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Adsorptive transfer of methylene blue from aqueous solutions to hazelnut husk carbon activated with potassium carbonate

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ABSTRACT

Removal of methylene blue (MB) using activated carbon prepared from hazelnut husk by potassium carbonate (HHPCAC) chemical activation was investigated batchwise. In order to optimize the process, the effect of pH, contact time and initial MB concentration was studied. MB adsorption was favorable at near to neutral conditions. The adsorption of MB also depended on the contact time and reached equilibrium at 120 min. The MB equilibrium was modeled by Langmuir and Freundlich's isotherm equations. The MB adsorption onto prepared activated carbon was found to be compatible with the Langmuir isotherm providing a monolayer adsorption capacity of 333.3 mg g^{-1}. The adsorption kinetics was evaluated with pseudo-first-order, pseudo-second-order kinetic and intraparticle diffusion models. The prepared hazelnut husk activated carbon was found to be an effective adsorbent for removal of MB from aqueous solutions.

Keywords: Methylene blue; Adsorption; Hazelnut husk; Activated carbon; Chemical activation; Potassium carbonate

1. Introduction

Compensation of increasing demands, due to the human population, has necessitated the industrialization of production processes. Wastewater discharges increase along with these processes, unfortunately causing the pollution of water resources and deterioration of their quality [1,2]. Water pollution, which has been a problem for a long time, induces the diminution of clean water resources and this leads researchers to work on wastewater cleaning [3].

A significant portion of the pollution in the aquatic environment is constituted by dyestuffs, which are prevalently applied in areas such as leather, textile, rubber, pharmaceuticals, food, cosmetics, printing and paper industries [4,5]. Discharging colored water into the receiving water environments has constituted a grave menace to the aquatic habitat, water resources and human health because some dye materials can be toxic or even carcinogenic. The plants and animals living in dye-contaminated water are exposed to the detrimental effects of dye; they are devoid of the sunlight they need because the dyestuff reduces the penetration of light into the water [4–6].

Methylene blue is widely used as a model adsorbate to check the adsorption properties of sorbents for dyes in aqueous phases [7]. It is also frequently used in processes such as paper, cotton, wool, leather dyeing; temporary hair dye is also found in wastewaters [7–9]. While MB is not overly harmful, this does not mean that it is completely harmless. The effects of MB on human health as follows: nervous system damage, cardiac rhythm disorders and urinary tract infections, shock, nausea and vomiting, tissue damage, icterus and eye damage [1,8,9].

Adsorption [1], membrane filtration [10], coagulation-flocculation [11,12], liquid-liquid extraction [13], photochemical processes [14] and oxidation [15] are some of the purifying techniques applied in colored wastewater treatment. In the treatment of textile wastewater, chemi-

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cal, biological and photolytic methods are not sufficiently effective on stable chemical structures and the restriction of light permeability by dye molecules, respectively [16]. Numerous pieces of research have investigated adsorption as an easily applicable and inexpensive method without the need for any specialized equipment, which has proved its effectiveness for dye removal [16–23]. The basic component of the adsorption process is the adsorbent. Activated carbon has been a well-known and frequently used adsorbent since ancient times. The carbonaceous materials were converted to a porous structure with various activation processes, so their capacities were increased and they were called activated carbon [24,25]. There are many studies in the literature on the use of different activated carbons prepared from carbonaceous material such as fruit hulls [26], cocoa shells [27], industrial laundry sewage sludge [28], corn cobs [29], reeds [30], silk [31], cattail biomass [32], hazelnut husks [33] and rice hull [34] for dye or metal adsorption. In previous studies, hazelnut husk based novel activated carbon was prepared with chemical activation using potassium carbonate and successfully utilized for the removal of Pb(II) ions from aqueous solutions [24]. The highly efficient adsorption ability of the prepared activated carbon for Pb(II) ions motivated us to investigate its MB adsorption properties.

In this paper, the activated carbon produced by K_2CO_3 activation hazelnut husk (HHPCAC), which is an economical and environmentally friendly precursor material, was used for the MB adsorption by investigation of effective parameters such as solution pH, contact time, dosage and initial MB concentration. In addition, isotherm and kinetic model applications were also studied.

2. Materials and methods

2.1. Chemicals and instruments

Methylene blue stock solution at 1000 mg L^{-1} was prepared by dissolving 1.00 g of MB (319.86 g mol^{-1}, product of Riedel-de Haen AG, Seelze-Hannover, Germany) in 1.00 L of distilled water. Merck (Darmstadt, Germany) supplied the acid and base solutions (0.1 M of NaOH and HCl) used for the pH adjustments.

During the experimental work, an orbital shaker (KS 4000i control, IKA-Werke GmbH, Staufen, Germany) was used for shaking the HHPCAC-MB solution suspension, a digital pH meter (WTW pH 720) was used for pH control of the MB solution, and a spectrophotometer (Hitachi, U-1800, Tokyo, Japan) was used to determine equilibrium MB concentrations.

In order to determine particle size of the HHPCAC, Retsch AS 200, an electrical vibratory sieve shaker (Retsch Technology GmbH, Haan, Germany) was used: the various sieves ranged from 0.053 to 0.600 mm.

Preparation and characterization of the HHPCAC was detailed in the previous study. Briefly, equal amounts of K_2CO_3 and hazelnut husk (20 g) were added to 125 mL of deionized water and the suspension was mixed well using a drumstick. After their interaction at 60°C for 24 h, it was dried at 106°C for a further 24 h. Then, the mixture was pyrolyzed at 600°C under nitrogen atmosphere. The obtained activated carbon was washed with 0.1 M HCl solution, and then with deionized water. After drying the HHPCAC at 105°C, it was used in the experiments. BET surface area and pH_{pzc} values of HHPCAC were reported to be 980.9 $m^2 g^{-1}$ and 4.47, respectively [24]. The particle size range of the HHPCAC is given in Fig. 1.

2.2. Batch adsorption experiments

An MB solution of 50 mL was taken for all of the experimental runs. The MB solutions at two different concentrations (150 and 300 mg L^{-1}) were prepared and used for pH and contact time studies. The adsorbed MB amount part per gram of HHPCAC was investigated at varying pH (3.0–9.0) and contact time (5–240 min). To investigate the effect of the initial concentration, MB solutions (between 100 and 600 mg L^{-1}) were used after stirring for 120 min with 0.050 g of HHPCAC. The MB equilibrium concentrations were measured with a spectrophotometer at 663.0 nm. The adsorbed MB amount part per gram of HHPCAC was computed using Eq. (1):

$$q_t = (C_0 - C_t)\frac{V}{m} \tag{1}$$

where q_t is the amount of MB adsorbed by the HHPCAC (mg g^{-1}) at time t; C_0 and C_t are the initial and remaining MB concentration values (mg L^{-1}), respectively, m is the mass of HHPAAC (g), and V is the solution volume (L) of MB.

3. Results and discussion

3.1. Effect of solution pH

To investigate the effect of pH on adsorption of MB by HHPCAC, the solution pH was adjusted to values between 3.0 and 9.0 at MB concentration of 150 and 300 mg L^{-1}. In addition, MB solutions without any pH adjustment were used to monitor the adsorption at the original pH value (4.7). The results given in Fig. 2 show that the adsorbed MB amount by HHPCAC increased highly in line with pH values from 3.0 to 4.7. But, further increases in pH of the aqueous phase caused a small increase in the MB adsorption. Hence, the subsequent experiments were studied using the MB solutions at a pH of 4.7.

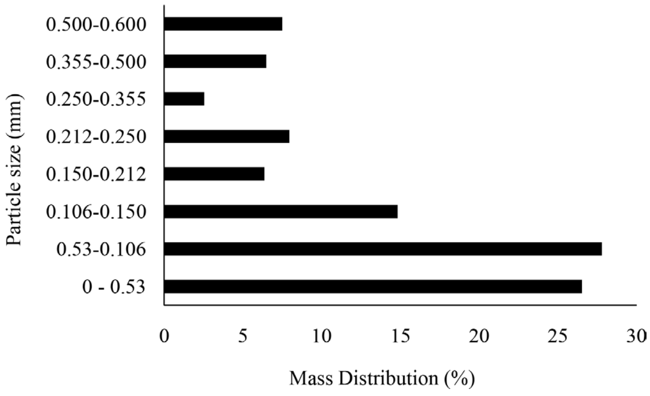

Fig. 1. Particle size distribution of HHPCAC.

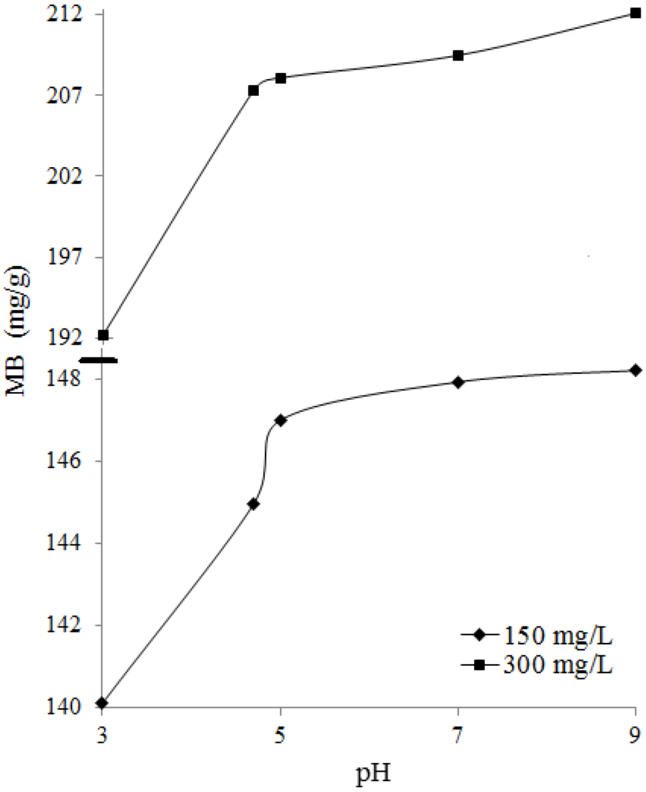

Fig. 2. Effect of pH on MB adsorption with HHPCAC.

The increased MB adsorption by increasing the sample pH can be explained as follows: the pH change in solution affects both the surface of the adsorbent and the ionic species in solution. The surface of the HHPCAC is positively charged below the pH_{pzc} value of 4.47, and negatively charged over this value [24]. The adsorption increased at pH values higher than 4.47 because of the opposite charge of the HHPCAC surface and MB molecules. However, at acidic pH values, a high concentration of hydronium ions in the solution will be in contention with MB molecules for the adsorption on the HHPCAC surface. This contention in basic pH values will abolish the adsorption amount of MB due to declining hydronium ions concentration, so the MB adsorption will be increased [6,8,17,35].

3.2. Effect of contact time

The effect of contact time was evaluated from 5 to 240 min time interval and at two different concentrations (150 and 300 mg L^{-1}). As can be seen in Fig. 3, more than 90% of the MB adsorption on the HHPCAC occurred within the first hour for all samples. There was also a slight increase up to 120 min, but there were minor changes afterwards. The adsorption rate, which was high in the first 60 min, decreased as the equilibrium state approached, depending on the inadequate adsorption sites on the HHPCAC surface for MB molecules. Since the adsorption sites at the beginning were completely unoccupied and easily accessible, the adsorption at the start-up time takes place rapidly. After some adsorption, the adsorption sites that were easily accessible were loaded with MB and the adsorption occurred in the inner pores of the HHPCAC, which requires more time and results in a slower adsorption rate than the beginning time [36,37]. Since the equilibrium between the MB molecules on the adsorbent surface and in the solution was observed over 120 min, the contact time of 120 min was used in subsequent studies.

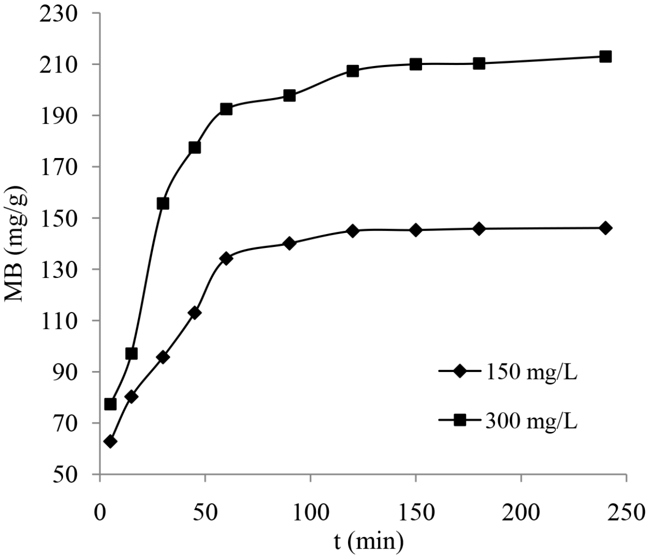

Fig. 3. The contact time effect on MB adsorption with HHPCAC.

3.3. Effect of initial MB concentration

The conducted studies at eight different initial MB concentrations (100–600 mg L^{-1}) and two different HHPCAC doses (0.030 and 0.050 g) showed that the amount of MB adsorbed per gram of HHPCAC increased by increasing the initial MB concentration from 100 to 300 mg L^{-1}. The adsorption amount of MB on the HHPCAC was seen to be independent of the input concentration at higher concentrations (Fig. 4). This is due to saturation of the adsorption sites on the HHPCAC [38,39]. The low q_e values of the 50 mg dosage may be due to clumping HHPCAC particles that hinder MB adsorption. The decrease in the adsorption percentage, by increasing initial MB concentration while the adsorbed amount of MB (q_e, mg g^{-1}) increases, is due to an inverse ratio between the HHPCAC dosage and the amount of MB uptake per gram of HHPCAC, as described in the literature [40,41].

3.4. Isotherm studies

Adsorption isotherms are modeling tools used to explain the adsorbate concentration balance in the solid and liquid phases; the most commonly applied isotherm models within studies of adsorbing pollution from wastewaters are Langmuir [42] and Freundlich's [43] equations. The linear forms of Langmuir and Freundlich's isotherms are shown in Eqns. (2) and (3), respectively:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \tag{2}$$

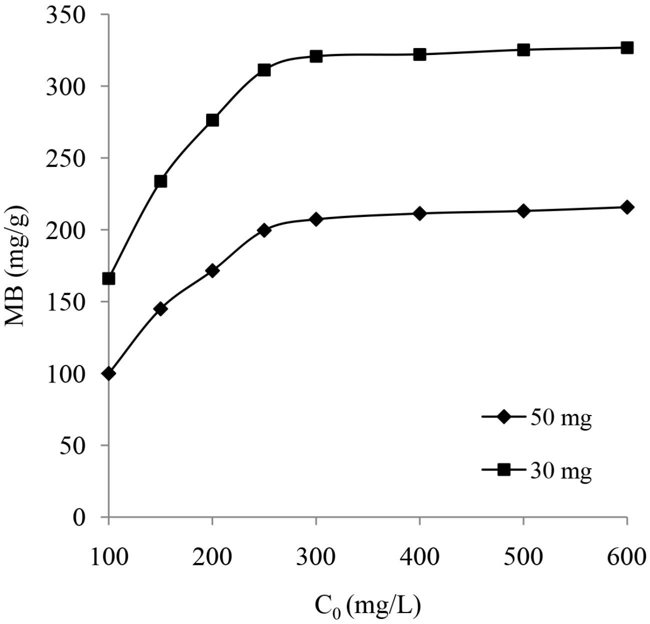

Fig. 4. Effect of initial MB concentration on the adsorption with HHPCAC.

$$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e \tag{3}$$

where C_e (mg L^{-1}) is the equilibrium MB concentration, q_e (mg g^{-1}) is the adsorbed MB amount per gram of HHPCAC, q_{max} (mg g^{-1}) is the maximum adsorption capacity, K_L (L mg^{-1}) is Langmuir's coefficient, which externalizes the relevance between the adsorbent and adsorbate, K_f (L g^{-1}) and $1/n$ are the Freundlich constants, which are related to sorption capacity and sorption intensity, respectively [44,45].

The data obtained as a result of the initial MB concentration studies were used to understand which isotherm model is better to define the MB adsorption on HHPCAC. Table 1 shows the calculated parameters for two isotherms at two different doses. The value of $1/n < 1$ indicates that MB adsorption on the prepared AC represents a convex, L-type (Langmuir-type) isotherm [46]. The regression coefficients (r^2) belonging to Langmuir are very close to unity, but not those of Freundlich, which means that the MB adsorption is defined by Langmuir's isotherm; this expresses a fixed number of adsorption sites with equal size and shape on the single-layer surface of adsorbent [47–49]. In addition, it is clearly seen in Fig. 5 that the experimentally obtained data is quite compatible with those calculated using the Langmuir equation. The lists of MB adsorption capacities of various adsorbents are presented Table 2, and the MB adsorption capacity of HHPCAC was compared with these adsorbents [1,2,9,26,29,36,37,41,49–56]. It is seen that the adsorption capacity of HHPCAC is higher than all of the listed adsorbents, with the exceptions of hazelnut husk carbon activated by zinc chloride and pine cone-activated carbon. Hence, HHPCAC can be acceptable among the adsorbents having high MB adsorption capacity.

Table 1
Parameters of Langmuir and Freundlich isotherms for MB adsorption at different dosage of HHPCAC

	Langmuir constants			Freundlich constants		
HHPCAC Dosage (mg)	q_{max} (mg g^{-1})	K_L (L mg^{-1})	r^2	K_f (mg g^{-1})	n	r^2
30	333.3	0.28	0.9999	191.2	10.0	0.9630
50	217.4	0.26	0.9997	138.9	13.0	0.9674

3.5. Kinetic studies

Pseudo-first-order [57], pseudo-second-order [58] and intraparticle diffusion models [59] were used for the evaluation of MB adsorption rate onto the HHPCAC. The equations for the models used are as follows:

Pseudo-first-order: $$\ln(q_e - q_t) = lnq_e - k_1 t \tag{4}$$

Pseudo-second-order: $$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

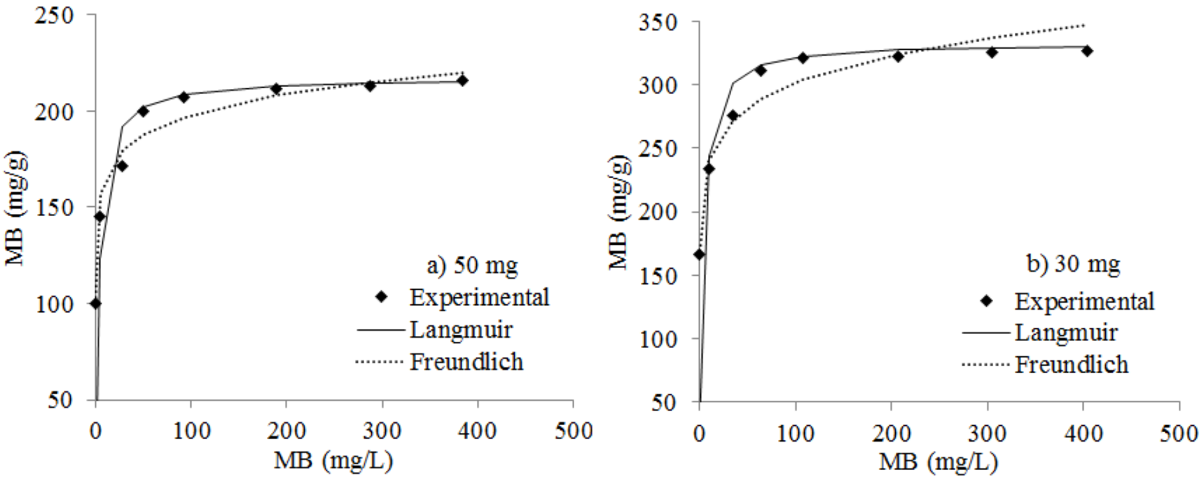

Fig. 5. The harmony comparison of MB adsorption with isotherm curves at different HHPCAC doses.

Table 2
The comparison of maximum adsorption capacities for MB using various adsorbents

Adsorbent	q_{max} (mg g^{-1})	Ref.
Activated lignin-chitosan	36.3	[37]
Corncob AC	82.7	[29]
Fruit hulls AC	239.4	[26]
BiOCl-NPls-AC	84.0	[9]
Canola residues AC	13.2	[49]
Chitosan flake AC	143.5	[50]
Silk powder	80.7	[36]
Vermiculite	203.0	[2]
Grafted MCM-41	204.1	[1]
Graphene oxide	96.2	[51]
Baker's yeast	141.8	[52]
Chitosan/sepiolite composite	41.0	[53]
Hazelnut husk AC by zinc chloride	476.2	[54]
Hazelnut husk AC by phosphoric acid	204.0	[41]
Pine cone-activated carbon	370.9	[55]
Dehydrated hazelnut husk carbon	285.7	[56]
HHPCAC	333.3	This study

Intraparticle diffusion model: $$q_t = k_{id} t^{\frac{1}{2}} + c \qquad (6)$$

where q_e and q_t are the adsorbed MB amounts on the HHPCAC at equilibrium and at time t, respectively. k_1 (min^{-1}), k_2 (g mg^{-1} min^{-1}) and k_{id} (mg g^{-1} min$^{-1/2}$) represent the adsorption rate constants for first order, second order and intraparticle diffusion models, respectively.

Lagergren first proposed the pseudo-first-order kinetic model for defining the adsorption from liquid to solid phase, built on solid capacity. The pseudo-second-order reaction model defines the amount of adsorbed species in equilibrium depending on the number of active binding areas on the adsorbent surface [60]. It is clearly understood from the calculated and presented parameters in Table 2 that the pseudo-second-order kinetic model best characterized the kinetic properties of the MB adsorption process between these two models (Fig. 6), as is the case with similar studies in the literature [61,62]. The closeness of the q_e values calculated by the pseudo-second-order equation and experimentally obtained, and the bigger values of r^2 are proofs of this status.

An intraparticle diffusion model is used to describe the rate control step for the adsorption of dyes or metal ions by solid porous adsorbents. The transports of adsorbates from solution to the solid adsorbent surface generally occur at three steps. The first step indicates the passing of adsorbate from the solution to solid surface (film diffusion). The second step represents the adsorbate transition to the inside of adsorbent particles (intraparticle diffusion), and the third step symbolizes the adsorption of molecules to the interior of adsorbent pores. The last step is very rapid and hence it is negligible [59,63–65]. As can be seen in Fig. 7, the adsorption of MB onto HHPCAC was shown in two regions; the first one is film diffusion and the second is intraparticle diffusion. Similar trends were observed in the literature for adsorption MB onto hazelnut husk AC [54] and Cr(III) adsorption by tea-industry waste activated carbon [65]. The constants calculated for both regions for the adsorption of MB by HHPCAC are presented in Table 3. The values of k_{id1} were higher than k_{id2}, showing that the rate-limiting step is intraparticle diffusion. However, the fact that the line does not pass through the origin indicates that the rate of adsorption is not only controlled by intra-particulate diffusion. Hence, it was concluded that the adsorption of MB by HHPCAC is a complex process and the rate of adsorption controlled by film diffusion and intraparticle diffusion [54,64,65].

4. Conclusions

The current work is a narrative of the successful removal of MB dye from aqueous solution with an adsor-

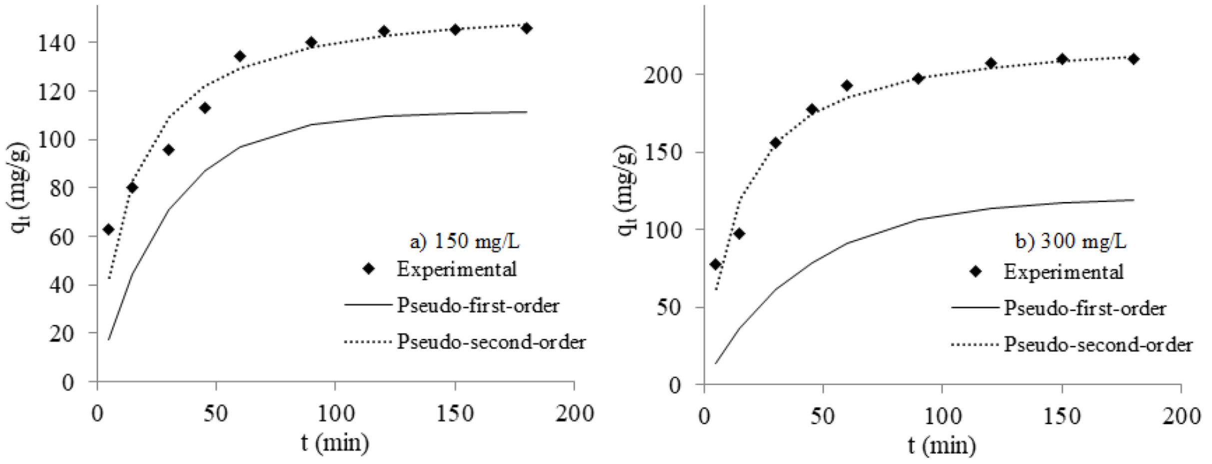

Fig. 6. Comparison of experimentally found q_e values with the predicted q_e values by pseudo-first- order, pseudo-second-order kinetic models.

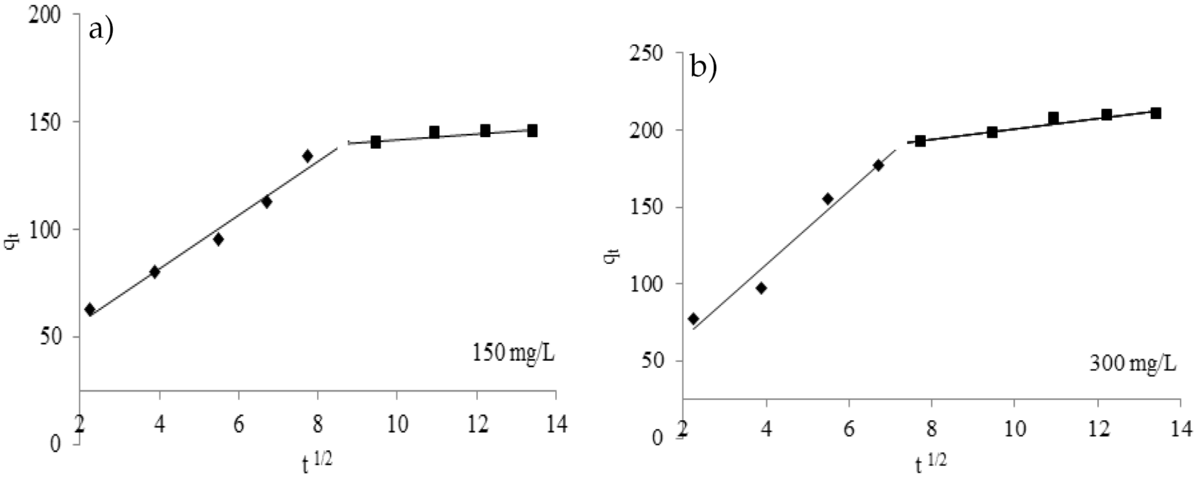

Fig. 7. Graph of intraparticle diffusion model for MB adsorption with HHPCAC.

Table 3
Parameters of kinetic models for MB adsorption onto HHPCAC

Kinetic model	Constants		C_0 (mg L^{-1})	
			150	300
Pseudo first order	$q_{e\,exp}$	(mg g^{-1})	146.1	213.0
	$k_1 \times 10^2$	(min^{-1})	3.4	2.3
	$q_{e\,cal}$	(mg g^{-1})	111.7	121.0
	r^2		0.9840	0.9656
Pseudo second order	$q_{e\,exp}$	(mg g^{-1})	146.1	213.0
	$k_2 \times 10^3$	(g mg^{-1} min^{-1})	0.5	0.3
	$q_{e\,cal}$	(mg g^{-1})	158.7	227.3
	r^2		0.9963	0.9977
Intraparticle diffusion	k_{id1}	(mg g^{-1} min$^{-1/2}$)	12.5	23.9
	r^2		0.9780	0.9613
	k_{id2}	(mg g^{-1} min$^{-1/2}$)	1.4	3.4
	r^2		0.7614	0.9223
	c	(mg g^{-1})	55.4	73.6

bent obtained by inexpensive, environmentally friendly, easily accessible starting material. The resulting capacity (333.3 mg g^{-1}) is quite satisfactory. It can certainly be said that it is an easy-to-apply process that does not require pH adjustment and does not need to wait more than 120 min for the equilibrium. Langmuir's and pseudo-second-order models better define the isotherm and kinetic characters of MB adsorption process on HHPCAC, respectively. HHPCAC has been shown to be a promising and effective adsorbent for MB removal from wastewaters.

Acknowledgments

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