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Removal of methylene blue from aqueous solution using acid/base treated rice husk as an adsorbent

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ABSTRACT

An agricultural waste, cheap and easily available rice husk is chemically modified with acid/base and used as an adsorbent for the removal of methylene blue (MB) (one of the industrially important dye) from aqueous media. The adsorption data were evaluated by Freundlich, Langmuir and Dubinin–Radushkevich isotherm models. Langmuir model showed best fit to the data indicating the formation of monolayer. The adsorption capacity (q_m) of the chemically modified rice husk was found to be 93.5 mg/g at a temperature of 298 K which is higher than that reported earlier in the literature which suggests that the treated rice husk can be efficiently used for the removal of MB. The adsorption kinetics was investigated by pseudo-first-, pseudo-second-order kinetic and intra-particle diffusion models. The q_e value calculated from pseudo-second-order kinetic model is in agreement with the experimental value with higher correlation coefficient (0.9988). The non-linearity of intra-particle diffusion model is an indication that more than one mechanism is involved in the adsorption process.

Keywords: Methylene blue; Rice husk; Adsorption kinetics; Langmuir model

1. Introduction

Dyes stuffs are widely used substances in industries including textile, pharmaceutical, food, leather, pulp mills and paper [1–2]. There are more than 10,000 commercially available dyes with over 7×10^5 tones of dyestuff produced annually across the world [3]. The release of dyes can pollute the environment, especially in the form of wastewater. Dyes and other organic compounds form foam which cover the surface of water and reduces oxygen diffusion through the water surface [4]. These complex aromatic structures of dyes make them more stable and difficult for biodegradation. Furthermore, the excess of dyes can cause serious health-related issues while certain dyes are carcinogenic and mutagenic in nature [5]. It is estimated that 10–15% dyes from only textile industry is released with effluent while total textile consumption is more than 10^7 kg per annum [6]. Methylene blue (MB) is also used in textile, printing, leather and pulp mills and the effluents are released in the lakes and rivers [7,8]. MB can cause eye injury for both human and animals [8]. On inhalation it can give rise to short period of rapid or difficult breathing [9], ingestion through mouth produces burning sensation and may cause nausea, vomiting, profuse sweating, diarrhoea, gastritis, mental confusion and

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methmoglobinemia [10–12]. Thus the removal of MB from industrial effluents has become one of the major environmental concerns.

Various physical and chemical processes have been employed for the removal of such coloured effluents from water such as coagulation, ozonation, flotation, oxidation, photo-degradation and reverse osmosis. But adsorption is a well-known and superior technique for the removal of dyes and other organic hazardous materials because of its easy operation, insensitivity to toxic substances, ability to treat concentrated forms of the dyes and the possibility of reusing the spent adsorbent via regeneration [13,14]. Many low-cost adsorbents have been used for this purpose such as Bentonite, yellow passion fruit peel, papaya seeds, orange peels, saw dust, walnut shells, Zeolite synthesized from fly ash, swelling clay, cedar saw dust and crushed bricks [15–20], but there is still a need for adsorbents which are cheap, easily available and efficient.

The present study reports the removal of MB by chemically modified rice husk from aqueous media. Different adsorption isotherms such as Freundlich, Langmuir and Dubinin–Radushkevich (D–R) models have been applied to the adsorption data. The adsorption kinetics and mechanism is also investigated in the present work.

2. Experimental

2.1. Chemicals used

The chemical used were MB (82%, Fluka), sodium hydroxide (≥97%, Fluka) and sulphuric acid (98%, Merck). These chemicals were used as received without further purification. The rice husk was collected from the local rice mill and chemically modified for further studies.

2.2. Activation of rice husk

Rice husk was thoroughly washed with deionized water to remove muddy materials after its collection from the local rice mill. After washing, it was soaked in 0.1 N sodium hydroxide solution (the solution was prepared in deionized water) for four hours to remove lignin-based coloured materials. After that this material was then dipped in 0.1 N H_2SO_4 for two hours and finally washed again with deionized water until the neutral pH was obtained. It was dried in an oven overnight and was then grinded up to 20–40 mesh. This was washed again with deionized water several times and finally dried in oven at 373 K for 12 h and cooled to room temperature [21]. The final material was stored in a desiccator and was used for all the further studies.

2.3. Time optimization

In order to optimize the shaking time, 25 ml of 5×10^{-4} M solution of the MB was taken in 12 different conical flasks. Pre-optimized amount (1 g) of acid/base-treated rice husk was added in each flask and was shaken in an electric shaker at 120 strokes/min for various times from 5 to 60 min. The solution was then filtered and the absorbance was taken at λ_{max} (665 nm) of MB and the amount of dye adsorbed per gram of the adsorbent was calculated using the following equation:

$$q_e = \frac{C_{ad} \times A \times V}{m \times 1,000} \tag{1}$$

where q_e (mg/g) is the amount adsorbed per gram of the adsorbent, C_{ad} (mol/L) the concentration of dye adsorbed on the adsorbent, A (g/mol) molecular weight of MB, V (L) the volume of the dye solution used for adsorption purpose and m (g) is the amount of adsorbent used. The plot between q_e and time shows that the equilibrium was attained at 30 min so this shaking time was chosen for further studies. These data were also used for the kinetic studies.

2.4. Adsorption studies

The aqueous solutions of different concentrations of MB ranging from 1×10^{-4} to 1×10^{-3}M were prepared in deionized water. The optimized amount of adsorbent (1 g) was then added to 25 mL solution of the dye in conical flasks. These flasks were shaken in an electric shaker at the rate of 120 strokes/min for an optimized time of 30 min. The solutions were filtered and the absorbance of filtrate was recorded at the λ_{max} (665 nm). The amount of dye adsorbed q_e was calculated by Eq. (1) and obtained data were used for various adsorption isotherm models.

3. Results and discussion

3.1. Scanning electron microscopy

The scanning electron microscopy (SEM) images for the unmodified, modified rice husk before and after adsorption are shown in Fig. 1(a)–(c). It is clear from the figure that the rice husk without modification (Fig. 1(a)) is less porous as compared to the chemically modified rice husk (Fig. 1(b)). The higher porosity in the acid/base-treated rice husk indicates

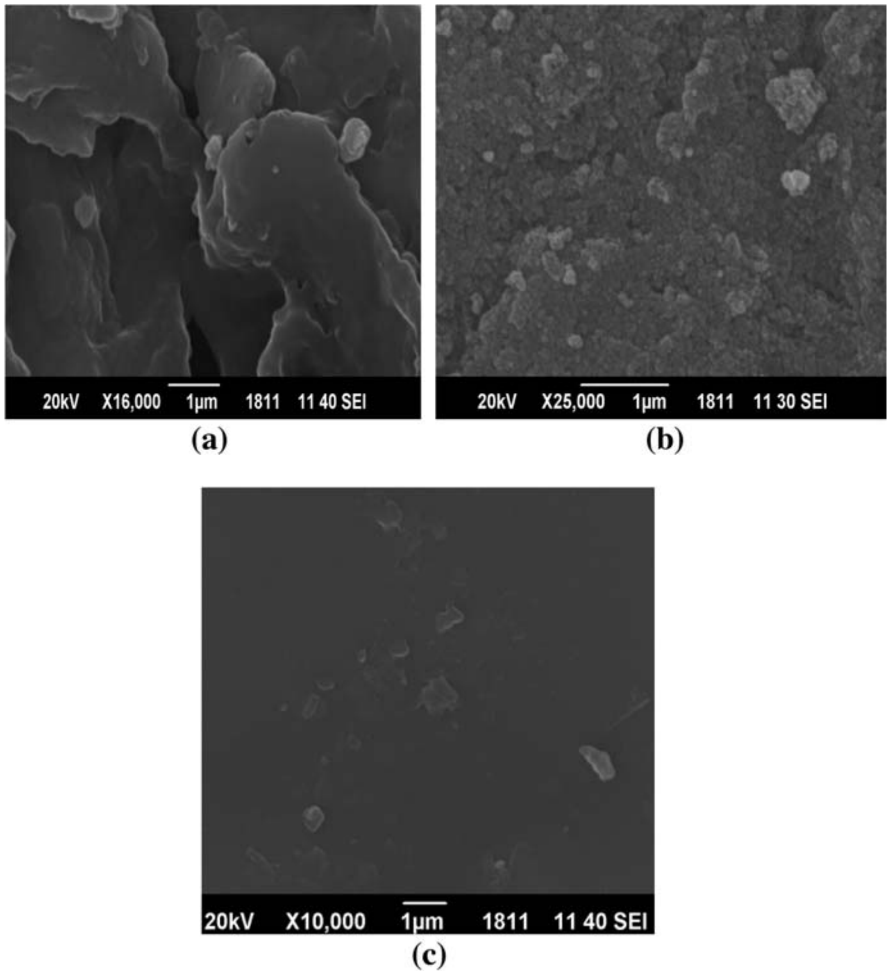

Fig. 1. SEM images for rice husk: (a) unmodified, (b) modified before adsorption and (c) modified after adsorption process.

that it can be a better adsorbent. The SEM image after the adsorption of MB is shown in Fig. 1(c) and shows that all the pores are filled with the adsorbate and shows smooth surface.

3.2. Adsorption isotherms

The graph is plotted between the amount of dye adsorbed (q_e) and equilibrium concentration (C_e) and is shown in Fig. 2. The graph shows the L-type isotherm, indicating that the MB has good affinity towards the adsorbent. The adsorption data was fitted to isotherms models such as Freundlich, Langmuir and D–R in order to get information about the properties and mechanism of adsorption process.

3.3. Freundlich model

Freundlich isotherm is an empirical model used for non-ideal adsorption on the heterogeneous surfaces system. The linear form of Freundlich isotherm is given as [22]:

$$\ln q_e = K_F + \frac{1}{n} \ln C_e \tag{2}$$

where C_e (mol/L) is the equilibrium concentration of dye at equilibrium time, q_e (mg/g) is the equilibrium amount of adsorbate adsorbed per gram of the adsorbent, the K_F and n are the Freundlich constants. The values of Freundlich constants i.e. K_F and n obtained from the intercept and slope of the linear plot of ln q_e vs. ln C_e, respectively. The n (dimensionless) is related to the surface homogeneity and gives indication of how favourable the adsorption process is while K_F (mg/g) is related to the relative adsorption capacity. When "n" is greater than unity then the adsorption process is favourable, if it is equal to one then the adsorption is homogeneous and there are no interactions between adsorbed species and when it is less than unity then adsorption is unfavourable. In the

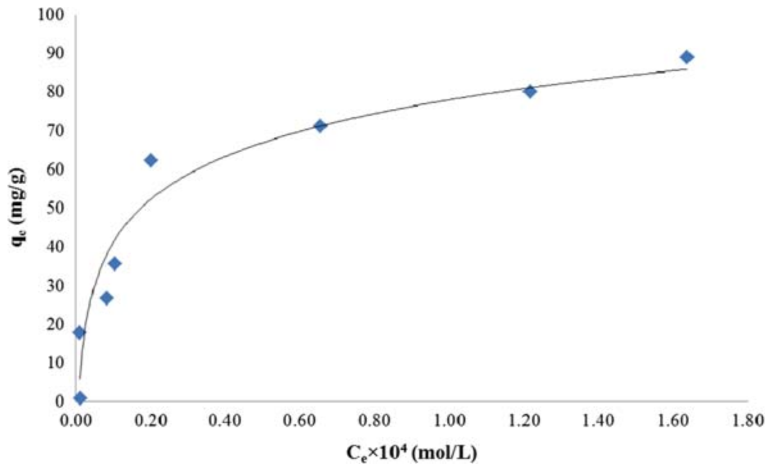

Fig. 2. Adsorption isotherm for the adsorption of MB on the surface of modified rice husk at 298 K.

present investigation, the value of "n" is greater than unity i.e. 3 (Table 1) which indicates that the adsorption is favourable. The larger value of K_F (1542.7 mg g^{-1}) shown in Table 1 indicates that the acid/base-treated rice husk has good adsorption capacity for MB. The value of K_F in the present study is greater than that of earlier reported adsorbents used for MB from aqueous solution [23–25].

3.4. Langmuir model

The Langmuir adsorption isotherm has been widely used for the adsorption of solute from liquid solution and gives information about the adsorption capacity of the adsorbent. This model is based on the assumption that adsorption takes place on the homogeneous surface having large number of identical active sites and represents the monolayer adsorption. The linear form of Langmuir model is given as [8]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + a_L \frac{C_e}{K_L} \quad (3)$$

where K_L (L/mg) and a_L (g/L) are the Langmuir constants which correspond to the energy of adsorption and binding force between adsorbent and adsorbate, respectively. The linear plot of C_e/q_e vs. C_e gives the values of K_L and a_L from the intercept and slope of this plot, respectively and the values of both the constants are reported in Table 1. The Langmuir model gives better fit to the adsorption data of MB onto the surface of treated rice husk with higher correlation coefficient (R^2) of 0.9891 as compared to that of Freundlich isotherm having R^2 value 0.9571. This indicates the homogeneous surface of the rice husk. The Gibbs free energy (ΔG) is also calculated and is found to be –38.2 kJ/mol and this high negative value of free energy indicates that the adsorption process of MB on rice husk is spontaneous.

Table 1
Analysis of the results of adsorption of MB onto acid/base-treated rice husk

Isotherms models	Parameters	Values
Freundlich model	$n \pm 0.1$	3.00
	K_F (mg/g) ± 2.0	1,542.7
	R^2	0.9571
Langmuir model	q_m (mg/g) ± 1.0	93.5
	a_L (g/L) ± 3.0	5.4×10^4
	K_L (L/mg) ± 2.0	5.0×10^6
	R^2	0.9891
D–R model	E (kJ/mole) ± 1.0	235
	A_m (mg/g) ± 1.0	75.04
	R^2	0.7871

The adsorption capacity of the adsorbent q_m (mg/g) is calculated by following relation [8]:

$$q_m = \frac{K_L}{a_L} \quad (4)$$

The value of q_m in the present work is compared with number of recently reported adsorbents used for the adsorption of MB in Table 2. It is evident from Table 2 that the value of adsorption capacity in the present work (93.5 mg/g) is higher than many of adsorbents reported in literature [26–41]. The value of q_m is also compared with rice husk and the materials obtained from rice husk such as activated carbon and found higher adsorption capacity as compared to Refs. [26,37] but lower than the activated carbon obtained from rice husk [39,41]. Furthermore, being an agriculture waste, the rice husk is easily available and a cheap material in agricultural countries such as Pakistan, India and Bangladesh, so it can be used as potential adsorbent for the removal of MB.

3.5. D–R model

The D–R isotherm model has been used in order to gain information that the adsorption of MB on the rice husk is chemisorption or physical adsorption. The D–R isotherm model can be expressed as follows [25]:

$$\ln q_e = \ln A_m - \beta \varepsilon^2 \quad (5)$$

where A_m (mg/g) is the maximum amount of dye adsorbed on the rice husk to form monolayer, β is related to the sorption energy and ε is calculated from following equation [25]:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

The linear plot between $\ln q_e$ and ε^2 gives the values of β and A_m from the slope and intercept, respectively and their values are given in Table 1. The value of β is used to calculate the sorption energy using following equation:

$$E = \frac{\beta^{-1/2}}{\sqrt{2}} \quad (7)$$

The calculated value of sorption energy (E) for the adsorption of MB onto acid/base-treated rice husk is found to be 235 kJ/mol (Table 1) indicating the chemisorption of this dye.

Table 2
Comparison of adsorption capacity (q_m) of various adsorbents reported in literature and rice husk (present work)

Adsorbents	Q_m/mg/g	References
Indian rosewood sawdust (formaldehyde treated)	11.8–51.4	[26]
Rice husk (grinded to powder)	40.58	[27]
Neem leaf (powder)	8.76–19.61	[28]
Papaya seeds (crushed)	555.557	[29]
Jute processing waste	22.47	[30]
Eggshell and eggshell membrane	0.80–0.24	[31]
Fly ash	13.42	[32]
Wheat shells (grinded to powder)	16.56–21.50	[33]
Activated date pits (500℃)	12.9	[34]
Activated date pits (900℃)	17.3	[34]
Banana peel (washed and dried)	20.8	[35]
Pumpkin seed hull (crushed)	141.92	[36]
Garlic peel at various temperature	8.62 (303 K)	[37]
	123.4 (313 K)	
	142 (232 K)	
Rice Husk (washed and dried)	4.41	[38]
Rice Husk's activated carbon	441.52	[39]
Peanut Husk (powder)	72.13	[40]
Rice Husk (washed and dried)	312	[41]
Present work	**93.5**	

Table 3
Pseudo-first-order and pseudo-second-order kinetics parameters for the removal of MB onto rice husk

q_e (exp.)/mg g^{-1}	Pseudo-first-order			Pseudo-second-order		
	q_e/mg g^{-1} (10^5)	k_1/min^{-1} (10^2)	R^2	q_e/mg g^{-1} (10^5)	k_2/g mg^{-1} min^{-1} (10^{-3})	R^2
2.76×10^{-5}	6.10	4.36	0.9356	2.80	2.27	0.9988

3.6. Adsorption kinetics

The mechanism of adsorption depends upon the physical and chemical properties of the adsorbent as well as the mass transport process [42]. Three different adsorption kinetic models namely pseudo-first-order, pseudo-second-order and intra-particle diffusion model were used in order to determine the mechanism of MB onto the rice husk.

The linear form of pseudo-first kinetic model is given as [43]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{8}$$

where q_e is the equilibrium amount of dye adsorbed on the adsorbent at equilibrium time, q_t is adsorbed amount at specific time, t the shaking time and k_1 is the specific rate constant for first order. The values of k_1 and q_e are obtained from the slope and intercept of the plot $\ln(q_e - q_t)$ vs. time as shown in Fig. 3 and the values are given in Table 3.

The pseudo-second order-kinetic equation is as follows [43]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

where k_2 is the specific rate constant for pseudo-second-order and other parameters have the same definitions. The linear plot of t/q_e and t gives the values of k_2 and q_e from intercept and slope as shown in Fig. 4. The values of both the parameters are given in Table 3. The correlation coefficient (R^2) for the pseudo-second-order is found to be 0.9988 which is higher than that of pseudo-first order 0.9356 indicating that the adsorption kinetic for the MB on the rice husk follows the pseudo-second-order kinetic model. Secondly, the q_e value calculated from pseudo-second-order model is found to 2.87×10^{-5} mg/g is found to be very close to the experimental value 2.76×10^{-5} mg/g. But the q_e value calculated from pseudo-first-order model is found to be 0.0061 mg/g which is not matching the experimental value which confirms that the adsorption process for MB on rice husk follow the pseudo-second-order kinetics.

The intra-particle diffusion model has also been fitted to the adsorption data in order to see the adsorption mechanism of MB onto the rice husk. The intra-particle diffusion equation is given as [43]:

$$q_t = k_{ID}\sqrt{t} + C \tag{10}$$

where k_{ID} (mg g^{-1} min$^{-1/2}$) is the rate constant, while C is the constant related to the thickness of boundary layers. It has been reported that the plot of q_t vs. $t^{1/2}$ should be a straight line if diffusion play a role in the adsorption rate and if intra-particle diffusion is the rate-determining step then the plot should give zero

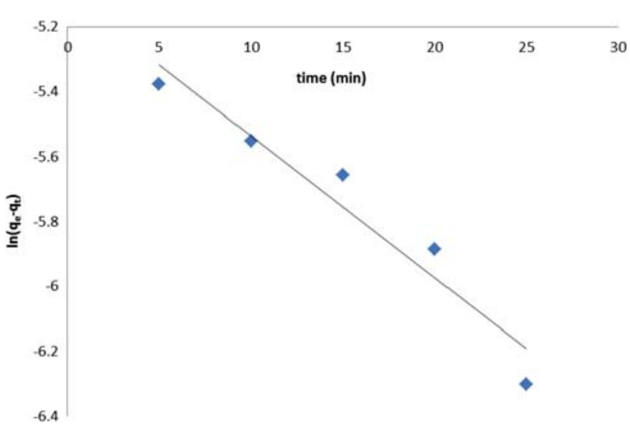

Fig. 3. Pseudo-first-order kinetics plot for the adsorption of MB on rice husk.

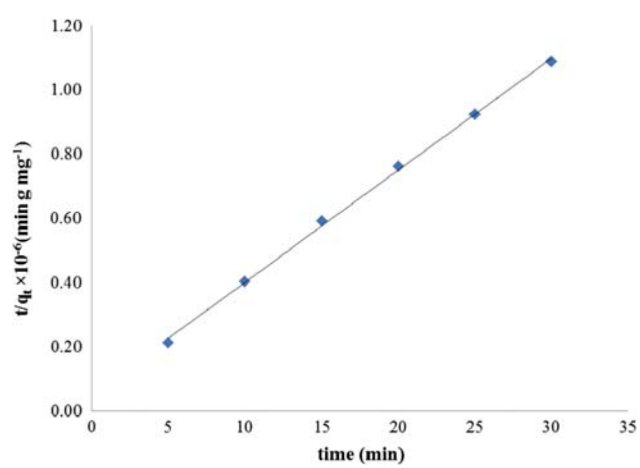

Fig. 4. Pseudo-second-order kinetics plot for the removal of MB from rice husk.

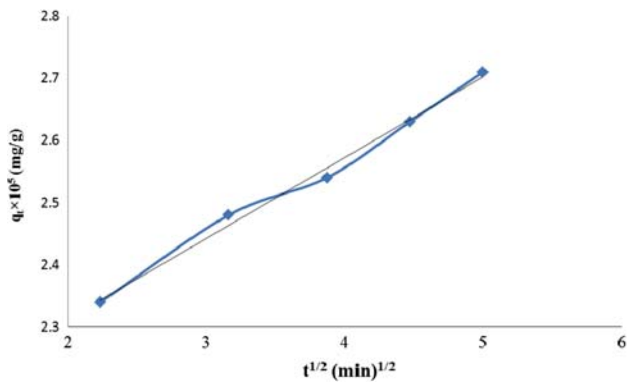

Fig. 5. Intra-particle diffusion model plot for the adsorption of MB on rice husk.

value of intercept [43]. In the present work, non-linearity of the graph between q_t and $t^{1/2}$ (Fig. 5) indicates that different mechanism with different rate constants involved in the adsorption process. Fig. 5 shows two linear regions. The first linear region (0–10 min) can be related to mass transfer effects taking place with boundary layer diffusion, while the second linear parts indicate intra-particle diffusion. The first linear part may be attributed to the diffusion through larger pores while the second part indicates the diffusion through micro and meso-pores. The higher value of k_ID_1 (2×10^{-5} mg g^{-1} min$^{-1/2}$) than that of k_ID_2 (1×10^{-5} mg g^{-1} min$^{-1/2}$) indicates the diffusion through larger pores is greater than micro and meso-pores. The line did not pass through the origin, indicating that the intra-particle diffusion is not the rate-limiting step.

3.7. Effect of pH

The change in pH affects the surface properties of the adsorbent due to adsorption of hydrogen and hydroxyl ions. Fig. 6 shows the variation of amount of MB adsorbed on the surface of rice husk and pH. It is obvious from the figure that the removal of MB increases with the increase in pH. At lower pH, the H^+ ions are adsorbed and create a positive charge on the surface of rice husk. Increase in pH results in the reduction of hydrogen ions on the surface which results in the reduction of positive charge on the surface. Consequently, the adsorption of MB increases as it is cationic in nature.

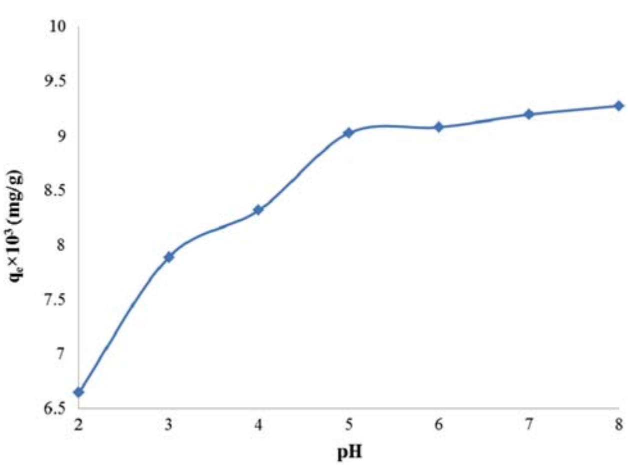

Fig. 6. Effect of pH on the adsorption of MB on rice husk.

4. Conclusions

(1) The adsorbed amount of MB i.e. 93.5 mg/g onto chemically treated rice husk is higher than that of many other adsorbents reported in the literature suggesting that the acid/base-treated rice husk can be efficiently utilized for the removal of MB from aqueous media.
(2) The adsorption data follow the Langmuir model well indicating the formation of monolayer.
(3) The higher value of activation energy (235 kJ/mol) and negative value of Gibbs free energy (–38.2 kJ/mol) indicate that the chemisorption takes place on the surface of adsorbent and the adsorption process is spontaneous, respectively.
(4) The value of equilibrium amount of dye adsorbed on the adsorbent calculated by pseudo-second-order kinetic model is in agreement with that of experimental value suggesting that the adsorption process follow the pseudo-second order kinetic model.
(5) The two linear regions in the Intra-particle diffusion model plot indicate that mass transfer effects taking place with boundary layer diffusion and diffusion through micro and mesopores.

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