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Methylene blue adsorption onto modified lignin from sugar cane bagasse

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Abstract: The adsorption kinetics and equilibrium of methylene blue (MB) onto reticulated formic lignin (RFL) from sugar cane bagasse was studied. The adsorption process is *pH*, temperature and ionic strength (μ) dependent and obeys the Langmuir model. Conditions for higher adsorption rate and capacity were determined. The faster adsorption (12 hours) and higher adsorption capacity (34.20 mg.g⁻¹) were observed at *pH* = 5.8 (acetic acid-sodium acetate aqueous buffer), 50 °C and 0.1 ionic strength. Under temperature (50 °C) control and occasional mechanical stirring it took from 1 to 10 days to reach the equilibrium.

Keywords: methylene blue; lignin; adsorption.

Introduction

Water is polluted as a consequence of the domestic and industrial men activity. This includes varying extents and types of pollutants. It is a complex problem that sometimes is not always considered with the proper seriousness. Many scientists are putting efforts to understand these systems and to propose new methods to overcome this problem. Such methods include precipitation, flocculation, adsorption, and biodegradation processes [1]. In general, different processes must be combined to achieve the desired contaminants removal level.

Colored effluents receive special attention because they are easily detected and on the other hand, the chemical structure of such dyes varies enormously. Certain methods can work very well for the uptake of a specific group of dyes but sometimes they can be inefficient to remove other

different types of dyes. Adsorption methods have received great attention because they are effective and their application processes are relatively simple. Activated carbon is the most widely used adsorbent for color removal. It has the ability to adsorb large amounts of various types of dye. Due to its relatively high cost, other lower cost materials have been also investigated as adsorbents for dye removal from aqueous media. Some of these materials are: chitin [2], Fuller's earth and fired clay [3], cellulose based polymers [4], peat [5] and wood [6]. Lignin-based materials were also investigated: post-vanillin lignin for cationic and anionic dyes [7, 8] and hydrolytic lignin modified with cationic surfactant for anionic dye adsorption [9]. The results have shown that through lignin chemical modification and/or by just varying the adsorption conditions, the use of lignin as an adsorbent for dye removal from aqueous media can be significantly

enhanced. In some cases it showed a higher adsorption capacity than activated carbon.

In this work is presented the use of reticulated formic lignin as an adsorbent material for methylene blue removal from aqueous media. Lignin was obtained from sugar cane bagasse, an abundant agro-industrial residue in various regions of Brazil. The adsorption equilibrium and kinetic studies were carried out by varying the temperature, *pH* and ionic strength (μ).

Experimental details

Formic lignin from sugar cane bagasse

Sugar cane bagasse was obtained from a local Sugar and Alcohol Industry (USACIGA). The sample was firstly washed with excess of deionized water, dried at room temperature (25 °C), and then it was grounded in a knife mill. The fraction up to 100 mesh of particle size was isolated for further studies. From the sugar cane bagasse powder (200 g), extractives were removed by using a soxhlet apparatus, in three stages using the following solvents (0.5 L): n-hexane (Mallinckrodt – AR), ethanol (Synth) and deionized water (this sequence), until the liquid remained uncolored in each solvent. Lignin was then extracted under reflux (~100°C) during three hours in the presence of formic acid (80%) (J. T. Baker). Aqueous 1 % (w/v) hydrochloric acid (HCl) (Merk) used as catalyst and the liquid-to-solid ratio was 115 mL to 10 g. The liquor obtained was concentrated in a rotary evaporator until a viscous liquid was obtained. The lignin precipitation was obtained by adding deionized water (drop by drop) to the viscous liquid, where hemicelluloses remains dissolved. The lignin was isolated and it was then dissolved in hot formic acid followed by precipitation by adding water. The resulting lignin precipitate was filtered and the solid portion collected. The filtrate (solid portion, lignin) was then oven dried at 60°C during 60 minutes. The formic lignin (FL) obtained was grounded by using a ceramic mortar and pestle and it was then stored in dark glass flasks. In order to obtain an insoluble lignin sample, FL was reticulated as described below.

Formic lignin reticulation

As reticulating agent acidic formaldehyde (Synth) solution was used. 10 mL of 40% formaldehyde and 5 mL of 37 % HCl aqueous solution were added to 0.4 g of FL and the resulting mixture was maintained under reflux (~100 °C) during 30 min. The dispersion was then filtered and the resulting solid material was washed and vacuum (mechanical) dried at 60°C until the sample presents a constant weight.

Solubility of lignin samples

Aqueous sodium acetate/acetic acid buffer solutions (*pH* = 4.5 and 5.8), aqueous HCl solution (*pH* = 2), and aqueous sodium hydroxide (*pH* = 8.0) were prepared.

50 mg of lignin sample was added to a round bottom volumetric flask containing 25 mL of aqueous sodium acetate/acetic acid *pH* = 4.5 buffer solution. The solubility of lignin sample in buffer system was monitored by measuring absorption increments at 280 nm (HITACHI U-2000 spectrophotometer). The exact same procedure as described above was repeated except that the following aqueous systems were used: (1) aqueous sodium acetate/acetic acid *pH* = 5.8 buffer solution; (2) *pH* = 2.0 HCl aqueous solution; (3) *pH* = 8.0 sodium hydroxide (NaOH) aqueous solution. The lignin samples used were FL and RFL, respectively.

Adsorption experiments

Methylene blue (MB) aqueous solution (10.0 mg.mL⁻¹) was prepared by using deionized water and a buffer aqueous solutions (*pH* = 4.5 and 5.8). 50 mg of RFL was added to a round bottom volumetric flask containing 25 mL of MB aqueous solution and it was then left inside a thermostatic bath during 0.5 to 10 days with occasional mechanical stirring. The resulting dispersions were then centrifuged and the MB concentration of the supernatant solution was determined by absorption measurements at 662 nm (HITACHI U-2000 spectrophotometer). The amount of MB adsorbed was calculated from the difference between the MB concentration in the solutions before and after the adsorption studies.

For adsorption equilibrium studies, the RFL-MB contact time used was 10 days, at various temperatures (30, 40, 50 °C).

The ionic strength (μ) controlled experiments were carried out by adding sodium chloride (NaCl) to deionized water to attain ionic concentration of 0.5 and 1.0. The exact amount of NaCl added prepare pH and μ controlled aqueous solutions was calculated using the Henderson-Hasselbach modified equation [10]. All experiments of adsorption were performed in duplicate.

Results and discussion

The solubility of the FL and RFL samples in aqueous solutions was quantified by measuring the UV absorption intensity at 280 nm. It was observed that RFL presented the lowest solubility in all studied systems, i.e. aqueous buffer solution ($pH = 4.5$ and 5.8 , maximum of absorption intensity = 0.06 a.u.) and HCl and NaOH aqueous solutions ($pH = 2.0$ and 8.0 , maximum of absorption intensity = 0.11 a.u.). The FL presented relatively high solubility in all systems studied, where the maximum of absorption intensity at 280 nm was higher than 1.6 a.u.. Therefore, RFL was used for the MB adsorption studies.

Figure 1 shows the dye concentration decay for MB initial concentration of 10.0 mg.mL^{-1} in the presence of RFL at 30°C . The rate of MB uptake from buffered aqueous solutions at $pH = 5.8$ and 4.5 , respectively, is much faster than from the unbuffered aqueous solution at $pH = 5.9$. When the MB (10.0 mg.mL^{-1}) was kept in the presence of RFL during five days in a $pH = 5.8$ buffered aqueous solution almost all MB

was removed from the liquid phase. These results suggest that the μ plays an important role in the adsorption process. The μ of the buffered aqueous solutions ($pH = 5.8$, $pH = 4.5$) is higher than of the unbuffered aqueous solutions ($pH = 5.9$).

In order to analyze the temperature influence in this MB adsorption process, adsorption experiments were carried out in the three different aqueous solutions (buffered aqueous solutions $pH = 5.8$, $pH = 4.5$ and unbuffered aqueous solutions $pH = 5.9$). The temperatures studied were: 40 , 50 and 60°C . The results are summarized in Figs. 2-4. In two different systems, i.e. unbuffered ($pH = 5.9$) and buffered ($pH=4.5$), the MB adsorption presented a maximum in the temperature range of $30 - 60^\circ\text{C}$, namely at 40°C and 50°C , respectively. In the $pH = 5.8$ buffered aqueous solution, MB is completely removed from the liquid phase at 30°C and at 50°C . At 60°C some of the adsorbed MB is desorbed from the RFL surface. The minimum time interval required to reach the adsorption equilibrium, with complete dye removal, was approximately 12 hours (at $pH = 5.8$ and 50°C). With the unbuffered aqueous solution, the complete dye removal was not obtained and the minimum time interval required to reach the adsorption equilibrium was approximately 2 days (at $pH = 5.8$ and 50°C).

The three step model proposed by McKay and McConvey [11] for basic and acidic dyes adsorption on wood was used to analyze the adsorption data from this work. This model calculates the change in adsorbate concentration (C_t) as a function of the time of adsorption (t) by the equation described below:

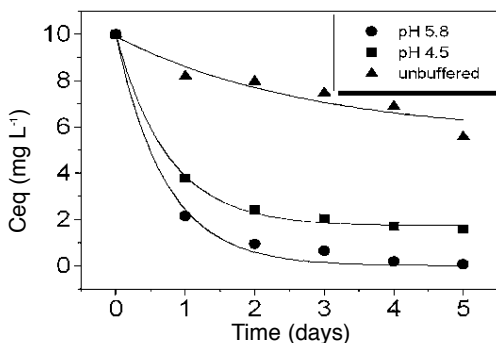


Figure 1. MB uptake by RFL in different aqueous media at 30°C .

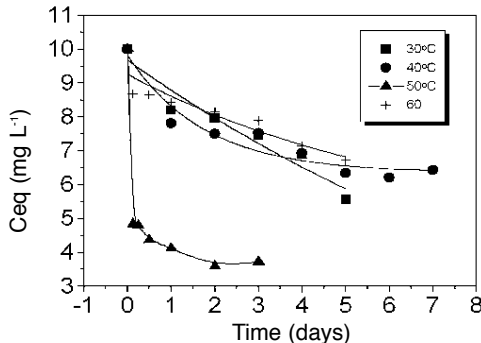


Figure 2. Temperature influence in MB adsorption onto RFL from unbuffered solution at $pH = 5.9$.

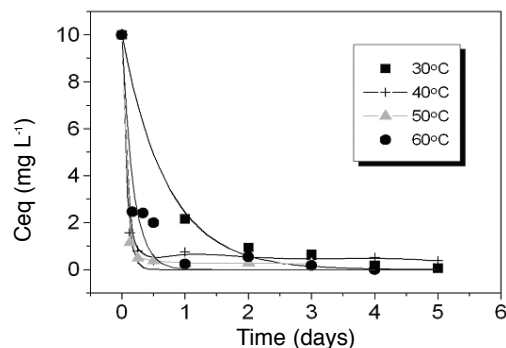


Figure 3. Temperature influence in MB adsorption onto RFL from buffered solution at $pH = 5.8$.

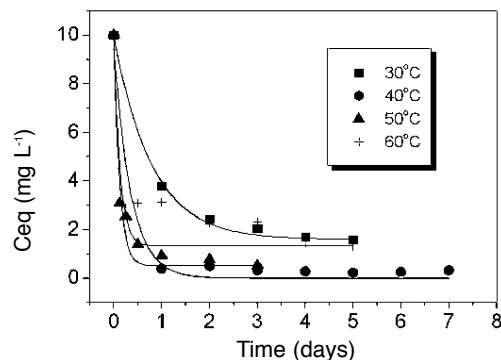


Figure 4. Temperature influence in MB adsorption onto RFL from buffered solution at $pH = 4.5$.

$$\frac{dC_t}{dt} = \beta S(C_t - C_s) \quad \text{and} \quad C_t = C_0 \quad \text{at} \quad t = 0$$

where C_s is the adsorbate concentration in the liquid phase near the outer surface of the adsorbent particle ($\text{mg} \cdot \text{dm}^{-3}$), β is the external mass transfer coefficient ($\text{cm} \cdot \text{s}^{-1}$), S is the outer surface of the adsorbent particles per volume unit of particle free slurry (cm^{-1}).

The βS product was determined from the slope at $t \rightarrow 0$ of the C_t/C_0 versus t plot. The results are presented in Table 1. A high increment in βS is observed when the temperature is increased from 30 to 40°C in the buffered aqueous solutions, and from 40 to 50°C in the unbuffered aqueous solution. On the other hand, a decrease in βS is observed when the temperature increases from 50 to 60°C in the three systems described above. The βS values calculated from experiments carried out at the same

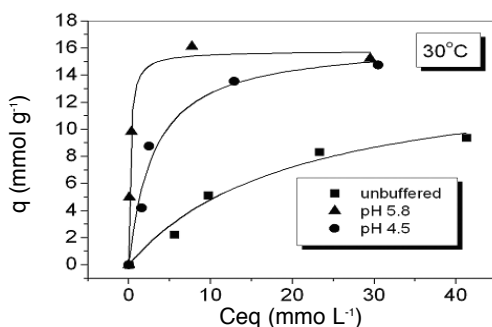
temperature for the three systems describe above increases as follows: unbuffered solution ($pH = 5.9$) < buffered solution ($pH = 4.5$) < buffered solution ($pH = 5.8$). It can be observed that the adsorption kinetic depends on all three parameters, temperature, pH and μ . The effect of the temperature on the MB adsorption behavior on RFL is probably related to an increase of the adsorption rate with the increase of the temperature up to a limit value (50 °C). This increase in the MB adsorption rate is due to the increase of the MB diffusion coefficient. At relatively high temperatures, i.e. 60 °C, the desorption process is favored and thus the amount of adsorbed MB decreases. The effect of the pH on the MB adsorption process may be related to the increase of the ionization degree of the carboxylic groups present in the lignin structure when the pH is increased. This increase in the ionization degree of the carboxylic groups might enhance the interaction process between the adsorbate (MB), a cationic dye and the adsorbent (RFL), which results in a driving force for adsorbate diffusion in the region near the surface of the lignin particles. The μ influence is evident when data from buffered and unbuffered aqueous solutions with $pH = 5.8$ and 5.9, respectively, are compared. βS values calculated from $pH = 5.8$ buffered aqueous solutions are much higher than βS values calculated from $pH = 5.9$ unbuffered aqueous solution. Therefore, it indicates that the μ of the buffer system play an important role in the adsorption process.

Adsorption equilibrium experiments were also done. A MB adsorption time of 10 days was used. The influence of the aqueous medium, i.e. pH and μ , and temperature was also analyzed. The Langmuir model fits well to all isotherms obtained in this study, as it can be seen from in Fig. 5. Figure 5 shows an increase on the adsorbed adsorbate concentration (q) with the increase of the adsorbate concentration in the liquid phase at the equilibrium (C_{eq}) up to a C_{eq} limit value, after which no further change in q values is observed. The C_{eq} limit value is equal to 10 mmol L^{-1} at $pH = 5.8$ (buffer system). In other hand, the unbuffered system ($pH = 5.9$) did not reach a C_{eq} limit value. The Langmuir isotherm can be written as described below:

$$q = \frac{q_m K_L C_{eq}}{1 + K_L C_{eq}}$$

Table 1. βS data for the adsorption of MB on RFL obtained from sugar cane bagasse.

T °C	βS (day ⁻¹)		
	pH=5.9	pH=5.8	pH=4.5
	Unbuffered	Buffered	Buffered
30	0.18	0.78	0.62
40	0.22	4.54	4.78
50	4.12	7.08	5.54
60	1.06	6.75	4.93

**Figure 5.** Adsorption isotherms of MB on RFL in the presence of three different aqueous solutions, as indicated in the figure. Solid lines are theoretical Langmuir isotherms and symbols are experimental data.

where C_{eq} is the adsorbate concentration in the liquid phase at equilibrium, q is the adsorbed adsorbate concentration at equilibrium, q_m is the adsorbent capacity, K_L is a measure of the adsorption intensity (Langmuir constant).

The q_m and K_L data for all adsorption equilibrium experiments were obtained from the fit of the experimental data to the Langmuir equation. These results are shown in Tables 2 and 3.

The data from Tables 2 and 3 shows that the adsorption rate behavior do not fit to the adsorption capacity behavior. Data for unbuffered aqueous solution at 30 °C are the most particular ones, where the slower process results to an adsorption capacity similar to those obtained from buffered aqueous medium at the same temperature. At the two other temperatures (40 and 50 °C) the adsorption capacity of the RFL in buffered solution is more than three times higher than the corresponding adsorption capacity of the unbuffered aqueous solution. On the other hand, for the unbuffered aqueous solution the higher adsorption capacity occurs at the lower temperature (30 °C), and for the buffered aqueous solutions the higher adsorption capacity occurs at the higher temperature (50 °C). There is no definite tendency of K_L data when the temperature is changed but at a constant temperature it increases in the following order: unbuffered aqueous solution ($pH =$

Table 2. Effect of the adsorption system conditions (pH, μ , temperature) on the Langmuir parameters for the adsorption of MB onto RFL.

T °C	Unbuffered, pH=5.9		Buffered, pH=5.8		Buffered, pH=4.5	
	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)
30	14.57	0.049	15.72	5.70	16.50	0.33
40	4.11	0.22	20.17	1.43	14.95	0.51
50	5.64	0.35	34.20	0.71	20.06	0.51

Table 3. Adsorption capacity according to Langmuir model, for MB adsorption onto RFL, in relation to pH, temperature and μ .

T °C	q_m (mg g ⁻¹)					
	pH=4.5			pH=5.8		
	$\mu=0.1$	$\mu=0.5$	$\mu=1.0$	$\mu=0.1$	$\mu=0.5$	$\mu=1.0$
30	16.50	6.21	3.55	15.72	6.82	3.96
50	20.06	17.62	21.82	34.20	31.55	31.71

5.9) < buffered aqueous solution ($pH = 4.5$) < buffered aqueous solution ($pH = 5.8$).

In Table 3 it can be observed that, at 30°C, the 0.1 μ gives the higher adsorption capacity. At 50°C this parameter has a little effect on the adsorption capacity, which might indicate that in this condition the temperature effect is more important. Comparing the results from unbuffered aqueous solution ($pH = 5.9$) presented in Table 2 ($q_m = 5.64 \text{ mg.g}^{-1}$ at 50°C) with the results from buffered aqueous solution ($pH = 5.8$) presented in Table 3 ($q_m = 34.20 \text{ mg.g}^{-1}$ at 50°C) it can be concluded that q_m reach's a maximum at an μ of approximately 0.1. The effect of μ lower than 0.1 in buffered aqueous solution could not be analyzed due to acetic acid/sodium acetate minimum concentrations that are required to prepare the buffer systems.

The Scatchard equation that is described below

$$\frac{\theta}{C_{eq}} = K_L(1 - \theta) \quad \text{where} \quad \theta = \frac{q}{q_m}$$

is often used to study binding to macromolecules [12]. If the adsorption model considered is valid, a plot of q/C_{eq} versus q will be linear, the intercept is $K_L q_m$, and the slope is equal to $-K_L$. When the Scatchard plot does not give a unique straight line, this indicates that the binding sites are not identical or are not independent. Figure 6 shows the Scatchard plots for the MB adsorption onto RFL at 30°C. Similar plots were obtained at 40°C and

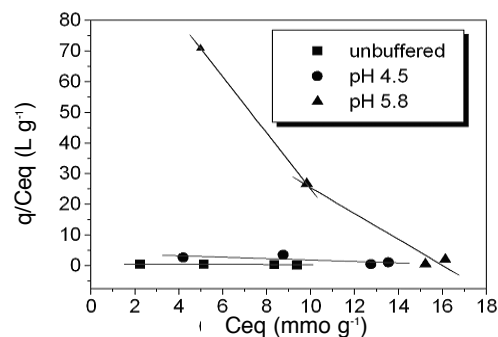


Figure 6. Scatchard plots for the adsorption equilibrium of MB onto RFL at 30°C.

50°C. Comparing the results from Fig. 6 with the results from Fig. 5, it can be seen that the adsorption data obtained at $pH = 5.8$, which shows a deviation from the linearity in Fig. 6, corresponds to the isotherm that has achieved the saturation. This behavior is related to the fact that, at higher θ , interactions between binding sites become more likely.

The Scatchard's plots for the adsorption systems under study in the conditions mentioned in Table 2 were analyzed. Table 4 shows the Scatchard parameters, K_L and q_m . They coincide with the corresponding Langmuir parameters only in the cases in which two straight lines are obtained, when they are computed from the lower one. In the other cases the Langmuir parameters are always higher than the corresponding Scatchard parameters, indicating

Table 4. Scatchard's parameters for the adsorption of MB onto LFB.

	Temperature (°C)	K_L	Q_m
Unbuffered, pH 5.9	30	0.02	21.96
Buffered, pH 4.5	30	0.23	18.68
Buffered, pH 5.8 (upper)	30	11.03	12.23
(lower)		4.76	15.43
Unbuffered, pH 5.9	40	0.04	8.80
Buffered, pH 4.5	40	1.48	13.09
Buffered, pH 5.8 (upper)	40	78.6	9.71
(lower)		1.48	20.01
Unbuffered, pH 5.9	50	0.35	5.71
Buffered, pH 4.5	50	0.59	19.54
Buffered, pH 5.8 (upper)	50	0.64	27.94
(lower)		0.75	34.12

Table 5. Factors and levels of a factorial design 2³ for the adsorption of MB onto RFL.

Symbol – Variable	Data (level)	Data (level)
A: μ	0.5 (-)	1.0 (+)
B: pH	4.5 (-)	5.8 (+)
C: Temperature (°C)	30 (-)	50 (+)

Table 6. Results of the factorial design for the adsorption of MB onto LFR.

Experiment	A	B	C	q_m (mg g ⁻¹)
1	-	-	-	6.21
2	+	-	-	3.55
3	-	+	-	6.82
4	+	+	-	3.96
5	-	-	+	17.62
6	+	-	+	21.82
7	-	+	+	31.55
8	+	+	+	31.71

Variable	Answer
I	14.75
A	-0.50
B	6.00
AB	-1.00
C	20.00
AC	2.50
BC	6.00
ABC	-1.00

that in the first case the final portion of the isotherm is more important and the Scatchard treatment is more sensible to the initial portion of that curve. The non linear Scatchard plots cannot be attributed to higher adsorption capacity or adsorption process rate as can be seen comparing with data in Tables 1 and 2. There are βS and K_L data of the unbuffered ($pH = 5.9$) and the buffered ($pH = 4.5$) aqueous systems in the same interval as the data of buffered aqueous system ($pH = 5.8$), which show a linear behavior in the Scatchard plot.

To q_m data, a full 2³ factorial design (three factors, each at two levels) was applied. The standard experimental matrix for the factorial design and the results of q_m are shown in Table 5. A statistical analysis was performed on these q_m results, and the main effects and interaction effects for the dif-

ferent variable combinations were calculated. The results (Table 6) show that temperature is the most important factor in the MB adsorption. Increasing the μ (A), the adsorption decreases, even when pH (B) and temperature (C) increases, as showed by the results of interactions AB, AC and ABC.

Conclusions

Formic lignin from sugar cane bagasse can be reticulated through a simple reaction with formaldehyde to obtain a product with low solubility in aqueous media. This material was able to be used as an adsorbent for MB removal from aqueous media. The adsorption process showed pH , temperature and ionic strength dependence and obeyed the

Langmuir model. The general tendencies observed with the adsorption capacity are:

- It decreases when the μ increases in the range of 0.1 to 1.0,
- It increases when the temperature increases in the range of 30 to 50°C,
- It increases when the pH increases in the range from 4.5 to 5.8, in buffered aqueous solutions.
- The faster adsorption and higher capacity were observed at 50°C, $pH = 5.8$ and 0.1 of μ , for which interactions between binding sites were detected through Scatchard analysis.
- μ is a very important variable especially at 30°C in all pH values studied. Increasing I , q_m decreases dramatically at this temperature.
- The q_m values of methylene blue adsorbed onto reticulated lignin from sugar cane bagasse can be described by the equation
- $q_m = 14.75 - 0.5(I) + 6.00(pH) - 1.00(I)(pH) + 20.00(t) + 2.50(I)(t) + 6.00(pH)(t) - 1.00(I)(pH)(t)$

- when the experiments are carried out according to the factorial design described in Table 5.
- The adsorption of MB onto RFL is exothermic process when it is carried out at $pH = 5.8$
- It is possible to prepare adsorbents at low cost from lignin that can adsorb methylene blue, since sugar cane bagasse is relatively cheap material and it can be found in any region of in Brazil.

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N. Consolin Filho, E. C. Venancio, M. F. Barriquello, A. A. W. Hechenleitner, E. A. G. Pineda, Adsorção de azul de metileno em lignina modificada obtida do bagaço de cana de açúcar.

Resumo: Estudou-se neste trabalho, a cinética de adsorção e o equilíbrio de adsorção do azul de metileno (AM) em lignina fórmica reticulada (LFR) obtida do bagaço de cana de açúcar. O processo de adsorção é dependente do pH , temperatura e força iônica (μ) e obedece ao modelo de Langmuir. Algumas condições como a alta capacidade e velocidade de adsorção foram determinadas. Observou-se rápida adsorção (12 horas) e alta capacidade de adsorção (34,20 mg.g⁻¹) em $pH = 5,8$ (tampão acetato de sódio-ácido acético), 50°C e 0,1 de força iônica. Para alcançar o equilíbrio de adsorção, o sistema foi termostatizado com tempos de 1 a 10 dias, com agitação ocasional.

Palavras-chave: azul de metileno; lignina; adsorção.

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