ESTUDO CINÉTICO NA REMOÇÃO DE CORANTE EM SOLUÇÃO AQUOSA PELO CARVÃO DE COCO DE BABAÇU MODIFICADO COM ÁCIDO CÍTRICO

KINETIC STUDY IN REMOVAL OF DYE IN AQUEOUS SOLUTION BY THE BABASSU COCONUT CHARCOAL MODIFIED WITH CITRIC ACID

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RESUMO

Os corantes estão entre a classe de compostos considerados perigosos para a flora e fauna aquáticas, por isso é importante tratar as águas residuais contaminadas por estas substâncias. Entre as diferentes técnicas de tratamento, a adsorção mostra um método eficiente e barato para tratar grande quantidade de resíduos. O carvão de coco de babaçu (CCB) surge como uma alternativa à produção de carvão vegetal, pois é uma biomassa bastante encontrada em várias regiões do Brasil. O CCB foi tratado com ácido cítrico e o carvão de coco de babaçu modificado com ácido cítrico (CCBMod) foi utilizado nos testes de adsorção com o azul de metileno (AM). Os resultados mostram que o ácido cítrico agiu sobre a superfície do carvão sem ser incorporado na sua estrutura. A cinética de adsorção neste estudo é regida pelo modelo de pseudo-segunda-ordem, onde a quantidade adsorvida no equilíbrio foi de 1,5424 mg g^{-1} de acordo com o valor calculado para este modelo de 1,5625 mg g^{-1}. Dentre os modelos empregados neste estudo para isotermas de adsorção, o que melhor se aplicou aos dados experimentais foi o modelo de Langmuir, com um coeficiente de correlação de 0,9870.

Palavras-chave: *Carvão de coco de babaçu, azul de metileno, ácido cítrico, tratamento de efluentes*.

ABSTRACT

Dyes are among the class of compounds considered dangerous to aquatic flora and fauna, thus it is important to treat waste water contaminated by this substances. Among different treatment techniques, adsorption shows an efficient and inexpensive method for treating large amount of waste. Babassu coconut charcoal (BCC) arises as an alternative to charcoal production, because it is a quite biomass found in several of Brazil. The BCC was treated with citric acid and the babassu coconut charcoal modified with citric acid (BCCMod) was used in the adsorption tests with the methylene blue (MB). The results show that citric acid acted on the charcoal surface without being incorporated into their structure. The adsorption kinetics in this study is governed by the pseudo-second-order model, where the amount adsorbed in the equilibrium was 1.5424 mg g^{-1} agreement with the value calculated for this model 1.5625 mg g^{-1}. Among the models employed in this study for adsorption isotherms, what better applied to the experimental data was the Langmuir model, with a correlation coefficient of 0.9870.

Keywords: Babassu *coconut charcoal, methylene blue, citric acid, wastewater treatment*.

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INTRODUTION

There are several substances that are considered dangerous to aquatic life. The dyes are among the class of compounds which damage the aquatic plants and animals once form a pigment in the water surface that hamper the penetration of solar radiation and compromises the process of photosynthesis (Luna *et al*., 2013). Moreover, the treating of the hydrous resources is characterized as an important step for survival on earth. It is estimated that our planet is constituted by 70% of water, of this total water available on the planet only 2.5% is potable water, in which approximately 98% is held in glaciers and deep subsoils (*Projeto Brasil das águas*, 2015).

Dyes have wide application potentiality including textile, cosmetics, plastics, food industry and among others sectors that use dyes to give color to their products. The main causes of water contamination occurs due disposal of textile waste without preliminary treatment once sewage treatment plants do not degrade the effluent and these end up contaminating water from rivers, ponds and others (Vieira *et al*., 2011, Djilani *et al*., 2015).

Several technologies are reported in the literature as a source of water treatment: biological treatments (Almeida e Corso, 2014; Chakraborty *et al*., 2013), electrochemical degradation (Körbahti *et al*., 2011; Torres e Gutiérrez, 2010), photocatalysis (Kant *et al*., 2014; Mozia *et al*., 2010), adsorption (Aboua *et al*., 2015). Among these methods mentioned, adsorption appears as an effective alternative and low cost for waste treatment in aqueous solutions and increasingly their application has been highlighted in literature (Han et al., 2016).

The babassu is a native palm tree of Latin America that can be easily found in Brazil in the Amazon, Atlantic Forest, Cerrado and Caatinga. This palm tree produces a fruit, the babassu coconut, which has wide potentiality since the production from farinaceous food up to the production of cleaning supplies such as shampoos, soaps and others (Carrazza *et al*., 2012, Cruz *et al*., 2012). In this perspective, the babassu coconut gains importance, because a large amount of agricultural waste can be generated after processing of babassu, so these residues can easily be used in coal production both for burning in furnaces and in the production activated carbon.

The goal of this work is to treat wastewater containing textile dyes with babassu coconut charcoal (BCC) and to study its adsorption kinetics and isotherm.

MATERIALS AND METHODS

2.1. Materials

The BCC used in the study was obtained from the state of Maranhão, charcoal was crushed, pulverized and sieved and after treated with citric acid 1.0 mol L^{-1} for 4 hours. Thus, it was obtained babassu coconut charcoal modified with citric acid (BCCMod).

2.2. Characterization of the material

The BCCMod was characterized by infrared spectroscopy (FTIR) Shimadzu, model FTIR- 8400S da série IRAffinity - 1 in the region 4000-400 cm^{-1} with a resolution of 4 cm^{-1} using KBr pellets. To characterize the crystalline structure, the parameters was used for Ray diffraction-X As on a Bruker D2 Phaser device using CuKα radiation (λ = 1,54Å) with a Ni filter, with step 0,02º, current of 10 mA, voltage 30kV using a Lynxeye detector. This procedure was performed in a Scanning Electron Microscope - model Philips XL-30. To obtain images, it was the following experimental conditions: 5 V, beam diameter 4.0 (increased according to the needs of each sample). Samples were affixed to the support using carbon tape. The images were processed in Philips XL software - 30.

2.3. Adsorption kinetics

The adsorption kinetic was obtained by suspending 100 mg of BCCMod in 30 mL of methylene blue (MB) in aqueous solution in the concentration of 6 mg L^{-1} under agitation 150 rpm ± 1. The tests were performed at room temperature and at natural pH of the solution (pH 6.0) in the time interval from 0 to 100 minutes. 5 mL aliquots of the adsorbate was collected each 10 minutes and centrifuged for 10 minutes. After separation, the supernatant solution was brought to the spectrophotometric determination in a spectrophotometer model UV-1800 from Shimadzu. The amount absorbed by unity mass of adsorbent in the equilibrium q (mg g^{-1}) it was obtained using Eq. 1.

$$q_e = \frac{V}{M}(C_i - C_e) \quad \text{(Eq. 1)}$$

where Ci and Ce represent the dye initial and equilibrium concentrations (mg L^{-1}), respectively, V is the solution volume (L) and M is the mass of adsorbent (g). In order to obtain kinetic parameters, the models of pseudo first order (Eq. 2), pseudo second order (Eq. 3) and intraparticle diffusion (Eq. 4) were applied.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{(Eq. 2)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(Eq. 3)}$$

$$q_t = k_{dif} t^{0.5} + c \quad \text{(Eq. 4)}$$

where q_e is the quantity of adsorbate adsorbed in equilibrium (mg g^{-1}), qt the amount adsorbed at time t (mg g^{-1}) and k_1(min^1) e k_2 (g mg^{-1} min^{-1}) are the rate constants of pseudo first and pseudo second order. k_{dif} is the constant intraparticle diffusion expressed in (mg g^{-1} $min^{-0.5}$).

2.4. Adsorption isotherms

The adsorption isotherm was obtained following the experimental procedure similar to the adsorption kinetics. In this stage, it was used concentrations of MB from 2 to 16 mg L^{-1} in a time determined by the adsorption kinetic, suspending 100 mg of BCCMod in 30 mL of MB under agitation 150 rpm ± 1 at room temperature. The solid was separated by centrifugation for 10 minutes and was brought to spectrophotometric determination in the visible region. In order to determine the constants involved in adsorption, it was applied the isotherm models of the *Langmuir* (Eq. 5), the *Freundlich* (Eq. 7) and *Temkin* (Eq. 8), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \quad \text{(Eq. 5)}$$

Where C_e (mg L^{-1}) and q_e (mg g^{-1}) are respectively, the concentration and the amount of adsorbate in the equilibrium, K_L is the *Langmuir* equilibrium constant and q_m is maximum amount of adsorbate which can be adsorbed. The *Langmuir* isotherm model can also be expressed in terms of adimensional constant (R_L) (Eq. 6), known as the separation factor, which can be used to determine if the adsorption is favorable or not.

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{(Eq. 6)}$$

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e) \quad \text{(Eq. 7)}$$

C_e (mg L^{-1}) and q_e (mg g^{-1}) represent the same as has already been mentioned for the *Langmuir* model, K_F is the *Freundlich* constant that indicates the capacity of adsorption and n is the heterogeneity factor.

$$q_e = a_T \ln K_T + a_T \ln C_e \quad \text{(Eq. 8)}$$

K_T is the *Temkin* binding constant in the equilibrium and a_T is associated to heat of adsorption.

RESULTADOS E DISCUSSÃO:

3.1. Characterization of the material

The infrared spectrum (IR) (Figure 1) for BCCMod appear to be similar to the IR spectrum of BCC, indicating that there was not incorporation of citric acid in its structure, however, citric acid possibly acted causing a masking functional groups or lixiviation the surface, because after the treatment with citric acid IR results show a reduction in complexity of the bands. However, the main bands that characterize this type of plant material were not changed. The axial deformation of the group - OH in the region 3680-3166 cm^{-1}, bands between 2992 and 2840 cm^{-1} characteristic of the axial deformation of the CH_2 and CH_3 groups. A low intensity band at 1769 cm^{-1} characteristic of the axial deformation of the C = O group and 1566 cm^{-1} an axial deformation of the C = C bonds characteristic of aromatic rings (Silverstein *et al.*, 2006, Vieira *et al.*, 2009).

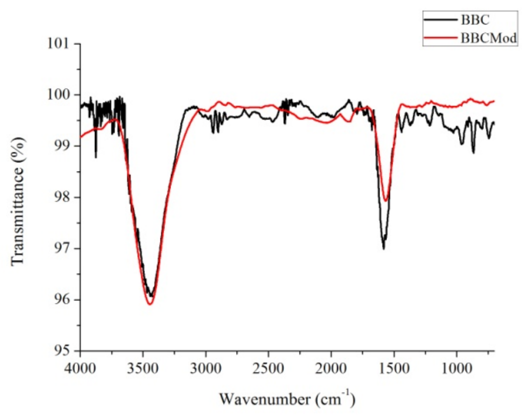

Figure 1. *Infrared spectrum of BCC and BCCMod.*

The X-rays' diffractograms (Figure 2) show that the amorphous carbon structure was not changed after treatment with citric acid, indicating again that there was not the incorporation of the acid in the charcoal structure. In the XRD were only observed reflections in 2Θ near 23° and 43° as mentioned in the literature like a characteristic for this type of material (Shimabuku *et al.,* 2013).

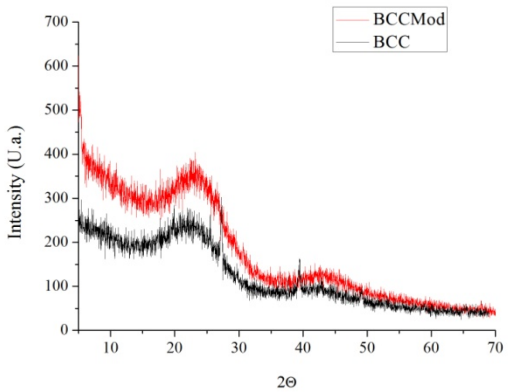

Figure 2. *X-ray diffractograms of the BCC and BCCMod.*

The Scanning Electron Micrographs (Figure 3) show that before treatment with citric acid, charcoal appearance was irregular with small heterogeneous and non-uniform cavities, in which after the acid treatment, the surface of the material appeared more uniform and regular, this being a good indication for the adsorption once that surface is better distributed and available to adsorb dye molecules in the effluent to be treated.

3.2. Adsorption kinetic

To investigate the best contact time for this study, it was necessary to get the equilibrium condition for the adsorption of the dye in BCCMod. The amount of dye q_e was established as a function of time t. The Figure 4 shows the curve indicating in which time occurred the adsorption equilibrium, as can be noted, this time was 60 minutes. Despite the system show certain linearity in points previous at 60 minutes, it was from this time that the points oscillate less in relation to each other and thus fixed the equilibrium in this time mentioned.

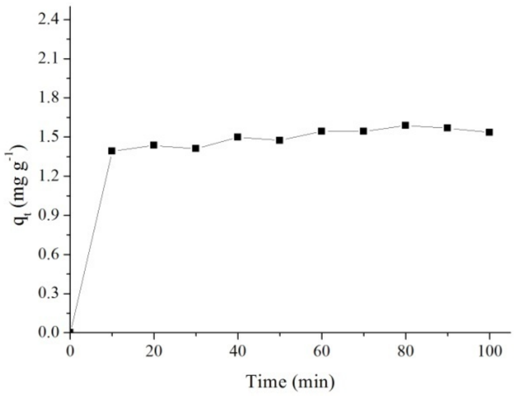

Figure 4. Adsorption of MB in aqueous solution on BCCMod in function of time, pH 6.0, temperature 25 ± 1 ° C, agitation rate150 rpm ± 1.

To evaluate the mechanisms that control the adsorption kinetics were employed models of pseudo-first-order, pseudo-second-order and intraparticle diffusion. These models applied to the experimental data include the main actions that occur in the adsorption process: transport in solution, adsorption on the external surface and intraparticle diffusion and adsorption (Vucurovic *et al*., 2014). The data obtained by the pseudo first-order model are not in agreement with the experimental data as shown in Table 1, especially the amount adsorbed in the equilibrium for this model was 0.1907 mg g^{-1} and experimental data was 1.5424 mg g^{-1}. The pseudo-second-order model showed a better fit to the experimental data, where q_e calculated for this model was 1.5625 mg g^{-1} and experimental data was 1.5424 mg g^{-1} as mentioned, indicating that this kinetic model can be used to describe the adsorption process as mentioned by (Carvalho, 2010). Others data obtained for this model are summarized in Table 1. Finally, it was also tested intraparticle diffusion model to the experimental data, with a linear correlation coefficient of 0.7186. This value indicates that even charcoals being porous materials, which would be an advantage for the intraparticle diffusion model, there is not applicability of this model to the experimental data, since this process is characteristic of an external diffusion and already proven by the application the pseudo-second-order data. Figures 5, 6 and 7 show the curves for the three models mentioned above.

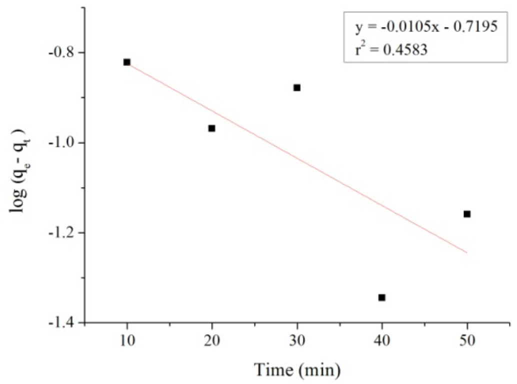

Figure 5. *Kinetic model of pseudo-first-order in the adsorption of MB on BCCMod, pH 6.0, temperature 25 ± 1 ° C, agitation rate 150 ± 1 rpm.*

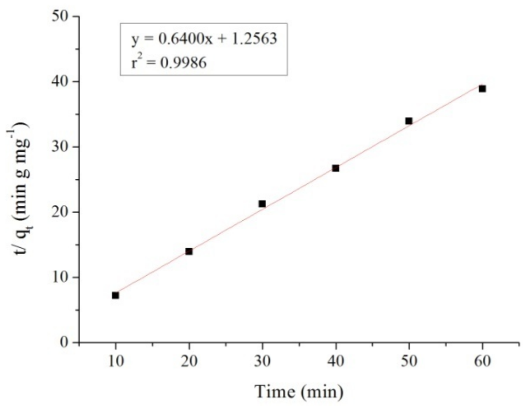

Figure 6. *Kinetic model of pseudo-second-order in the adsorption of MB on BCCMod, pH 6.0, temperature 25 ± 1 ° C, agitation rate 150 ± 1 rpm.*

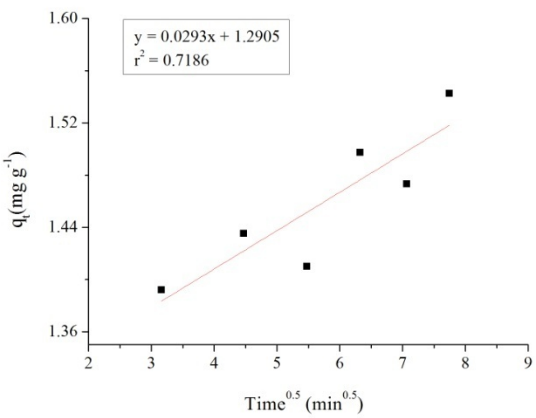

Figure 7. *Intraparticle diffusion kinetic model of the adsorption of MB on BCCMod, pH 6.0, temperature 25 ± 1 ° C, agitation rate 150 ± 1 rpm.*

3.3. Adsorption isotherms

The isotherms models employed provide physical-chemical data on the adsorption process. Thus, to interpret the experimental data of the adsorption were used the *Langmuir*, *Freundlich* and *Temkin* isotherms. Among these models employed, what better applied to the experimental data was the Langmuir model (Figure 8), with a correlation coefficient of 0.9870. The maximum amount adsorbed q_m and constant Langmuir K_L are respectively 2.1612 mg g^{-1} and 4.4792 L mg $^{-1}$. These data provide this adsorption occurred by formation of monolayers homogeneously distributed over the surface of BCCMod as previously reported by the literature for this type of materials (Vucurovic *et al*., 2014, Melo, 2016). The separation factor R_L is a dimensionless unit that can be classified as follows: If the value of (R_L > 1) the adsorption process is unfavorable, if (R_L = 1) the isotherm is linear, in cases where (0 < R_L < 1) the adsorption is favorable and for (R_L = 0) the adsorption process is irreversible (Vucurovic *et al.,* 2014). The R_L values obtained for the concentrations used in this study show a variation of (0.0263 - 0.5534), indicating that the adsorption process is favorable once it is in the range (0 < R_L < 1) as already mentioned above.

Freundlich (Figure 9) and Temkin (Figure 10) models showed a correlation coefficient values equal to 0.7568 and 0.7036 respectively, indicating that these values are widely dispersed not adapting the models presented. The summary of the data presented for each model are shown in Table 2.

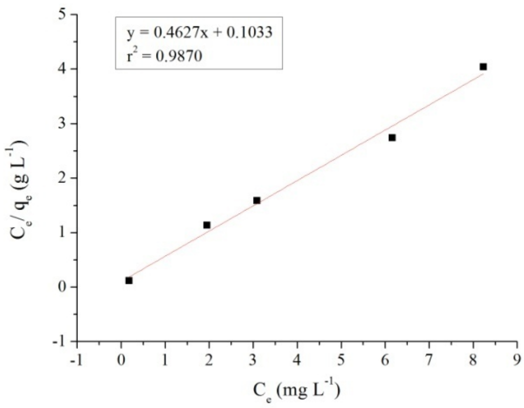

Figure 8. *Isotherm linearized of Langmuir to adsorption of the MB on BCCMod, pH 6.0 temperature 25 ± 1 ° C, agitation rate 150 rpm ± 1.*

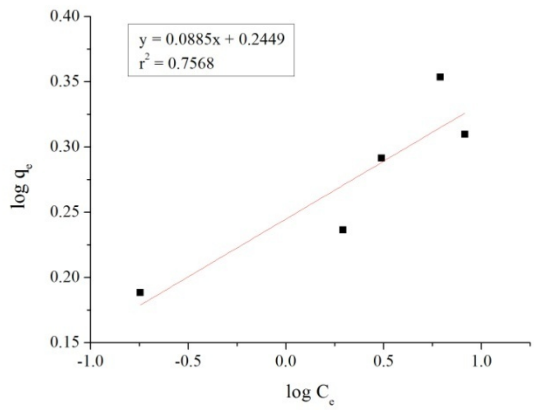

Figure 9. *Isotherm linearized of Freundlich to adsorption of the MB on BCCMod, pH 6.0 temperature 25 ± 1 ° C, agitation rate 150 rpm ± 1.*

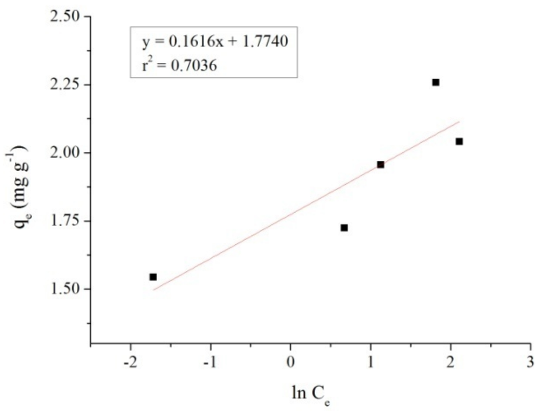

Figure 10. *Isotherm linearized of Temkin to adsorption of the MB on BCCMod, pH 6.0 temperature 25 ± 1 ° C, agitation rate 150 rpm ± 1.*

CONCLUSIONS

The results of this study show that acid treatment carried out with the charcoal did not generate impregnation of citric acid on the surface of BCC, acting only in the acid leaching in the material surface as shown by the data of IR, XRD and SEM. The pseudo-second-order equation is the model that best describes the adsorption kinetics of MB on BCCMod with a linear correlation coefficient of 0.9965 and the value of q_e is consistent with the value of $q_{e,exp}$ being 1.5625 and 1.5424 mg g^{-1}, respectively. The *Langmuir* isotherm model is the model that best describes the adsorption isotherm showing a linear correlation coefficient of 0.9870, featuring a homogeneous monolayer adsorption. It is concluded that the BCCMod is a good adsorbent in the removal of MB.

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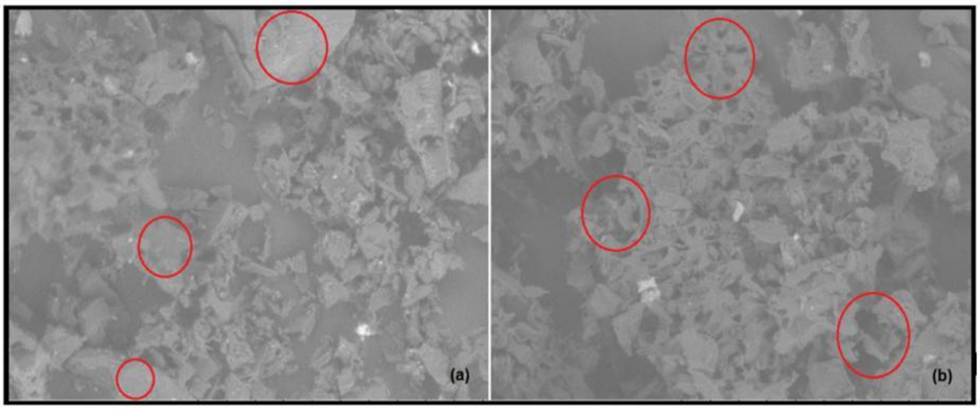

Figure 3. *Scanning electron microscopy of BCC (a) e of the BCCMod (b).*
Fonte: Silva, 2015.

Table 1 - *Kinetic parameters obtained by removal of the MB from the BCCMod.*

Kinetic models					
$q_{e,exp}$ (mg g^{-1})			1.5424		
Pseudo-primeira-ordem		**Pseudo-segunda-ordem**		**Difusão intrapartícula**	
k_1 (min^{-1})	0.0241	k_2 (g mg^{-1} min^{-1})	0.3260	k_{dif} (mg g^{-1} min$^{-0.5}$)	0.0293
q_e (mg g^{-1})	0.1907	q_e (mg g^{-1})	1.5625	C	1.2904
r^2	0.4583	r^2	0.9965	r^2	0.7186

Table 2*. Isothermal parameters obtained by removal the MB from the BCCMod.*

Isotherms models					
Langmuir		**Freundlich**		**Temkin**	
k_L (L mg^{-1})	4.4792	K_F (L mg $^{-1}$)	1.7575	α_T	0.1616
q_m (mg g^{-1})	2.1612	1/n	0.0885	k_T (L mg^{-1})	5.8554 x 10^4
r^2	0.9870	r^2	0.7568	r^2	0.7036