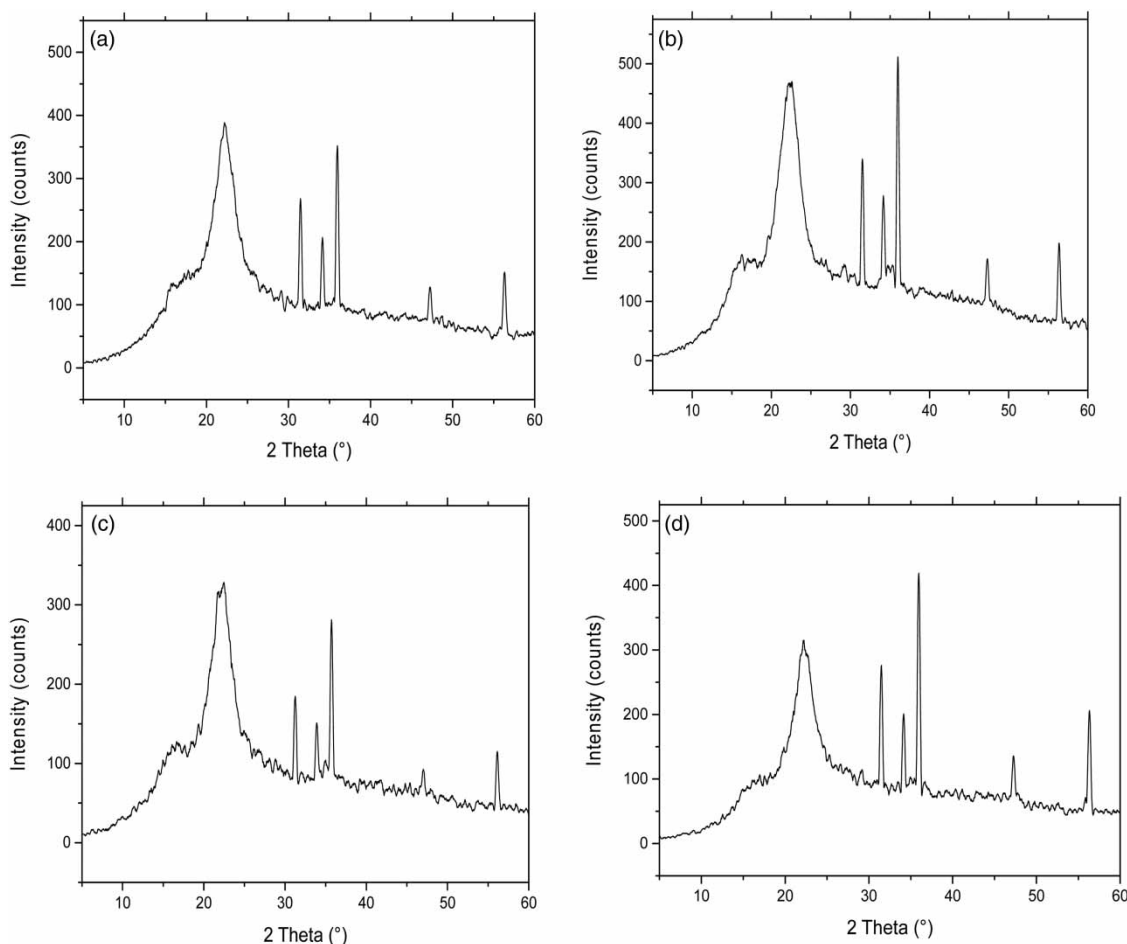
where  $q_{i,\text{model}}$  is each value of  $q$  predicted by the fitted model,  $q_{i,\text{exp}}$  is each value of  $q$  measured experimentally,  $\bar{q}_{i,\text{exp}}$  is the average of  $q$  experimentally measured and  $n$  is the number of experimental points.

## RESULTS AND DISCUSSION

### Characteristics of raw and modified rice husks

The FT-IR spectra of raw rice husk —, NaOH-rice husk —, UA-rice husk — and  $\text{SCO}_2$ -rice husk — are shown in Figure 1.

For all samples, the major intense bands were found at  $3,450 \text{ cm}^{-1}$  (OH stretching vibrations),  $2,910 \text{ cm}^{-1}$  (C-H alkane stretch),  $1,650 \text{ cm}^{-1}$  (C=O),  $1,429 \text{ cm}^{-1}$  (C-C, C-O ring),  $1,065 \text{ cm}^{-1}$  (Si-O-Si asymmetric stretch),  $450 \text{ cm}^{-1}$  (Si-O-Si bend). These groups are common for lignocellulosic



**Figure 2** | XRD patterns of the raw rice husk (a), NaOH-rice husk (b), UA-rice husk (c) and  $\text{SCO}_2$ -rice husk (d).

materials, which contain cellulose, hemicellulose and lignin (Thakur 2014). In particular the NaOH-rice husk has demonstrated a lower intensity in the  $1,650\text{ cm}^{-1}$  region. These groups can be potential sites for dye adsorption. For the other samples, the spectra were similar. This indicates that only physical modifications occurred in the rice husk.

The XRD patterns of raw rice husk, NaOH-rice husk, UA-rice husk and  $\text{SCO}_2$ -rice husk are shown in Figure 2. All the samples exhibit the same diffraction planes. Only the intensity was affected. This behavior indicates that the surface treatment changed the rice husk crystallinity. The likely hypothesis is that silica was dragged by pressure in the ultrasound and supercritical treatments, or transferred to the solution when sodium hydroxide was used. This can result in new active sites for MB adsorption.

The SEM images of raw rice husk, NaOH-rice husk, UA-rice husk and  $\text{SCO}_2$ -rice husk are shown in Figure 3. For raw rice husk the lemma and the silicate deposit can be seen (Figure 3(a)), which is common for this material. In Figure 3(b) (NaOH-rice husk), it can be verified that strong ruptures on the lemma appeared. As a consequence, the endocarp structure (tube cells) was exposed. This can be favorable for the adsorption process, since it allows the diffusion of the MB molecules. For the UA-rice husk (Figure 3(c)), the absence of silicate deposits can be seen. This can be favorable for the adsorption process, since it exposes the organic region to be new interaction sites. The  $\text{SCO}_2$ -rice husk (Figure 3(d)) also presents ruptures on the lemma, but, less intense than NaOH-rice husk.

From the EDS analysis (figure not shown), it was found that the raw rice husk surface is composed mainly of C, O

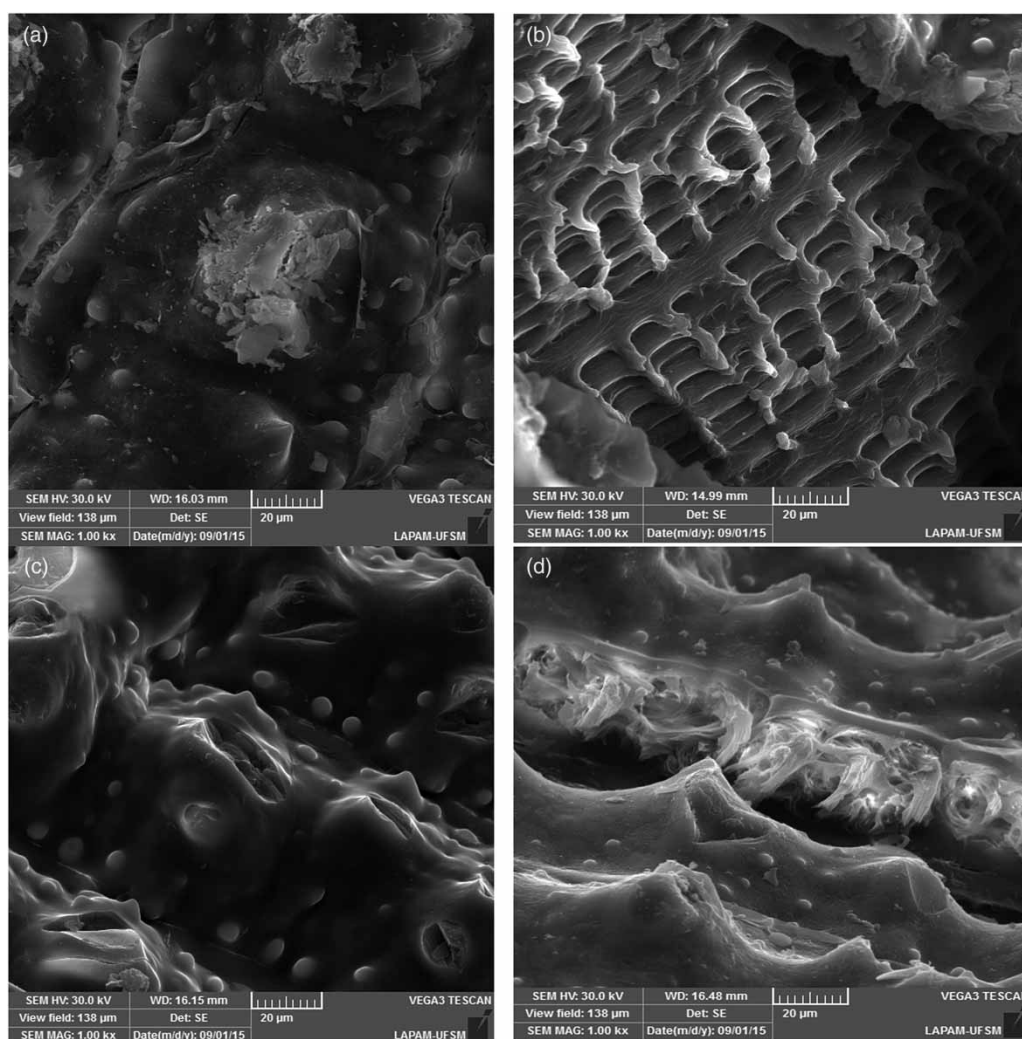
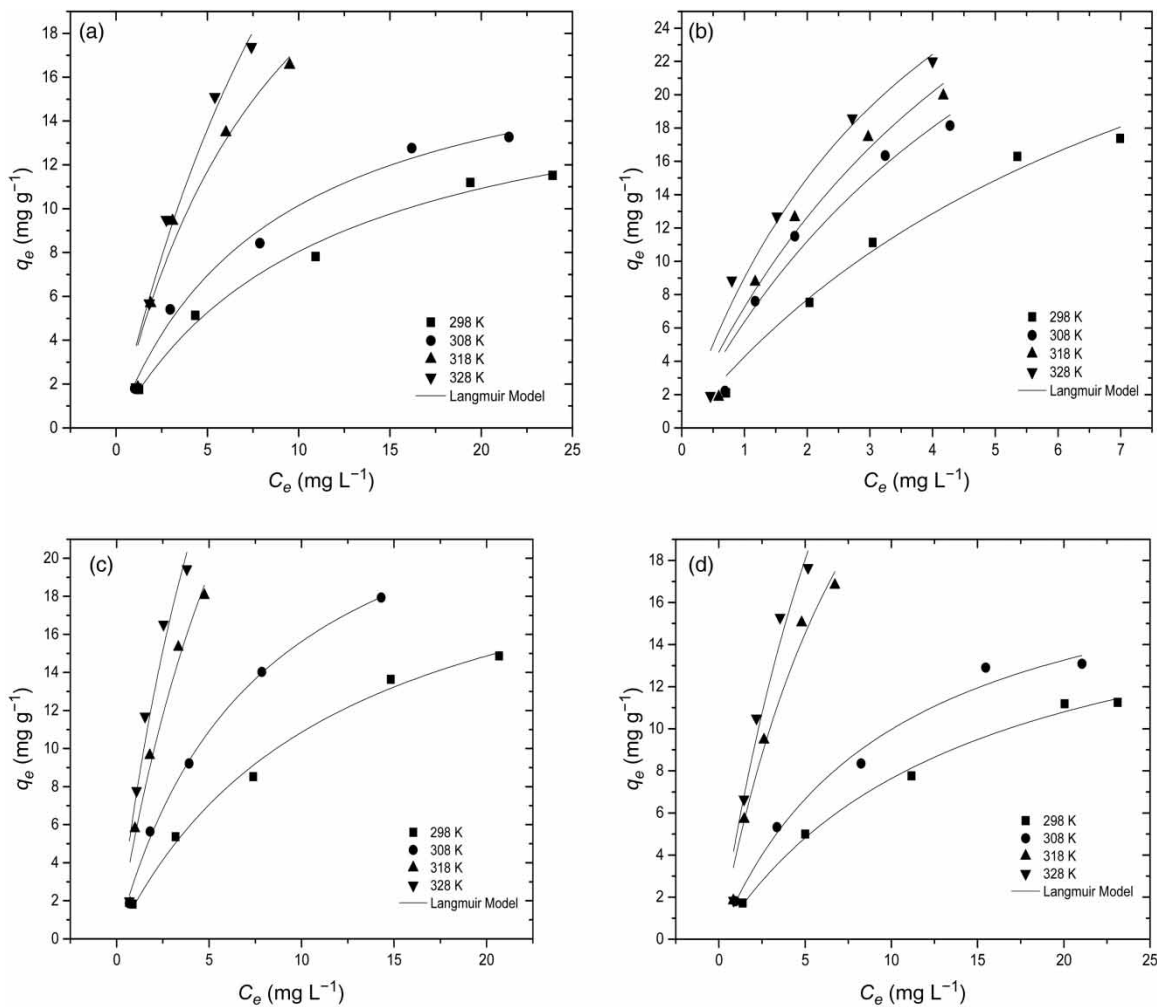


Figure 3 | SEM images of the raw rice husk (a), NaOH-rice husk (b), UA-rice husk (c) and  $\text{SCO}_2$ -rice husk (d).



**Figure 4** | Equilibrium curves for MB adsorption by raw rice husk (a), NaOH-rice husk (b), UA-rice husk (c) and  $\text{SCO}_2$ -rice husk (d) (Langmuir fitted data) (temperatures of 298, 308, 318 and 328 K; initial MB concentration ranging from 10 to 100  $\text{mg L}^{-1}$ ; adsorbent dosage of  $5.0 \text{ g L}^{-1}$ ; pH of 11.0 and 150 rpm until equilibrium).

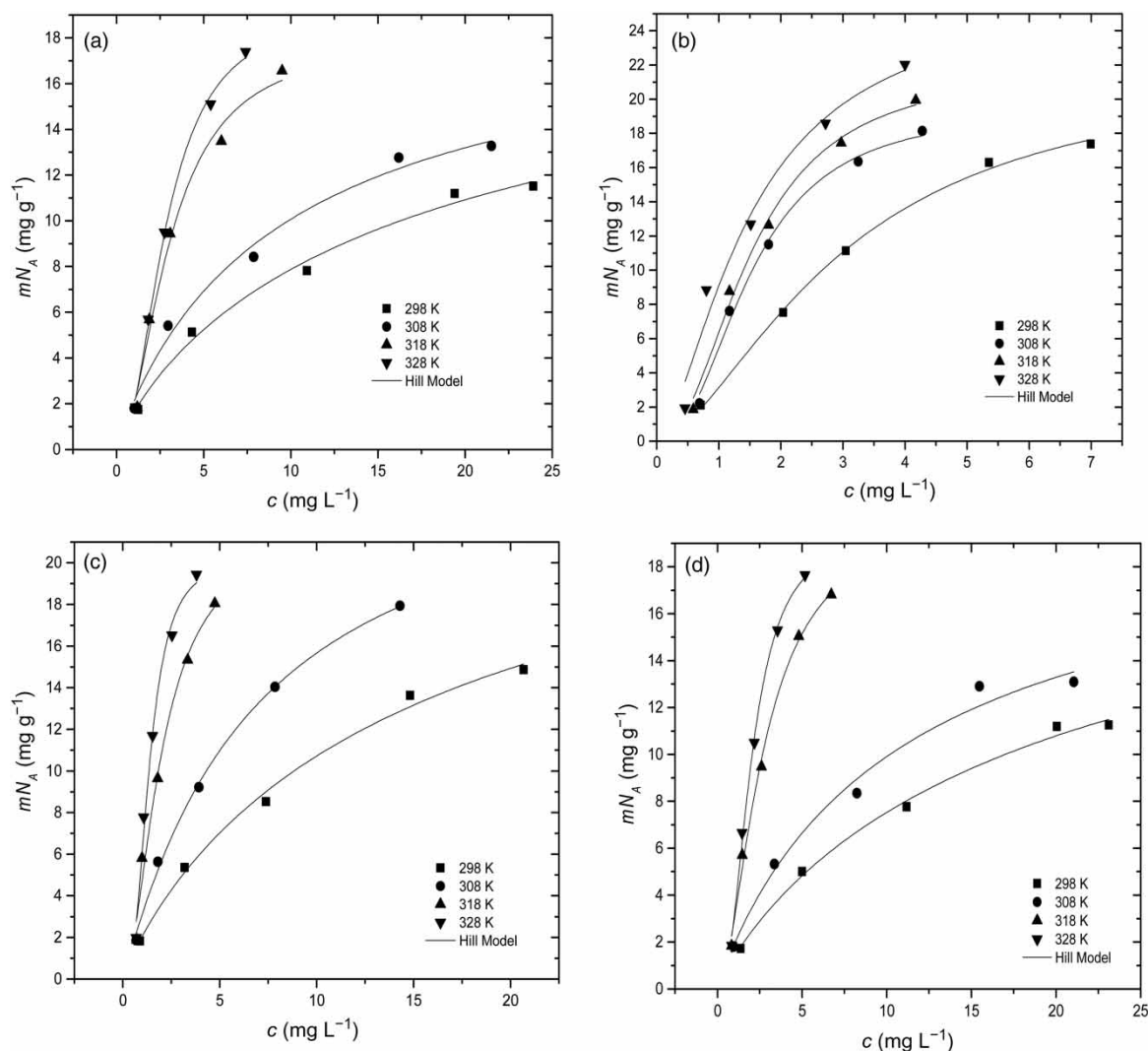
and Si. For the others samples (NaOH-rice husk, UA-rice husk and  $\text{SCO}_2$ -rice husk), Si was not detected on the surface. These results corroborate the XRD and SEM analyses. Therefore, it is possible to affirm that the organic fraction of rice husk surface was exposed by the treatments.

#### Influence of the treatments and temperature on the adsorption isotherms of MB

The equilibrium curves for MB adsorption by the adsorbents are shown in Figure 4 (Langmuir fit) and Figure 5 (Hill fit). All the experiments attained equilibrium within 6 hours. Regarding to the temperature effect, it was found that the temperature increase caused an increase in the adsorption capacity. This influence of temperature can be observed for all surface

modifications. This suggests that the behavior is related to the overall rice husk composition. Also, this effect may be attributed to the increase in the number of active sites, or the increase of the diffusion rate (Chowdhury *et al.* 2011).

Regarding to the effect of surface treatments, it was found that, in general, the adsorption capacity followed the order: NaOH-rice husk > UA-rice husk >  $\text{SCO}_2$ -rice husk > raw rice husk. This shows that all modifications promoted improvements in the rice husk performance as adsorbent. The NaOH-rice husk presented a better adsorption capacity in comparison with the other surface modifications. This can be attributed to the exposure of the endocarp structure (tube cells). This exposure created new adsorption sites and new diffusion paths, which can help the adsorption process (Dotto *et al.* 2015a).



**Figure 5** | Equilibrium curves for MB adsorption by raw rice husk (a), NaOH-rice husk (b), UA-rice husk (c) and  $\text{SCO}_2$ -rice husk (d) (Hill fitted data) (temperatures of 298, 308, 318 and 328 K; initial MB concentration ranging from 10 to 100  $\text{mg L}^{-1}$ ; adsorbent dosage of 5.0  $\text{g L}^{-1}$ ; pH of 11.0 and 150 rpm until equilibrium).

### Interpretation of Langmuir and Hill models

Table 1 shows the Langmuir parameters for the MB adsorption onto raw rice husk, NaOH-rice husk, UA-rice husk and  $\text{SCO}_2$ -rice husk. The Langmuir model presented a satisfactory fit with the experimental data ( $R^2 > 0.95$  and  $ARE < 10\%$ ). It was found that, for all adsorbents, the temperature increase caused an increase in the  $q_m$  values, with the maximum values attained at 328 K. The  $q_m$  values were in the following order: NaOH-rice husk > UA-rice husk >  $\text{SCO}_2$ -rice husk. This behavior indicated that the MB adsorption capacity is favored by the use of NaOH-rice husk at 328 K. In general, the same trend was found for the  $K_L$  parameter. This indicated that the adsorbent-adsorbate affinity is higher at 328 K. Also, the higher affinity was found using

NaOH-rice husk, confirming that this adsorbent is the most adequate for MB.

From the perspective of the statistical physical Hill model ( $R^2 > 0.97$  and  $ARE < 10\%$ ), it is possible to describe and understand the influence of temperature and surface modifications on the MB adsorption. The Hill parameters are presented in Table 2. According to the literature (Khalfaoui *et al.* 2003; Franco *et al.* 2015; Dotto *et al.* 2016), the stoichiometric coefficient  $n$  describes the adsorption reaction and is a parameter which estimates the number of molecules per site during the adsorption process and the adsorbate position on adsorbent surface. This number can be less than, greater than or equal to 1. If this value is less than 1,  $1/n$  represents the anchorage number of one molecule on

**Table 1** | Langmuir parameters for the adsorption of MB onto raw rice husk, NaOH-rice husk, UA-rice husk and SCO<sub>2</sub>-rice husk

Adsorbent	Parameters	T (K)			
		298	308	318	328
Raw rice husk	$q_m$ (mg g <sup>-1</sup> )	17.0 ± 1.5	18.7 ± 1.5	33.5 ± 2.6	52.2 ± 1.3
	$K_L$ (L mg <sup>-1</sup> )	0.089 ± 0.009	0.118 ± 0.004	0.107 ± 0.005	0.069 ± 0.007
	$R^2$	0.987	0.986	0.959	0.956
NaOH-rice husk	$q_m$ (mg g <sup>-1</sup> )	39.2 ± 2.7	46.5 ± 2.4	49.7 ± 0.6	65.0 ± 0.4
	$K_L$ (L mg <sup>-1</sup> )	0.122 ± 0.007	0.158 ± 0.005	0.17 ± 0.001	0.209 ± 0.003
	$R^2$	0.979	0.958	0.959	0.954
UA-rice husk	$q_m$ (mg g <sup>-1</sup> )	23.5 ± 2.0	27.4 ± 1.2	52.6 ± 1.4	58.7 ± 2.1
	$K_L$ (L mg <sup>-1</sup> )	0.085 ± 0.001	0.131 ± 0.012	0.114 ± 0.008	0.138 ± 0.005
	$R^2$	0.979	0.958	0.959	0.954
SCO <sub>2</sub> -rice husk	$q_m$ (mg g <sup>-1</sup> )	18.4 ± 1.4	19.7 ± 2.2	42.0 ± 3.8	56.4 ± 0.6
	$K_L$ (L mg <sup>-1</sup> )	0.07 ± 0.001	0.101 ± 0.002	0.105 ± 0.005	0.093 ± 0.005
	$R^2$	0.979	0.958	0.959	0.954

**Table 2** | Hill parameters for the adsorption of MB onto raw rice husk, NaOH-rice husk, UA-rice husk and SCO<sub>2</sub>-rice husk

Adsorbent	Parameters	T(K)			
		298	308	318	328
Raw rice husk	$C_{1/2}$ (L mg <sup>-1</sup> )	18.3 ± 1.6	9.7 ± 1.8	3.0 ± 0.1	2.8 ± 0.2
	$nN_m$ (mg g <sup>-1</sup> )	21.0 ± 1.4	19.8 ± 6.6	17.9 ± 2.0	19.2 ± 1.2
	$n$	0.85 ± 0.25	0.94 ± 0.27	1.9 ± 0.44	2.15 ± 0.26
	$R^2$	0.983	0.983	0.978	0.994
NaOH-rice husk	$C_{1/2}$ (L mg <sup>-1</sup> )	2.9 ± 0.3	1.5 ± 0.1	1.5 ± 0.1	1.4 ± 0.6
	$nN_m$ (mg g <sup>-1</sup> )	19.4 ± 1.7	20.4 ± 1.3	21.8 ± 1.8	26.2 ± 1.3
	$n$	1.64 ± 0.16	2.31 ± 0.37	2.16 ± 0.39	2.58 ± 0.59
	$R^2$	0.996	0.989	0.987	0.976
UA-rice husk	$C_{1/2}$ (L mg <sup>-1</sup> )	16.5 ± 1.2	6.8 ± 1.9	1.9 ± 0.5	1.3 ± 0.1
	$nN_m$ (mg g <sup>-1</sup> )	27.5 ± 1.3	26.2 ± 1.3	21.5 ± 2.1	20.1 ± 1.4
	$n$	0.89 ± 0.21	1.04 ± 0.11	1.82 ± 0.50	2.72 ± 0.52
	$R^2$	0.989	0.996	0.973	0.983
SCO <sub>2</sub> -rice husk	$C_{1/2}$ (L mg <sup>-1</sup> )	20.6 ± 0.2	11.2 ± 0.9	2.6 ± 0.4	1.9 ± 0.1
	$nN_m$ (mg g <sup>-1</sup> )	21.8 ± 1.9	20.8 ± 1.3	20.2 ± 1.1	19.3 ± 1.0
	$n$	0.89 ± 0.20	0.94 ± 0.33	1.76 ± 0.28	2.37 ± 0.25
	$R^2$	0.990	0.972	0.991	0.995

several different receptor sites, i.e. the molecules adsorb in a parallel position (multi-anchorage) on the adsorbent. If the parameter is greater than to 1, a certain number of molecules are adsorbed on one receptor site. If the number of molecules per site is equal to 1, the molecule interacts by an inclined position (mono-anchorage) with the adsorbent surface. In Table 2, it can be noticed that  $n$  increased with the temperature. The higher  $n$  values were found for NaOH-rice husk. These results indicate that higher temperatures favored the MB aggregation into the adsorption sites. Also, they suggest that the

modification with NaOH was efficient, since the surface of NaOH-rice husk is able to interact with more than one molecule per site.

The concentration at half saturation ( $C_{1/2}$ ) decreased with the temperature increase (Table 2), for all used adsorbents. This shows that at higher temperatures, the MB remaining in the solution is low, when the half saturation is attained. One major observation is that, for the NaOH-rice husk, the  $C_{1/2}$  value is low, even for the lowest temperatures. This shows that, even at low temperatures, the NaOH-rice husk is a good adsorbent. The last Hill parameter is the adsorbed



**Table 3** | Thermodynamic parameters for the MB adsorption onto raw rice husk, NaOH-rice husk, UA-rice husk and SCO<sub>2</sub>-rice husk

Adsorbent	T (K)	$\Delta G^0$ (kJ mol <sup>-1</sup> )	R <sup>2</sup>	$\Delta S^0$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )
Raw rice husk	298	-18.14	0.952	0.14 ± 0.01	24.94 ± 1.73
	308	-19.70			
	318	-21.60			
	328	-22.33			
NaOH-rice husk	298	-20.97	0.950	0.13 ± 0.01	19.76 ± 1.18
	308	-22.77			
	318	-23.87			
	328	-25.20			
UA-rice husk	298	-18.80	0.990	0.18 ± 0.01	37.52 ± 1.53
	308	-20.95			
	318	-22.98			
	328	-24.51			
SCO <sub>2</sub> -rice husk	298	-17.75	0.986	0.19 ± 0.01	39.93 ± 1.36
	308	-19.45			
	318	-22.16			
	328	-23.33			

quantity at saturation ( $nN_M$ ). In general this parameter presented no clear tendency. However, for NaOH-rice husk, the adsorbed quantity at saturation increased with the temperature, corroborating the abovementioned parameters.

### Thermodynamic evaluation

The standard Gibbs free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) changes are shown in Table 3.

For all adsorbents, the  $\Delta G^0$  values were negative, confirming that the adsorption was a spontaneous and favorable operation. Also, the temperature increase provided more-negative  $\Delta G^0$  values, indicating that the adsorption was most favorable at higher temperatures. More-negative  $\Delta G^0$  values were found for NaOH-rice husk, showing that the use of this adsorbent was the most favorable. The  $\Delta H^0$  values were positive, indicating that the adsorption was endothermic in nature. The magnitude of  $\Delta H^0$  is typical of physisorption (Khalfaoui *et al.* 2003; Franco *et al.* 2015).  $T\Delta S^0$  contributed more than  $\Delta H^0$  to provide negative  $\Delta G^0$  values. This shows that the MB adsorption was an entropy-controlled process.

### CONCLUSION

In this work, techniques for surface modification were applied on the rice husk, in order to improve its adsorption potential regarding MB dye. FT-IR, XRD, SEM, and EDS analyses showed that the silica was dragged from the rice husk to the

solution and the organic fraction was exposed, creating new adsorption sites. The treatment with NaOH provided the most pronounced surface modification. Regarding to the MB adsorption, Langmuir and Hill models were adequate to represent the equilibrium data. The MB adsorption was favored by the temperature increase. The maximum adsorption capacities for the MB solutions, estimated from the Langmuir model at 328 K, were in the following order: NaOH rice-husk (65.0 mg g<sup>-1</sup>) > UA-rice husk (58.7 mg g<sup>-1</sup>) > SCO<sub>2</sub>-rice husk (56.4 mg g<sup>-1</sup>) > raw rice husk (52.2 mg g<sup>-1</sup>). The thermodynamic parameters demonstrated that the MB adsorption was a spontaneous, favorable, endothermic and entropy-controlled process. The magnitude of  $\Delta H^0$  is in agreement with physisorption. Based on these results, it is possible to affirm that mainly the NaOH treatment is an alternative to improve the potential of rice husk as adsorbent.

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