Synthesis of magnetic activated carbon from passion fruit seeds and its application in the adsorption of methylene blue dye

Síntese de carvão ativado magnético de sementes de maracujá e a sua aplicação na adsorção do corante azul de metileno

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ABSTRACT

Brazil is a large producer of passion fruit, approximately 600 thousand tons of this fruit were produced in the year 2019, but about 70% of the mass is considered waste. The waste from this production could be aggregated in the synthesis of activated carbons for the treatment of textile effluents. However, the activated carbons need to be changed periodically and these can be removed from the inserted medium using magnetic fields by incrementing particles sensitive to this field on the surface of the adsorbent reducing the cost of the operation. The present work presents a comparison of 3 different carbons: (i) conventionally activated carbon with NaOH as an activating agent from dried passion fruit seeds at 500 °C, (ii) magnetic field sensitive activated carbon synthesized in the laboratory using FeCl3 $6H_2O$ as magnetizing agent at 700 °C and (iii) commercial activated carbon. The three types of carbons were characterized using the analyses of: FTIR, PZC, TGA and nitrogen physisorption. The adsorption tests were performed on the adsorption of methylene in batch. Four kinetic models were evaluated to predict the adsorption kinetics: pseudo-first order, pseudo-second order, Elovich and Weber-Moris and four adsorption isotherm models: Langmuir, Freundlich, Temkin and Redlich-Peterson. The characterization of the conventional activated carbon presented an adsorbent with a degradation curve by TGA that followed the dry seeds, presenting low concentration of non-volatile material, the FTIR showed in its surface ketone groups and

CH_2, with a pH_{PZC} on the surface of approximately 5.46, with a microporous surface with 690 m^2 g^{-1} of type I for microporous surfaces and shows . The magnetization of this carbon significantly changed the properties on the surface, cation ionic surface; the TGA showed more non-volatile compounds, sensitivity of magnetic field, showing more acidic components on its surface such as hydroxyls and carboxyls and the surface pH_{PZC} is 4.14 and a microporous surface with 501 m^2 g^{-1} specific surface area. The kinetic and isothermal tests showed promising, the conventional activated carbon showed a higher adsorption capacity than the commercial one and the magnetic activated carbon showed a similar adsorption capacity as the commercially available. All the adsorbents presented very similar behaviors among them, presenting a kinetics with characteristics of physisorption of a pseudo-first order adsorption and the adsorption isotherms presented a favorable behavior, endothermic and with Langmuir adsorption. Thus, the present work infers in the potential use of magnetic activated carbons in relation to the ones available in the market, with similar performance.

Keywords: non-linear regression, chemical activation, favorable isotherm, passion fruit seeds, magnetic activated carbono.

RESUMO

O Brasil é um grande produtor de maracujá, aproximadamente 600 mil toneladas deste fruto foram produzidas no ano de 2019, mas cerca de 70% da massa é considerada um desperdício. Os resíduos desta produção poderiam ser agregados na síntese de carbonos activados para o tratamento de efluentes têxteis. Contudo, os carbonos activados precisam de ser mudados periodicamente e estes podem ser removidos do meio inserido utilizando campos magnéticos, aumentando as partículas sensíveis a este campo na superfície do adsorvente, reduzindo o custo da operação. O presente trabalho apresenta uma comparação de 3 carbonos diferentes: (i) carvão activado convencional com NaOH como agente activador de sementes secas de maracujá a 500 °C, (ii) carvão activado sensível ao campo magnético sintetizado em laboratório utilizando FeCl3 6H2O como agente magnetizante a 700 °C e (iii) carvão activado comercial. Os três tipos de carbonos foram caracterizados utilizando as análises de: FTIR, PZC, TGA e fisisorção de azoto. Os testes de adsorção foram realizados sobre a adsorção de metileno em lote. Quatro modelos cinéticos foram avaliados para prever a cinética de adsorção: pseudo primeira ordem, pseudo segunda ordem, Elovich e Weber-Moris e quatro modelos de isoterma de adsorção: Langmuir, Freundlich, Temkin e Redlich-Peterson. A caracterização do carvão activado convencional apresentou um adsorvente com uma curva de degradação por TGA que seguiu as sementes secas, apresentando baixa concentração de material não volátil, o FTIR mostrou nos seus grupos de cetonas de superfície e CH2, com um pHPZC na superfície de aproximadamente 5,46, com uma superfície microporosa com 690 m² g-1 de tipo I para superfícies microporosas e mostra . A magnetização deste carbono alterou significativamente as propriedades na superfície, superfície catiónica iónica; a TGA mostrou mais compostos não voláteis, sensibilidade do campo magnético, mostrando componentes mais ácidos na sua superfície como hidroxilos e carboxilos e a superfície pHPZC é de 4,14 e uma superfície microporosa com 501 m² g-1 de superfície específica. Os testes cinéticos e isotérmicos revelaram-se promissores, o carvão activado convencional mostrou uma capacidade de adsorção superior à comercial e o carvão activado magnético mostrou uma capacidade de adsorção semelhante à comercialmente disponível. Todos os adsorventes apresentaram comportamentos muito semelhantes entre eles, apresentando uma cinética com características de fisisorção de uma adsorção de pseudo primeira ordem e as isotermas de adsorção apresentaram um comportamento

favorável, endotérmico e com adsorção de Langmuir. Assim, o presente trabalho infere na potencial utilização de carbonos magnéticos activados em relação aos disponíveis no mercado, com desempenho semelhante.

Palavras-chave: regressão não linear, activação química, isoterma favorável, paixão sementes de frutos, carvão activado magnético.

1 INTRODUCTION

The passion fruit is one fruit of Passiflora genus with Brazil and Colombia being the largest producers in the world, according EMBRAPA (2019), Brazil produced around 600 thousand tons of passion fruit and which of approximately half is residues without an appropriate disposal. There is an emerging potential for the development of other products involving the waste generated by this industry, once these can be processed and add value in the development of products for industry and even in the treatment of effluents. The seeds of this fruit are low in moisture, about 10%, and rich in fiber, with approximately 53.40% detergent fibers and 20.54% pure lignin, being an alternative for synthesis of activated carbons and could be higher yield of synthesis (Faleiro, Junqueira, 2017)

The term "conventional activated carbon" was employed by Ao et al. (2018) to refer to the synthesis in induction heated muffle furnace, but there are other ways of synthesis that can be applied, could be syntesis in microwave and others. However, after the adsorption process there is the need for separation of this adsorbent, employing the use of filters or decanters, a relative cost operation associate, however, using materials with magnetic fields could facilitates separation processes once magnetic removal is a low-cost operation (Cazetta, 2016).

According to Khan et al. (2022) one of the largest applications of methylene blue dye is in the dyeing of garments made of cotton wood and silk and others. This dye its non-biodegradable and can be harmful to health in excess causing various problems in human health, such as nausea, vomiting, increased heart rate, cyanosis and even tissue necrosis.

Thus, the present work aims to present an alternative to the passion fruit seed industry by proposing the synthesis of a magnetic activated carbon, developing a product with market value and an appropriate destination for this waste, while studying its applicability in methylene blue removal.

2 MATERIAL AND METHODS

First, dry passion fruit seeds were pyrolyzed in a muffle furnace at 500 °C for 1 h with nitrogen flow (150 mL min^{-1}) and heating ramp of 10 °C min^{-1}. Next, for carbon activation, the seeds were infused in a NaOH solution (1:3) and heating on a muffle furnace at 500 °C nitrogen flow (150 mL min^{-1}) and heating ramp of 10 °C min^{-1} for 2 h. A part of the AC was separated for adsorption tests and another part was magnetizated with a solution of $FeCl_3$ $6H_2O$ (1:2) and then taken to the muffle furnace for heating at 700°C for 1.5 h, with nitrogen flow (150 mL min^{-1}) with a heating ramp of 10 °C min^{-1}.

The adsorption tests were carried out in batches using methodology employed Mousav et al. (2022) for methylene blue adsorption with some modifications.

For the adsorption Kinects, arranged in several erlenmayers flasks each with 50 mg of adsorbent material and 50 ml of solution, under stirring at 180 RPM. For the kinetics tests, different erlenmayers were used and remained in the shaker for residence times of: 1 min, 5 min, 10 min, 15 min, 20 min, 30 min, 40 min, 1h, 2h, 4h, 6h, 8h,12h, 16h, 20h and 24h each with a solution of 200 mg L^{-1} and apply in follow kinetic adsorption models: Pseudo-first-order, Pseudo-second-order, Elovich and Weber-Moris.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

$$\frac{t}{(q_e - q_t)} = \frac{1}{q_e^2} + k_2 t \quad (2)$$

$$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t) \quad (3)$$

$$q_t = k_D . t^{0,5} + C \quad (4)$$

For the adsorption isotherm, several erlenmayers were used with concentrations of 50, 100, 200, 300, 400 and 500 mg L^{-1} at temperatures of 25, 35 and 45 °C and apply in follow isotherm adsorption models: Langmuir, Freundlich, Temkin and Redlich-Peterson

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = k_F C_e^{\frac{1}{n}} \quad (6)$$

$$q_e = \frac{RT}{b_T} \ln(k_T C_e) \quad (7)$$

$$q_e = \frac{K_{RP}.C_e}{1 + a_{RP} C_e^g} \quad (8)$$

After performing all kinetic and isothermal tests, the samples were centrifuged and then exposed to the spectrophotometer at wavelength 665 nm for determination of the concentration methylene blue after adsorption. With all the concentration results, it was possible to make graphs and determine the parameters using the statistica softwere and the indexes R^2 and c^2 were used to choose the best fitting model

3 RESULTS AND DISCUSSION

The verification of activated carbon magnetization was carried out by approaching a magnet to the sample, the visual result is shown in Figure 1.

Figure 1 – Verification of magnetic proprieties of the MAC

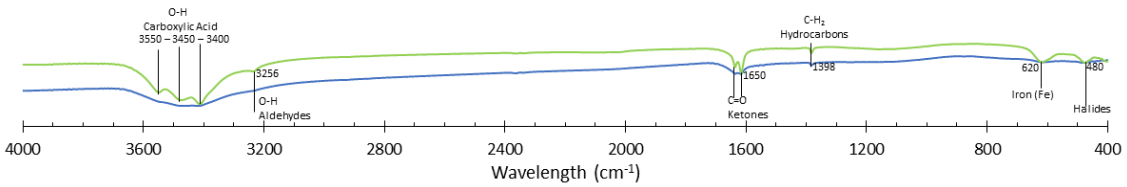
3.1 CHARACTERIZATION

The Infrared scanning by FTIR were performed with samples of Convention Activation Carbon (AC) and Magnetic Activation Carbon (MAC). The results of bands are shows in Figure 2.

The AC sample by detection of the 1388 cm^{-1} band may contain alcohol group C-O-H, but may represent CH_3 unfolding. By detection of the 1600 cm^{-1} and 1650 cm^{-1} band it may contain weak C=C medium alkene groups and C=O ketone group with conjugation of aromatic rings.

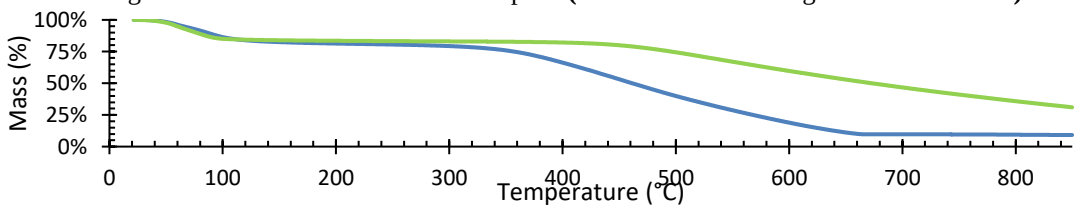
The MAC sample showed bands similar to the AC bands and further enhanced the bands 620, 719 may be the relationship between the iron chloride with the groups present on the surface, and the bands: 3256, 3400, 3450, and 3550 cm^{-1} typical of acidic groupings as hydroxyls and carboxylic acid, possibly associated with the magnetizing agent, iron III chloride.

Figure 2 – FTIR of AC and MAC samples (blue line for AC and green line for MAC)



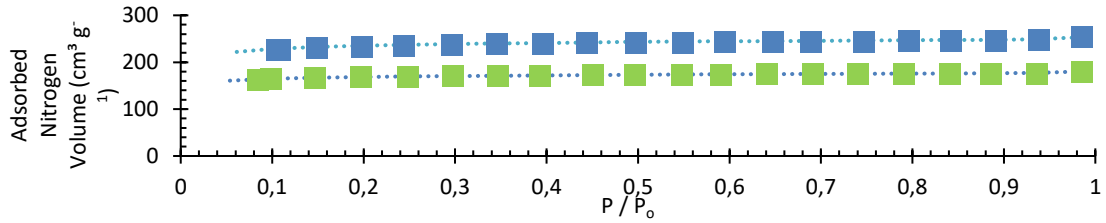
Note that the TGA degradation, shows in Figure 3, in AC curve result a small amount of non-volatile material (about 7%) indicating a possibility of containing a high pore number, however, the magnetic activated carbon showed a higher accumulation of non-volatile material (about 30%) possibly due to the high temperatures in magnetization step accumulated iron on surface.

Figure 3 – TGA of AC and MAC samples **(**blue line for AC and green line for MAC**)**



The nitrogen physisorption, shows in Figure 4, indicates that there were two very similar structures porous, probably the similarity is due by the activated carbons step using the sodium hydroxide agent noted in the AC and MAC curves. According Thommes et al. (2015), these curves are characteristic of TYPE I curves; related to microporous adsorbents The reduction in the volume of adsorbed nitrogen among the MAC samples and may be related to incorporation of iron nanoparticles on the surface of the adsorbent Cazetta (2016).

Figure 4 – Nitrogen fissoration of AC and MAC samples (blue square for AC and green square for MAC)



The PCZ showed that the adsorbent generated from the passion fruit seed samples have a more acidic interaction on its surface (pH_{PZC} less than 7,00), ideal for the adsorption of materials with negative charges in its structure.

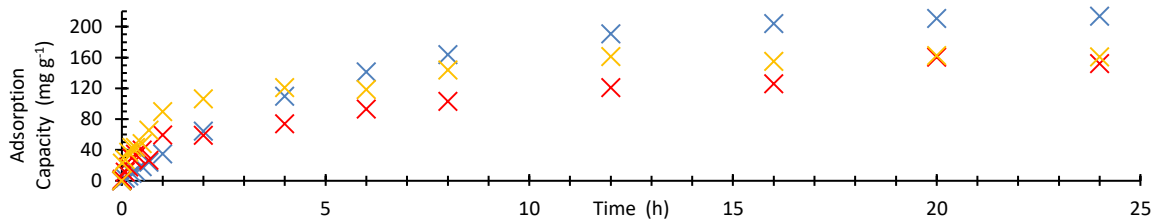
Table 1 - pH_{PZC} ratio of the adsorbents AC and MAC

Matherial	pH_{PCZ}	Matherial
AC	5,46	AC
MAC	4,14	MAC

3.2 EQUILIBRIUM ADSORPITION

The kinetics, in Figure 5, occurred in a 24 h interval when it was observed that all adsorbents reached their equilibrium. For AC the equilibrium time was 16 h with a q_{MAX} of 209.29 mg g^{-1}, for MAC the equilibrium time was 20h with a q_{MAX} of 156.13 mg g^{-1} and for CAC the equilibrium time was 12h with a q_{MAX} of 159.78 mg g^{-1}. In this first analysis it can be inferred that the carbon synthesized without the magnetic application provided an adsorptive capacity greater than the commercial activated carbon and in turn the magnetized activated carbon has similar removal capacity to the commercial activated carbon, demonstrating that this synthesis route has the potential to be accepted commercially.

Figure 5 – Experimental adsorption kinetic profiles of the AC, MAC and CAC adsorbents **(**blue marks for AC, red marks for MAC and yellow marks for CAC**)**



According to the modeling by figure 6, it can be noted that almost all the models obtained good acceptance, for the CA sample the model that presented the best statistical index was the Pseudo First Order, indicating that the adsorption has a more physical character possibly associated with the microporous surface. Unlike CAM and CAC that had better acceptance for the Elovich model, which is expected for adsorbents and dye removal, possibly these two adsorbents have a relationship with diffusion effects between the adsorbent and the dye (Wu et al, 2009)

The difference between the pseudo first-order and Elovich model statistical confidence indices were not very different for the AC and MAC, suggesting that it may also have physical adsorption effects on its surface.

Figure 6 – Modeling profiles of adsorption kinect for each adsorbent AC, MAC and CAC (X mark for experimental points, Greenline for Pseudo-first order, Blueline for Pseudo-second Order, redline for Elovich, and purpleline is for Weber -Morris model. a) for AC; b) for MAC and c) for CAC**)**

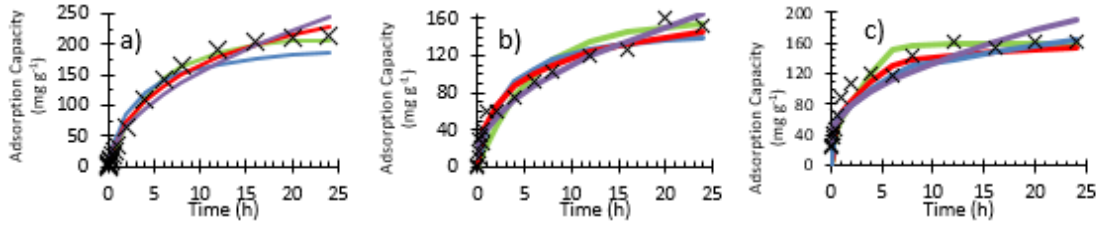


Table 2 – Parameters of the models applied on each adsorbent for adsorption Kinect

AC		MAC		CAC	
		Pseudo First order			
k_1	0,1902 ±0,0032	k_1	0,1685 ±0,0238	k_1	-0,7024±0,1053
R^2	0,9990	R^2	0,8931	R^2	0,9109
□²	1,233	□²	259,6077	□²	279,4414
		Pseudo Second Order			
k_2	0,0016±0,0002	k_2	0,0023 ±0,0003	k_2	0,0070 ±0,0008
R^2	0,963475	R^2	0,9355	R^2	0,9656
□²	122,17	□²	127,6622	□²	99,37886
		Elovich			
□	0,0128±0,1793	□	0,0295 ±0,3110	□	0,0024 ±0,0122
□	57,65±6,2252	□	104,2 ± 23,13	□	28,72 ± 1,680
R^2	0,9921	R^2	0,9673	R^2	0,9785
□²	41,604	□²	62,24059	□²	67,65968

			Weber-Morris		
k_D	51,78±2,351	k_D	31,61 ± 1,417	k_D	32,63 ± 2,960
C	-8,548±5,557	C	9,414 ± 3,350	C	31,02 ± 6,997
R^2	0,9700	R^2	0,9707	R^2	0,8901
□²	154,86	□²	61,54842	□²	292,7422

Figure 7 – Modeling profiles of adsorption isotherm for each adsorbents AC, MAC and CAC (blue marks for AC, red marks for MAC and yellow marks for CAC)

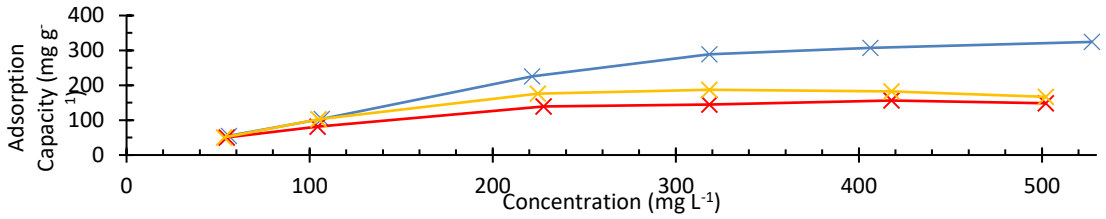
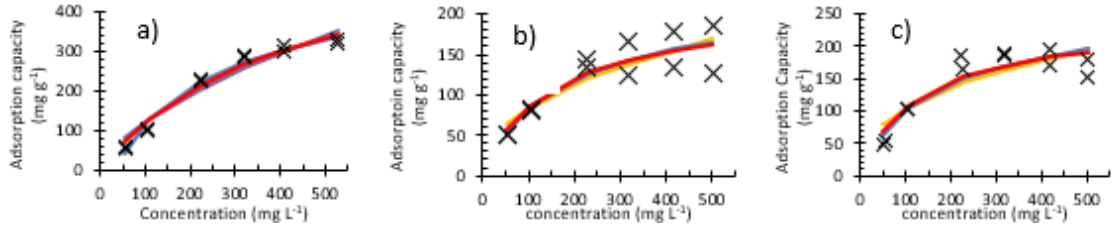


Figure 8 demonstrates the modeling of the activated carbons in relation to experimental data. It can be concluded that the Langmuir modeling was well accepted, the Redlich-Peterson modeling coincided with the Langmuir modeling, but within what was expected, since the g parameter resulted in 1 and the Langmuir modeling was well accepted among the 3 adsorbents.

Figure 8 - Modeling profiles of adsorption isotherm for each adsorbent AC, MAC and CAC (X mark for experimental points, Greenline for Pseudo-first order, Blueline for Pseudo-second Order, redline for Elovich, and purpleline for Weber -Morris model. a) for AC; b) for MAC and c) for CAC)



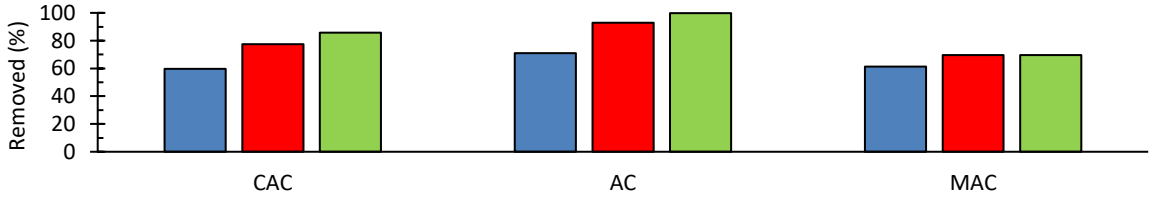
According to Table 3 the parameters can result in certain analyses; by the Langmuir model when performing the R_L Separation Factor we obtained in all carbons a result less than 1, that is, all isotherms resulted in a favorable curve, the same is noted by the n factor of Freundlich, in which resulted in a number less than 1 indicating a favorable adsorption (Nascimento et al., 2014).

According to Silva et al. (2018) the parameter b_T is related to the enthalpy of adsorption, as it results in a value greater than zero, it can be stated that the adsorption may be endothermic, confirmed by the tests of temperature variation in which the highest temperature offered the greatest removal according to Figure 9

Table 3 - Parameters of the models applied on each adsorbent for adsorption isotherm

AC		MAC		CAC	
		Langmuir			
q_{max}	618,9 ± 79,73	q_{max}	214,2 ± 28,87	q_{max}	240,2 ± 26,17
k_L	0,0024 ±0,0005	k_L	0,0064 ±0,0024	k_L	0,0077 ±0,0025
R^2	0,9700	R^2	0,8239	R^2	0,8530
χ^2	383,77	χ^2	415,48	χ^2	463,82
		Freundlich			
k_F	5,901 ± 2,515	k_F	10,88 ± 5,804	k_F	16,18 ± 8,562
n	0,6537 ±0,0722	n	0,4414 ±0,0922	n	0,4018 ±0,0917
R^2	0,9376	R^2	0,7777	R^2	0,7498
χ^2	798,53	χ^2	524,61	χ^2	789,57
		Tenkin			
b_T	20,22 ± 0,9318	b_T	51,82 ± 7,714	b_T	44,76 ± 6,319
k_T	0,0249 ±0,0021	k_T	0,0514 ±0,0192	k_T	0,0550 ±0,0200
R^2	0,9792	R^2	0,8186	R^2	0,8338
χ^2	266,27	χ^2	428,13	χ^2	524,49
		Redlich-Peterson			
k_{PR}	1,460 ±0,1623	k_{PR}	1,373 ± 0,3500	k_{PR}	1,845 ± 0,4315
a_{RP}	0,0024 ±0,0005	a_{RP}	0,0064 ±0,0024	a_{RP}	0,0077 ±0,0025
g	1	g	1	g	1
R^2	0,9700	R^2	0,8239	R^2	0,8530
χ^2	295,85	χ^2	461,65	χ^2	515,36

Figure 9 – Evaluation of the adsorption temperature for adsorbents AC, MAC and CAC (blue for 25°, red for 35° green for 45°)



4 CONCLUSIONS

The magnetization method significantly altered the surface properties of the adsorbent, causing a reduction of the specific surface area, the appearance of more acidic substances on its surface and a greater presence of non-volatile compounds. However, this process did not significantly alter the adsorption processes in which the carbons presented very similar kinetic and isothermal adsorption behavior. In addition, the magnetic adsorbent presented a removal capacity similar to that of adsorbents available in the market, showing a plausible alternative.

Nomenclature

a_{RP} – Redlich-Peterson isotherm constant
b_T - Temkin constant in relation to the heat of adsorption, J g mol^{-1} mg^{-1}
C - Concentration at equilibrium (mg g^{-1})
FTIR - Fourier Transformer Infrared
g - Redlich-Peterson constant
k_1 - Adsorption rate for the pseudo first order model, h^{-1}
k_2- Adsorption rate for the pseudo-second order model, g mg^{-1} h^{-1}
k_D - Adsorption rate for the Weber-Morris model
k_F - Freundlich adsorption constant, mg g^{-1} (L mg^{-1})$^{1/n}$
k_L - Langmuir adsorption constant, L g^{-1}
k_{epi} - Redlich adsorption constant, mg L^{-1} g^{-1}
k_T - Temkin adsorption constant, L mg^{-1}
n - Adsorption facility
pH_{PZC} - pH of Point of Zero Charge
PZC - Point of Zero Charge
q_{MAX} - maximum adsorption capacity
TGA- Thermogravimetric Analysis
α - Initial adsorption rate (mg g^{-1} min^{-1})
β – Desorption rate (mg g-1)

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