

Kinetics and Equilibrium Study of Black Krom KJR Dye Sorption by Bone-based Activated Carbon

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Abstract: In this work, the sorption capacity of a bone-based activated carbon for the Black Krom KJR dye removal was investigated in a batch system. Preliminary sorption tests were performed in order to assess the effects of initial pH, sorption temperature, stirring speed and the particle size on the sorption process. The most reliable conditions were used to perform the kinetic and equilibrium tests in duplicate. From the kinetic sorption experiments, an equilibrium time of 24 h was achieved with a sorption capacity of 53 mg·g⁻¹. Kinetic dye sorption data was well represented by both the pseudo second order and Elovich models. Among used isotherm models, the Langmuir model exhibited best fit to the equilibrium sorption data, showing a maximum sorption capacity value of 154 ± 8 mg·g⁻¹ and affinity constant value of 0.0114 ± 0.0012 g·L⁻¹, respectively. Based on these results, it is remarkable the great potential exhibited by the bone-based activated carbon adsorbent for its application in industrial wastewater treatment systems.

Keywords: Adsorption, Bone-based activated carbon, Black Krom KJR dye uptake, Wastewater treatment.

Introduction

Continuous increasing of industrial activity and human population growth have contributed to the generation of several types of toxic pollutants, which when improperly released into the environment are the main cause of global water pollution.

The term “water pollution” refers to a substance or a material that alters the natural water quality of the physical, chemical and/or biological [18]. One of the major classes of pollutants are dyes [19], which are widely used in the textile, leather, paper, plastic, etc. [31].

The dye molecule has a complex aromatic structure [9], comprising two main components: the chromophores responsible for the color; and auxochrome which can complement the chromophore and also make the molecule soluble in water [19]. When released in natural water bodies, these molecules modify their color by increasing the chemical oxygen demand (COD), biological oxygen demand (BOD), dissolved and suspended solids [32]. Moreover,

dyes lower photosynthetic activity due to reducing light penetration, and many of them are toxic, carcinogenic and harmful to the human health [38]. Thus, strict standards have been stipulated by regulatory agencies to the removal of dyes before launching them into environmental receptors [8].

In order to meet the limits, several treatments methods have been used, such as Advanced Oxidation Processes (AOP) [25], chemical coagulation and flocculation [39], photo-catalysis [29], nanofiltration and reverse osmosis [37] and as well as adsorption [13, 27]. Among these treatment methods, the adsorption process is distinguished mainly in terms of low initial cost, simplicity of design, ease of operation and insensitivity to toxic pollutants [12].

The adsorption process consists at the concentration of fluid molecules (adsorbate) on the solid surface (adsorbent) [15]. When the fluid and solid phases are in contact, the diffusion of the dye molecules within the fluid phase to the surface of the adsorbent (external diffusion) occurs, and these molecules attach on the surface (surface reaction). The next step of the process is the diffusion of the dye from the surface into the pores of the adsorbent material (internal diffusion) [14]. The process continues until the dynamic equilibrium between the two phases (liquid-solid) is achieved.

The activated carbon (AC) is the most widely used adsorbent in the adsorption conventional systems [22, 34]. Although relatively costly and regeneration requirement, it is an excellent adsorbent material [34], because of its highly reactive surface, micro-porous structure and high specific surface area [28]. The characteristics of the AC depend on the employed activation method, as well as the properties of used raw material in the carbonization process [8] and they determine the level of adsorption of the pollutants. Evaluating mechanisms on the molecular level one may claims that groups in the carbon structure such as carboxyl, carbonyl, phenols, lactones, quinones, among others, are generally responsible for the phenomenon [2].

Numerous physical and chemical factors affect the adsorption of the dye by activated carbon. The most important are: the interaction between the adsorbate and the adsorbent surface area; porous structure and the adsorbent surface chemistry; structural characteristic of the dye molecule; particle size of the adsorbent; pH, temperature and contact time [26].

The objective of this study was to evaluate the ability to remove the Black Krom KJR dye from aqueous solution by using bone-based activated carbon. In order to achieve this goal, preliminary tests were conducted to evaluate the effect of initial pH of the solution, sorption temperature, stirring speed and particle size of the adsorbent on the removal process. The most reliable conditions obtained in preliminary tests were used in kinetic and equilibrium experiments. The pseudo-first order, pseudo-second order and Elovich kinetic models were fitted to experimental data, while Langmuir, Freundlich and Sips models were applied to describe equilibrium data.

Materials and methods

Reagents

The used dye in the tests was called Black Krom KJR (Kromatica ®) (BK-KJR). This was a mixture of dyes. The dye was obtained from an industry located at the western region of Paraná State, Brazil. A stock solution of 500 mg·L⁻¹ was prepared by using the dye and distilled water and subsequently diluted as needed. The stock solution was stored in dark amber bottle.

Adsorbent

The adsorbent used for BK-KJR removal was bone-based AC provided by the manufacturer Bonechar – AC from Brazil, whose specifications are shown in Table 1. The bone-based AC was grounded by a knife grinder type “Willye” (model TE 648) and further characterized by granulometric size distribution using Tyler sieves.

Table 1. Bone-based activated carbon specifications provided by the manufacturer

Specification	Value
Carbon conten	9-11%
Ash	< 3%
Insoluble ash	0.7
Tricalcium phosphate	70-76%
Calcium carbonate	7-9%
Calcium Sulphate	0.1-0.2%
pH	8.5-9.5
Total specific surface area (BET N ₂)	200 m ² ·g ⁻¹
Carbon surface area	50 m ² ·g ⁻¹
Iron	< 0.3%
Pore diameter	7.5-60.000 nm
Pore volume	0.225 cm ³ ·g ⁻¹
Moisture	< 5%
Apparent density	0.60-0.70 g·cm ⁻³
Hardness	> 80

Determination of the dye concentration

The determination of the BK-KJR concentration in solution, after each test of biosorption was performed by using UV-Vis spectrophotometer (Shimadzu UV-1800). Initially, a molecular absorption spectrophotometry was carried out in the wavelength range from 400 to 800 nm with the solution concentration of 100 mg·L⁻¹ in order to determine the wavelength characteristic of the maximum visible light absorption. After that, a standard curve was prepared where the absorbance value was a function of the dye concentration. For this purpose, the stock solution was diluted in order to obtain 12 solutions with different concentrations in the range from 1 to 100 mg·L⁻¹.

Preliminary tests

In order to determine the most favorable conditions for the adsorption process, preliminary tests were performed. The effect of initial pH (from 1 to 10), temperature of sorption (20, 30, 40 and 50°C), stirring speed (50, 100 and 150 rpm) and particle size of the bone-based AC adsorbent (< 0.177; 0.177-0.297, 0.297-0.420, 0.420-0.840; > 0.840 mm; a mixture of them) were evaluated on the BK-KJR dye removal by bone-based AC.

In 125 ml Erlenmeyer flasks 300 mg of bone-based AC adsorbent were placed in contact with 50 ml of BK-KJR dye solution with initial concentration of 100 mg·L⁻¹ for pH conditions test, whereas for other preliminary tests 300 mg·L⁻¹ dye concentration were used. The samples remained under constant stirring and temperature conditions at rotary orbital shaker (TECNAL: TE-424) for 24 h. After that, the samples were centrifuged at 3000 rpm for

5 minutes to separate the solid and liquid phases, and an aliquot of the supernatant was removed to determine the remnant dye concentration at UV-Vis spectrophotometer. The amount of dye adsorbed by bone-based AC was determined by using the mass balance:

$$q = \frac{(C_0 - C)V}{m}, \tag{1}$$

where q is the amount of dye adsorbed by adsorbent, ($\text{mg}^{-1}\cdot\text{g}$); C_0 and C are the dye concentrations in the initial and final solution, ($\text{mg}\cdot\text{L}^{-1}$), respectively; V is the solution volume, (L); m is the mass of adsorbent, (g).

Adsorption kinetics

For kinetic experiments, 50 mg of bone-based AC adsorbent in contact with 50 ml of BK-KJR dye solution with an initial concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ and $\text{pH} = 1$ were placed in 125 ml Erlenmeyer flasks. Samples remained during the whole experiment under agitation of 100 rpm and temperature 40°C . At predetermined intervals of time (5 min to 96 h), samples were taken out and then centrifuged at 3000 rpm for 5 minutes and an aliquot of the supernatant was removed for dye concentration analysis at UV-Vis spectrophotometer. The amount of dye adsorbed by the bone-based AC was calculated by Eq. (1). The pseudo-first order (Lagergren), pseudo-second order (Ho), and Elovich models were tested to describe the sorption kinetics (Table 2).

Table 2. Kinetic models of adsorption

Model	Equation	Reference
Pseudo-first order	$q = q_e (1 - \exp(-k_1 t))$	[23]
Pseudo-second order	$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	[20]
Elovich	$q = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln t$	[10]

In the equations in Table 2 k_1 and k_2 are the rate constants (h^{-1}) and ($\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$), respectively; q_e and q are the amounts of dye adsorbed at equilibrium and at a given time, respectively ($\text{mg}\cdot\text{g}^{-1}$); a is the adsorption rate ($\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) and b is the coefficient related with the extension of covered surface and activation energy of chemical-sorption ($\text{mg}\cdot\text{g}^{-1}$).

Adsorption equilibrium

For the equilibrium study, 50 mg of bone-based AC adsorbent in contact with 50 ml of BK-KJR dye solution with different initial concentrations (from 10 to $300 \text{ mg}\cdot\text{L}^{-1}$) at $\text{pH} = 1$ were placed in 125 ml Erlenmeyer flasks. Samples remained for 24 h under agitation of 100 rpm and temperature of 40°C . The samples were then centrifuged at 3000 rpm for 5 minutes and an aliquot of the supernatant was withdrawn for dye concentration analysis by UV-Vis spectrophotometer. The amount of dye adsorbed by the bone-based AC was calculated by Eq. (1). Langmuir, Freundlich and Sips isotherms were used to fit the equilibrium experimental data (Table 3), where q_{max} is the maximum adsorption capacity assuming a monolayer of the adsorbate on the adsorbent, ($\text{mg}\cdot\text{g}^{-1}$); b is the Langmuir affinity constant, ($\text{mg}\cdot\text{L}^{-1}$); C_{eq} is the concentration of adsorbate in solution at equilibrium, ($\text{mg}\cdot\text{L}^{-1}$); K_F and K_S

are Freundlich and Sips constants, respectively; n and n_s are the exponents of Freundlich and Sips, respectively.

Table 3. Isotherms adsorption models

Isotherm	Equation	Application	Reference
Langmuir	$q_{eq} = q_{max} b C_{eq} / 1 + b C_{eq}$	Monolayer, homogeneous surfaces	[24]
Freundlich	$q_{eq} = K_F (C_{eq})^{1/n}$	Multi-layer, heterogeneous surfaces	[16]
Sips	$q_{eq} = \frac{q_{max} (K_S C_{eq})^{n_s}}{1 + (K_S C_{eq})^{n_s}}$	Combination of Langmuir and Freundlich isotherms	[35]

Results and discussion

Preliminary tests

Effect of solution initial pH

An important factor that influences the adsorption process is pH. According to the Çeçen and Aktaş [4], the liquid phase adsorption of organic pollutants by activated carbons in general increases with a decreasing of pH. This is essential for the neutralization of negative charges on the AC adsorbent surface by reducing the diffusion resistance and directing the link to the most active sites. The pH also affects the electrostatic charges of the dye molecule surface. It is well known that cationic dyes removal decreases for lower pH values (acid solutions), while anionic dyes removal increases [33]. Thus, to determine the optimal pH of BK-KJR dye adsorption by bone-based AC, experiments were carried out in the pH range from 1 to 10. The results are exhibited in Fig. 1.

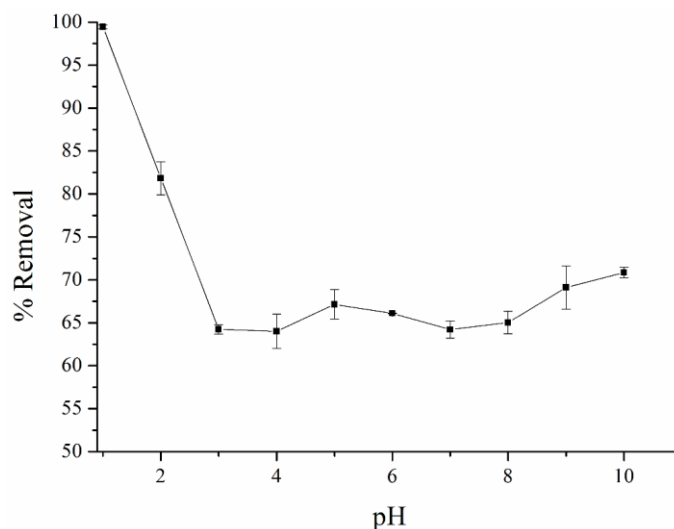


Fig. 1 Effect of pH on BK-KJR dye removal by bone-based activated carbon

Analyzing Fig. 1 one can see that lower initial pH values promoted the higher BK-KJR dye adsorptions by bone-based AC adsorbent, reaching a 98% maximum percentage of BK-KJR dye removal at pH = 1. Therefore, a pH value of 1 was used in subsequent tests.

Effect of sorption temperature

The effect of temperature (20, 30, 40 and 50°C) on the BK-KJR removal by bone-based AC was also investigated. The results are shown in Table 4.

Table 4. Effect of adsorption temperature on BK-KJR dye removal by bone-based activated carbon

Adsorption temperature, (°C)	BK-KJR dye removal, (%)
20	68.33 ± 2
30	98.28 ± 1
40	98.75 ± 1
50	81.19 ± 1

Results presented in Table 4, showing that the BK-KJR dye sorption capacity of the bone-based AC adsorbent increased by increasing the temperature and reaching a maximum value at 40°C where the dye removal value was approximately 98%. This is a well known phenomenon showing that the increase of temperature increases the kinetic energy of the molecules of the solute. In turn, the kinetic energy can be transferred to the internal energy by molecular collisions, leading them toward the activated sites, which are vulnerable to rupture of bonds and adsorption [14]. Moreover, increasing the temperature may result at an increasing of the rate of diffusion of the adsorbate molecules through the boundary layer and within the adsorbent pores due to decreasing of the viscosity of the solution [5, 7].

An increasing the temperature from 40 up to 50°C resulted in lower dye removal and the dye adsorption fell down from 98% to 81%, which can be explained by the following effect: the internal energy of the dye molecules exceeded the bonding strength between them and the adsorbent and then began a process of the desorption.

Effect of stirring speed

Stirring influences the distribution of the solute into the solution and the formation of the boundary layer. Increasing the agitation rate reduces the thickness of the boundary layer and thus improves the solute diffusion to the outer layer of the adsorbent (external diffusion). Table 5 shows the result of this phenomenon and the dependence on the stirring speed of the percentage removal.

Table 5. Effect of stirring speed on BK-KJR dye removal by bone-based activated carbon

Stirring speed, (rpm)	BK-KJR dye removal, (%)
50	91.83 ± 2
100	92.33 ± 3
150	87.12 ± 3

From Table 5, it can be seen that, within a standard deviation, an improvement on the BK-KJR removal by the bone-based AC was not observed with an increasing on the agitation speed independent, suggesting that the adsorption of BK-KJR dye by bone-based AC was not limited by external diffusion.

Effect of particle size

The mass diffusion resistance is greater in particles with greater size. Therefore, if adsorption process is mainly a surface phenomenon, the reduction of particle size conduces at faster removal kinetic processes. In addition, smaller adsorbent particle sizes have higher surface areas, increasing the number of available sites, and therefore the sorption capacity [36]. Thus, the effect of the adsorbent particle size on the removal process was evaluated and the results are shown in Table 6.

Table 6. Effect of particle size in the BK-KJR removal by bone-based activated carbon

Particle Size, (mm)	% of Removal
< 0.177	96.54 ± 1
0.177-0.297	92.58 ± 1
0.297-0.42	87.74 ± 1
0.42-0.84	85.48 ± 1
> 0.84	84.97 ± 1
Mixture of particles	87.30 ± 2

Analyzing Table 6, it was found that the sorption process was promoted by reducing the adsorbent particle size. This resulted in the highest percentage dye removal (about 96%) when was used mean particle size less than 0.177 mm. It has to be noted that the removal rate was around 10% higher than that obtained in a particle size mixture. Thus, considering non-sieving convenience, adsorbent particle size mixture was more appropriate for industrial applications (a reduction on the cost effective) and was used in subsequent tests.

Adsorption kinetic tests

The adsorption kinetics describes the speed with which the dye molecules are transferred from the aqueous solution to the surface area of the adsorbent. In a closed batch system, the amount of dye on the solid surface increased with time until equilibrium was reached, beyond which the solute removal within the fluid phase no longer occurred. The time required to achieve this state was called the equilibrium time and the amount of solute adsorbed at that time corresponded to the maximum amount of adsorbed component from the fluid phase by the adsorbent under determined operating conditions. In Fig. 2 it can be seen the dynamics of adsorption process and the amount of BK-KJR dye adsorbed by the bone-based activated carbon as a function of contact time.

Referring to Fig. 2 (in different scale), it has to be noted that during the first 15 min there was a removal of about 28 mg BK-KJR dye per bone-based AC gram, which correspond to 32% of dye removal. Above 15 min, the adsorption process rate slowed down, needing approximately 24 h to reach the dye sorption equilibrium. The total adsorbed amount was about 53 mg·g⁻¹ (mg of dye per g of bone-based AC). Similar results were obtained in other earlier works [3], removing Blue Turquoise QG and Reactive Yellow 3R dyes by activated carbon. In addition, the kinetic equilibrium times were 800 min and 1200 min for the blue and yellow dyes, respectively.

In order to properly interpret the kinetics of the adsorption process, and check the kinetics hypothesis, a series of theoretical and empirical models were developed and are available at the literature [17]. In our study, pseudo-first order (Lagergren), pseudo-second order (Ho) and

Elovich models were used. The parameters identification of these models were done by applying the Levenberg-Marquardt gradient search method using the OriginLab® Origin 8.0 software. The estimated values of the parameters are presented in Table 7.

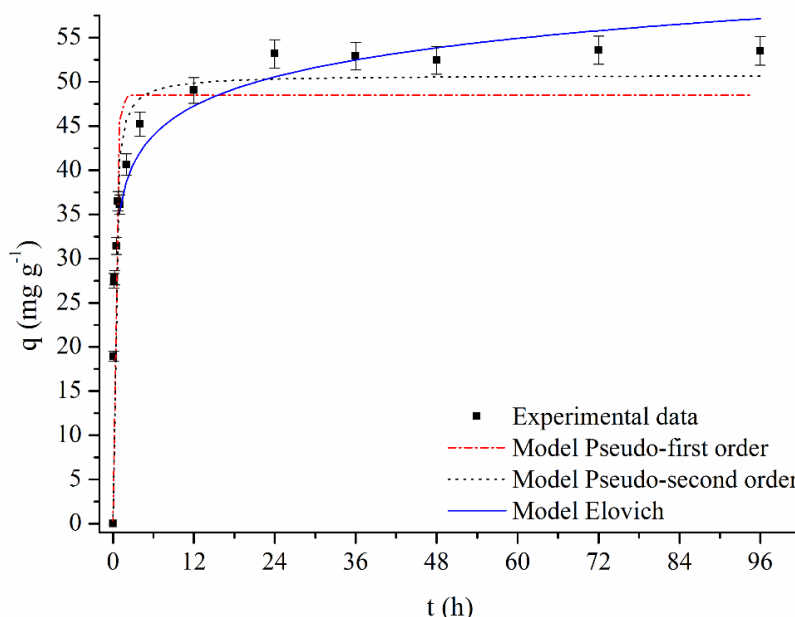


Fig. 2 Adsorption kinetics of BK-KJR dye by bone-based activated carbon

Table 7. Estimated values of parameters of kinetic models on the base of experimental data of BK-KJR dye sorption by bone-based activated carbon

Model	Parameters	Parameter value
Pseudo-first order	k_1 (h^{-1})	2.92 ± 0.6
	q_e ($\text{mg} \cdot \text{g}^{-1}$)	48.50 ± 2.1
	R^2	0.8390
Pseudo-second order	k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$)	0.088 ± 0.02
	q_e ($\text{mg} \cdot \text{g}^{-1}$)	50.78 ± 1
	R^2	0.9431
Elovich	a ($\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$)	8113 ± 3768
	b ($\text{g} \cdot \text{mg}^{-1}$)	0.2100 ± 0.012
	R^2	0.9764

From Table 7, pseudo second order and Elovich kinetic models well fitted to experimental data, according to coefficient of determination (R^2) values, suggesting that the adsorption process is chemical nature [30].

Adsorption equilibrium tests

A proper analysis of an adsorption treatment system require as a vital information the equilibrium data [11], which expresses the relationship between the amount of adsorbed dye by the unit mass of adsorbent (q_{eq}) and the concentration of dye in solution (C_{eq}) when the system reached equilibrium at a given temperature. Such relationship can be described by using many isotherms models [1, 6].

Hence, the models of Langmuir, Freundlich and Sips were fitted to the equilibrium sorption data of BK-KJR dye by the bone-based activated carbon. The estimation of isotherms models parameters was performed by using previously mentioned Levenberg-Marquardt gradient method and the OriginLab Origin 8.0 software ®. The estimated parameters values are shown in Table 8.

Table 8. Estimated values of isotherms parameters on the base of the sorption experimental data obtained on BK-KJR removal by bone-based activated carbon

Isotherms	Parameters	Parameters values
Langmuir	q_{max} (mg·g ⁻¹)	153.82 ± 8
	b (L·mg ⁻¹)	0.0114 ± 0.0012
	R^2	0.9886
Freundlich	K_F (L·g ⁻¹)	5.40 ± 1.2
	n	1.74 ± 0.14
	R^2	0.9547
Sips	q_{max} (mg·g ⁻¹)	129.44 ± 22
	K_S (L·mg ⁻¹)	0.0166 ± 0.006
	n_s	1 ± 0.2
	R^2	0.9742

As can be seen in Table 8, the Langmuir model was the best to fit the equilibrium data according to R^2 values where the estimated parameters of maximum sorption capacity was $q_{max} = 153.82 \pm 8 \text{ mg}\cdot\text{g}^{-1}$ and the affinity constant value $b = 0.0114 \pm 0.0012 \text{ mg}\cdot\text{L}^{-1}$. Moreover, the Sips model was reduced to Langmuir one because the estimated value n_s was equal to 1 [21]. These results of equilibrium data suggested that the sites were energetically homogeneous and the coverage of the adsorbate on the outer surface of the adsorbent occurred in monolayer. The equilibrium data and their simulation results by Langmuir, Freundlich and Sips models are plotted in Fig. 3.

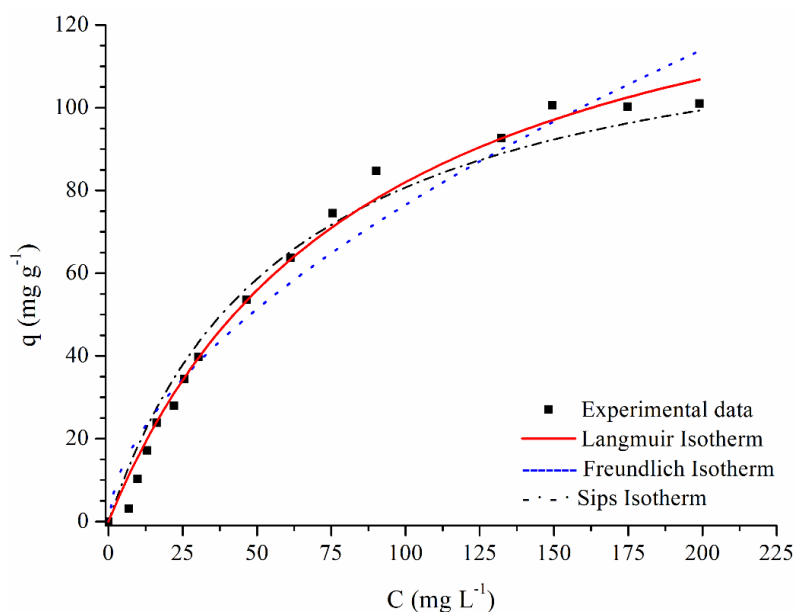


Fig. 3 Sorption equilibrium data and simulation results of the Langmuir, Freundlich and Sips isotherms of BK-KJR dye removal by bone-based activated carbon

Similar results were obtained by other authors [1]. They investigated the potential of the activated carbon prepared from agricultural by-products for tanning removal of dye (anionic dye) in aqueous solution. The results showed that the equilibrium data were well represented by the Langmuir isotherm with maximum adsorption capacity of a monolayer equal to $146.31 \text{ mg}\cdot\text{g}^{-1}$ at 25°C . Therefore, reaching high rates of removal in our system, bone-based AC was considered to be an effective adsorbent for BK-KJR dye removal.

Conclusion

The adsorption of BK-KJR dye by bone-based AC was studied in a batch system. Initially the effect of pH, particle size of the adsorbent, adsorption temperature and stirring speed on the removal of dye were investigated. The selected conditions were initial pH value of 1, mixture of the adsorbent particle sizes, sorption temperature of 40°C and stirring speed of 100 rpm, which were further used at the kinetic and equilibrium tests. During the kinetic experiments of sorption, it was found an equilibrium time of 24 h, with a sorption capacity of about $53 \text{ mg}\cdot\text{g}^{-1}$ and the kinetic data were well described by pseudo second order and Elovich models. The experimental data of equilibrium were best fitted by Langmuir isotherm. Therefore, the optimal results obtained in this study suggested that bone-based AC proved to be an effective sorbent for BK-KJR anionic dye removal from aqueous solution, and thus could be used to treat industrial effluents.

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