



## Equilibrium Modeling and Kinetic Studies on the Adsorption of Basic Dye by a Low Cost Adsorbent

Zohreh Saadati<sup>a,\*</sup>, Anita Makvandy<sup>a</sup>

<sup>a</sup>*Department of Chemistry, Islamic Azad University, Omidyeh Branch, Omidyeh, Iran*

### Abstract

An agricultural waste and eco-friendly biosorbent i.e. rice husk has been used as a cheap adsorbent for the removal of methylene blue dye from aqueous solutions. The physical properties of the developed adsorbent were characterized using FTIR. The study was realized using batch experiments. The effects of contact time, pH, initial dye concentration, biosorbent dose and temperature were investigated. The adsorption data were evaluated by Freundlich and Langmuir isotherm models. The adsorption isotherm is best fitted by the Freundlich model, while the adsorption kinetics is well described by the pseudo-second-order model. Different thermodynamic parameters i.e., changes in standard free energy, enthalpy and entropy have also been evaluated and it has been found that the dye adsorption onto rice was a spontaneous, endothermic and physical reaction.

**Keywords:** Rice husk; Biosorption; Kinetic study; Isotherm; methylene blue; basic dye

### 1. Introduction

Color is a visible pollutant and the presence of even a very minute amount of coloring substance makes it undesirable due to its appearance. The removal of color from dye-bearing effluents is a major problem due to the difficulty in treating such waste waters by conventional treatment methods. The sorption technique is proved to be an effective and attractive process for the treatment of these dye-bearing wastewaters [1,2]. The most widely used and effective physical method in industry is activated carbon, although running

costs are expensive [3]. If the adsorbent material used is of cheaper cost and does not require any expensive additional pretreatment step, this method will become inexpensive. In recent years, some papers had reported several kinds of agricultural by-product such as rice husk [4-5], cereal chaff [6], giant duckweed [7], sawdust [8] for the removal of methylene blue from its aqueous solutions.

Physical and chemical methods such as biological oxidation, adsorption, foam flotation, electrolysis, coagulation-flocculation, ozonation, oxidation, filtration, membrane separation, photo catalysis and electrochemical methods have been used for waste water decolourisation [9-20].

\*Corresponding Author

E-mail address: [zohrehsaadati@gmail.com](mailto:zohrehsaadati@gmail.com)

The adsorption process is one of the most efficient methods of reactive, acidic and direct dyes in neutral solutions removing pollutants from wastewater and provides an attractive alternative treatment, especially if the biosorbent is inexpensive and readily available [21].

The abundance and availability of agricultural by-products make them good sources of cheap raw materials for natural adsorbents. Rice husk, an agricultural waste, has been reported as a good adsorbent for many metals and basic dyes [22-23]. Rice husk consists of 32.2% cellulose, 21.4% hemicelluloses and 21.3% lignin [24-25]. The cellulose, hemicellulose and lignin form a very stable matrix structure. The inner surface of rice husk is smooth, and may contain wax and natural fats that provide good shelter for the grain. On the other hand, the presence of these impurities on the inner surface of rice husk also affects the adsorption properties of rice husk, both chemically and physically [26]. Scanning Electron Microscope (SEM) of rice husk showed the morphological features of outer epidermis raw rice husk, which is well organized in structure that resembles rolling hills [27].

In the purpose of this work, adsorption capacity of rice husk for the adsorption of methylene blue dye from aqueous solutions has been investigated and the obtained experimental data were analyzed using isotherm models namely, Langmuir and Freundlich. The effect of pH, adsorbent amount, contact time, biosorbent dose, temperature and initial dye concentration has been studied. Kinetic experiments have been also conducted to determine the rate of adsorption. Methylene blue is the most commonly used material for dyeing cotton, wood and silk. Methylene blue was chosen because of its known strong adsorption onto solids and it serves as a model compound for removing organic contaminants and colored bodies.

## 2. Materials and methods

All chemicals and reagents were of analytical grade. Basic dye used in this study was methylene blue (molecular formula:  $C_{16}H_{18}N_3ClS$ ,  $\lambda_{max} = 665\text{nm}$ ) purchased from Merck. The experimental solutions were obtained by diluting the stock solution in accurate proportions to different initial concentrations. The rice husk was obtained from a farm near Omidiyeh city, Khuzestan state, Iran. Rice husk was washed several times with water followed by filtration. The cleaned rice husk was oven dried completely at  $70^\circ\text{C}$ , then cooled and sieved to  $50\mu\text{m}$  size, which was used without further treatment.

### 2.1. Batch adsorption studies

Adsorption experiments were carried out by adding a fixed amount of rice husk to a series of Erlenmeyer flasks filled with 25 mL diluted solutions. The Erlenmeyer flasks were shaken at 300 rpm for 6 hours at room temperature. After equilibration, 10 mL of the suspension was centrifuged in a stopped tube for 10 min at 3000 rpm and 4 mL of the dye solution was taken from the tube by a filtered syringe for measurement. The color of dye concentrations were measured with a PerkinElmer Lambda 25 UV/Vis Spectrometer using maximum absorbance wave length values ( $\lambda_{max}$ ) for each dye. To determine the optimum conditions of the several parameters such as contact time, pH, initial dye concentration, biosorbent dose and temperature were studied for methylene blue dye. Using optimum conditions dye removal capacity, equilibrium values and kinetic studies were performed for methylene blue dye.

The amount of methylene blue adsorption at equilibrium,  $q_e$  (mg/g) was calculated from the following equation [28]:

$$q_e = \frac{(C_0 - C_e) \times V}{w} \quad (1)$$

Where  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium liquid phase concentration of dye solutions, respectively,  $V$  (L) the volume of the solution and  $W$  (g) is the mass of adsorbent. Decolourisation of dyes sorbed by rice husk was calculated using the following equation [28]:

$$\text{Removal percentage} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

### 3. Results and discussion

#### 3.1. Characterization of the adsorbent

FTIR spectroscopy was used for the characterization of rice husk. The FTIR spectrum (Fig. 1) indicated a broad band at  $3410.24 \text{ cm}^{-1}$  representing the bonded -OH groups. The C-H stretching vibration around  $2925.16 \text{ cm}^{-1}$  indicates the presence of alkane functional group. The peaks around  $1648.38$ - $1740 \text{ cm}^{-1}$  correspond to the C=O stretching that may be attributed to the hemicelluloses and lignin aromatic groups [29]. The peaks around  $1514.67 \text{ cm}^{-1}$  indicate the presence of C=C stretching vibrations of alkenes and aromatic functional groups. The peaks around  $1425.63 \text{ cm}^{-1}$  indicate the presence of  $\text{CH}_2$

and  $\text{CH}_3$  groups [30]. A peak at  $1376.64 \text{ cm}^{-1}$  band may be attributed to the aromatic CH and carboxyl-carbonate structures. The peaks in the  $1254.50$ - $1300 \text{ cm}^{-1}$  correspond to vibration of C-O group in lactones.

The peaks around  $1045.14$ ,  $578.92$  and  $465.93 \text{ cm}^{-1}$ , correspond to CHOH stretching, Si-O-Si stretching and Si-H groups, respectively. The presence of polar groups on the surface is likely to provide the considerable cation exchange capacity to the adsorbent [30].

#### 3.2. Effect of different parameters

##### 3.2.1. Effect of pH

The pH was adjusted using  $0.1 \text{ N NaOH}$  and  $0.1 \text{ N HCl}$  solutions. The pH of the dye solution plays an important role in the whole biosorption process and especially on the biosorption capacity. FTIR spectrum showed that rice husk has -OH groups. So, it seems that the pH value can affect the adsorbent efficiency of rice husk. The effect of pH of the solution on the adsorption efficiency of rice husk has been shown in Fig. 2. It can be seen from the figure that as the solution pH increases, the adsorption capacity increases.

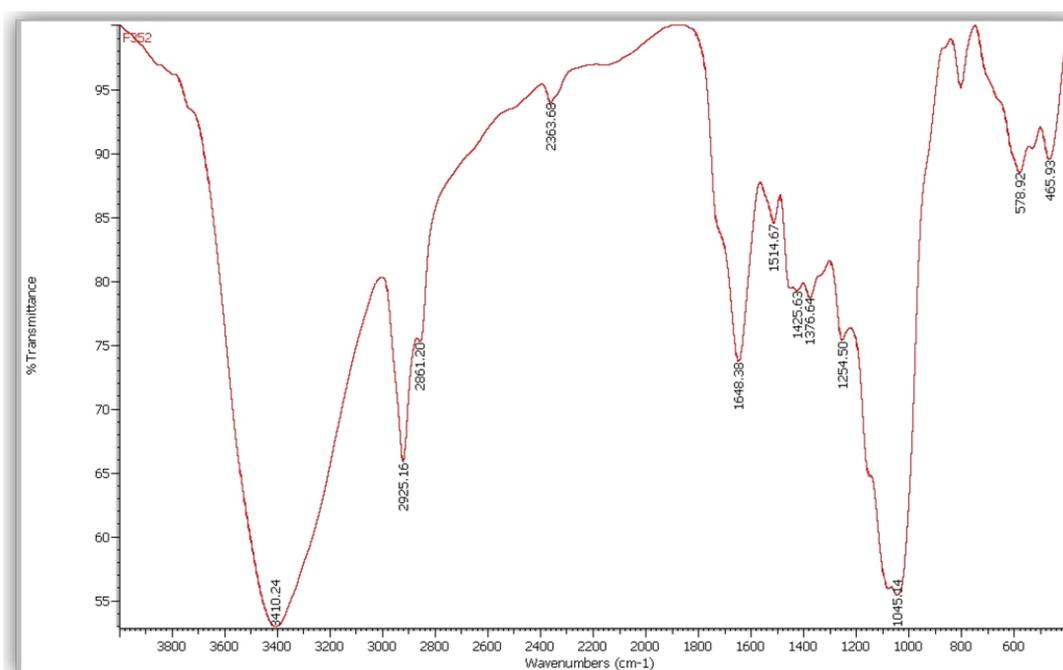
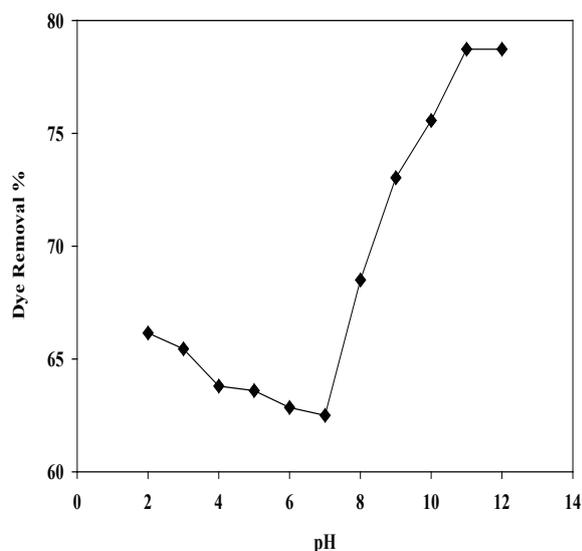
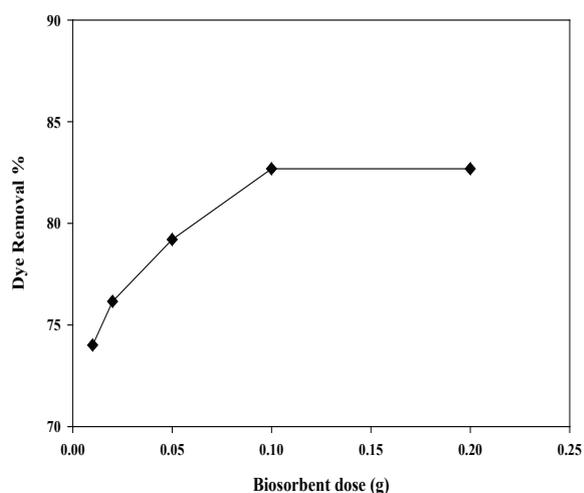


Fig.1. FTIR spectra of Rice husk.

Increasing solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enlarges the attraction between dye and adsorbent surface [31]. Generally, the net positive charge decreases with increasing pH value lead in the decrease in the repulsion between the adsorbent surface and the dye thus, improving the adsorption capacity.



**Fig. 2.** Effect of pH on the removal of methylene blue by rice husk (Contact time 6 h, biosorbent dose 0.1 g, initial concentration of dye 12 mg/L and 30°C).



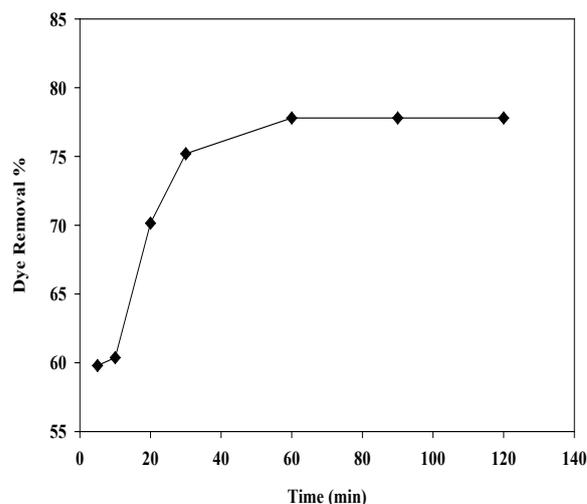
**Fig. 3.** Effect of biosorbent dose on the removal of methylene blue by rice husk (Contact time 6 h, pH 11, initial concentration of dye 12 mg/L and 30°C).

### 3.2.2. Effect of biosorbent dose

In order to evaluate the maximum biosorption capacity of the rice husk, the effect of biosorbent dose was investigated. The dose of respective biosorbent was varied from 0.01 to 0.2 g at a fixed pH, temperature and adsorbate concentration. After 0.1 g of the adsorbent, there was no change in the adsorption efficiency. So, 0.1 g of the adsorbent was chosen as an optimum amount. Results were shown in Fig. 3.

### 3.1.3. Effect of contact time

For the biosorption processes, biosorption experiments were carried out for different contact times with a fixed biosorbent dose 0.1 g, initial dye concentration 12 mg/L at solution pH 11 and at 30°C (Fig. 4). It is observed that the uptake of the dye increases with time. The uptake of adsorbate species was rapid in the initial stages of the contact period and became slow near the equilibrium. The percentage of dye removal at contact time of 60 min was 77.88%. After this time no further increase in the adsorption was observed. This result is expected because a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to occupy because of

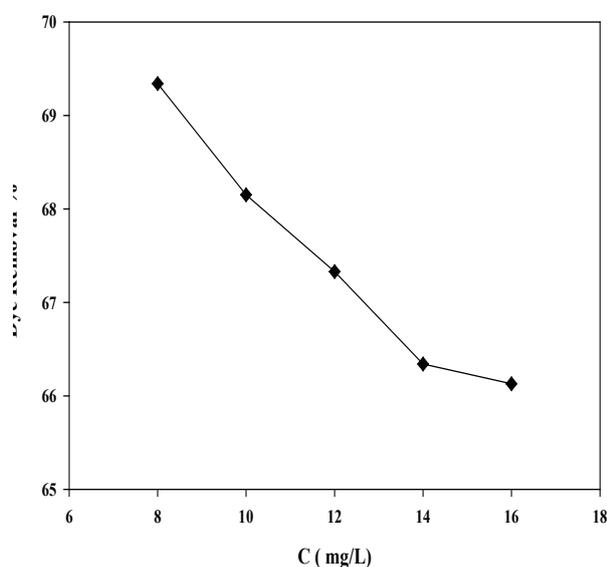


**Fig. 4.** Effect of contact time on the removal of methylene blue by rice husk ( Biosorbent dose 0.1g, pH 11, initial concentration of dye 12 mg/L and 30°C).

repulsion between the solute molecules of the solid and bulk phases [32].

### 3.1.4. Effect of dye concentration

Different methylene blue dye concentrations (8-16 mg/L) were used to determine the effect of dye concentration. The increase in the dye concentration leads to a decrease in the percentage of methylene blue removal (Fig. 5). As the dye/ sorbent ratio increases, sorption sites are saturated, resulting in decreases in sorption efficiency [33].



**Fig.5.** Effect of dye concentration on the removal of methylene blue by rice husk (Contact time 60 min, Biosorbent dose 0.1g, pH 11 and 30°C).

### 3.1.5. Effect of temperature

Biosorption experiments were carried out at different temperatures with a constant methylene blue concentration of 12 mg/L, biosorbent dose 0.1 g and pH 11. The removal percentage of methylene blue increases with increasing temperature, indicating that the sorption is **endothermic** process. This may be a result of increase in the mobility of dye with increasing temperature. Furthermore, the enhancement of sorption capacity might be due to the enhancement of sorptive interaction between the active site of rice husk and methylene blue or produce a swelling effect

within the internal structure of rice husk and enabling more dye molecules diffusion [34].

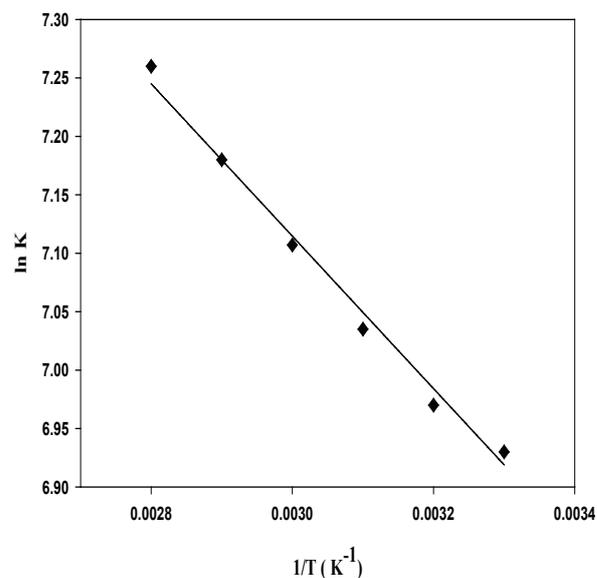
The thermodynamic parameters for the biosorption process,  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$ , were evaluated using the equation [35,36]:

$$\Delta G^0 = -RT \ln K \quad (3)$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (4)$$

$$G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

Where  $K$ , known as the distribution coefficient of the adsorbate, is equal to  $(qe/Ce)$ .  $R$  is the gas constant ( $8.314 \text{ J.mol.K}^{-1}$ ) and  $T$  is the temperature in Kelvin. The plot of  $\ln K$  vs.  $1/T$  is linear with the slope and the intercept giving values of  $\Delta H^0$  and  $\Delta S^0$ , respectively (Fig. 6). These values could be used to compute  $\Delta G^0$ . All these relations are valid when the enthalpy change remains constant in the temperature range. These thermodynamic parameters are given in Table 1. Generally, the change of free energy for physical biosorption is smaller than that of chemical biosorption. The positive value of  $\Delta H^0$  shows that the



**Fig. 6.** Plot of  $\ln K$  versus  $1/T$  for estimation of the thermodynamic parameters.

adsorption is endothermic process while positive  $\Delta S^0$  value reflects the increasing randomness at the solid/solution interface during the adsorption. The change in free energy for physical and chemical reactions are between - 20 and 0  $\text{kJ.mol}^{-1}$  and - 80 and - 400  $\text{kJ.mol}^{-1}$  respectively [37].

### 3.3. Biosorption isotherms

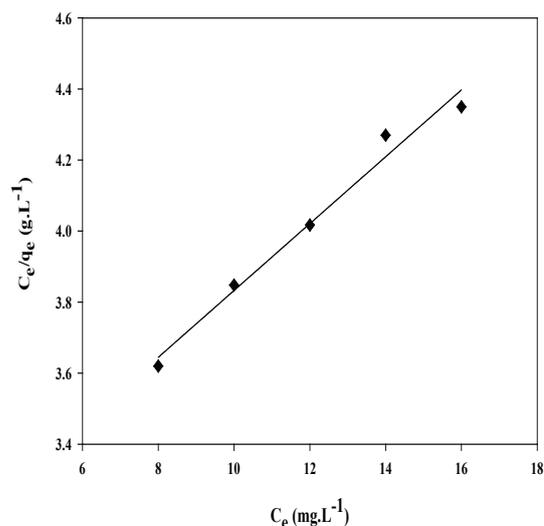
The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [38]. Biosorption isotherms are the most important information for analyzing and designing a biosorption process [39,40]. Several isotherm equations are available and two important isotherms are selected in this study, the Langmuir and Freundlich isotherms [41,42]. The Langmuir biosorption isotherm assumes that adsorption takes place at specific homogeneous sites within the biosorbent and has found successful applications for too many biosorption processes of monolayer adsorption.

The expression of the Langmuir model is given by Eq. (6) [43].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (6)$$

Where  $q_e$  (mg/g) is the adsorbed amount of the dye,  $C_e$  (mg/L), is the equilibrium concentration of the dye in solution,  $q_m$  (mg/g) is the maximum adsorption capacity

and  $K_L$  (L/mg) is the energy of adsorption.



**Fig. 7.** Langmuir isotherm for methylene blue sorption onto rice husk (Contact time 60 min, Biosorbent dose 0.1g, pH 11 and 30°C).

Fig.7.shows a linear plot of  $C_e/q_e$  versus  $C_e$ . The Langmuir constants  $q_m$  and  $K_L$  were determined from the slope and intercept of the plot and are presented in Table 2. The important characteristic of the Langmuir isotherm can be expressed by means of dimensionless constant separation factor, which is calculated using the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

Where  $K_L$  denotes the Langmuir constant and  $C_0$  is the initial concentration [44]. At all initial concentrations within studied range,  $R_L$  values presented in Table 3 have been found between

**Table 1:** Thermodynamic parameters for biosorption of Methylene blue on rice husk at different temperatures

Temperature (K)	$\Delta G^0$ (kJ.mol <sup>-1</sup> )	$\Delta H^0$ (kJ.mol <sup>-1</sup> )	$\Delta S^0$ (kJ.mol <sup>-1</sup> K <sup>-1</sup> )
303	-14.02	3.46	0.057
313	-14.59		
323	-15.16		
333	-15.79		
343	-16.41		
353	-16.89		

0 and unity (1), indicating thereby favorable processes for the adsorbent. Also higher  $R_L$  values at lower dye concentrations show that the adsorption is more favorable at lower dye concentrations.

**Table 2:** Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of methylene blue onto rice husk

Isotherm	Parameters
Langmuir	
$q_m$ (mg.g <sup>-1</sup> )	13.63
$K_L$ (L.mg <sup>-1</sup> )	0.038
$R^2$	0.981
Freundlich	
$K_F$	0.361
$n$	1.344
$R^2$	0.998

The Freundlich isotherm [45] is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as:

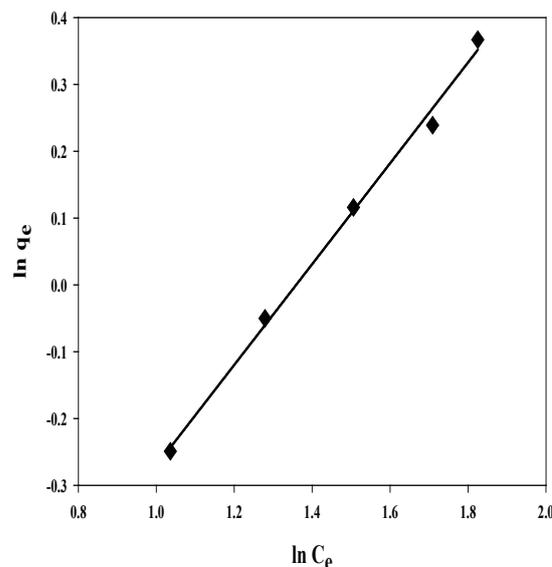
$$q_e = K_F C_e^{\frac{1}{n}} \quad (8)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

Where,  $K_F$  is biosorption capacity at unit concentration and  $1/n$  is biosorption intensity.  $1/n$  values indicate the type of isotherm to be irreversible ( $1/n = 0$ ), favorable ( $0 < 1/n < 1$ ) and unfavorable ( $1/n > 1$ ). The biosorption capacity depends on the properties of adsorbate and biosorbent. To determine the constants  $K_F$  and  $n$ , the linear form of the equation may be used to produce a graph of  $\ln(q_e)$  against  $\ln(C_e)$  (Fig. 8) All constants obtained by Freundlich models are listed in Table 2. By comparing the results of the values, it was found that the Freundlich isotherm generally represent the equilibrium sorption of methylene blue onto rice husk.

**Table 3:**  $C_o$  and  $R_L$  values for adsorption of Methylene blue onto rice husk

$C_o$	$R_L$
8	0.615
10	0.561
12	0.516
14	0.478
16	0.444



**Fig. 8.** Freundlich isotherm for methylene blue sorption onto rice husk (Contact time 60 min, Biosorbent dose 0.1g, pH 11 and 30°C).

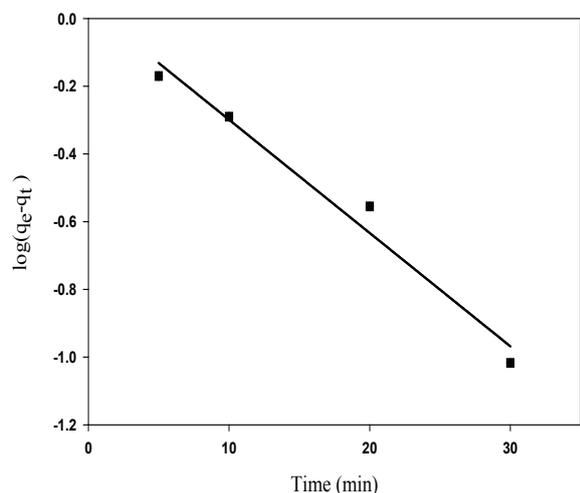
### 3.4. Adsorption kinetics

A linear form of pseudo-first-order model was described by Lagergren [46] in the form:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (10)$$

A linear plot of  $\log(q_e - q_t)$  against time allows one to obtain the rate constant (Fig. 9). If the plot was found to be linear with good correlation coefficient, indicating that Lagergren's equation is appropriate to methylene blue sorption on rice husk. So, the adsorption process is a pseudo-first-order process [46,47]. The Lagergren's first order rate constant ( $k_1$ ) and  $q_e$  determined from the model are presented in Table 4 along with the corresponding correlation coefficients. It was

observed that the pseudo-first-order model did not fit well. It was found that the calculated  $q_e$  value does not agree with the experimental  $q_e$  value (Table 4). This suggests that the adsorption of methylene blue does not follow first-order kinetics.



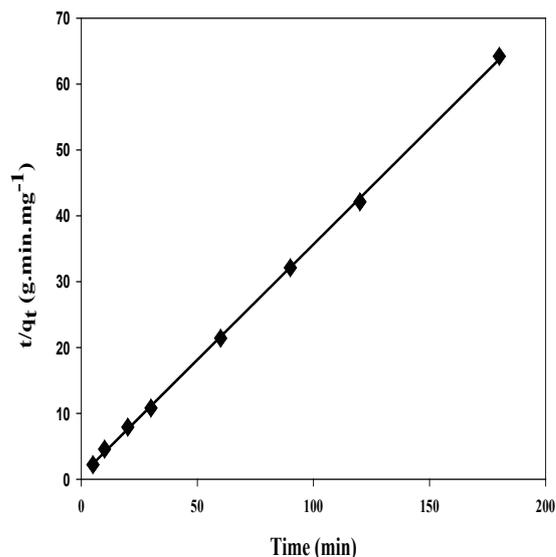
**Fig. 9.** Pseudo-first-order sorption kinetics for methylene blue sorption onto rice husk

The pseudo-second-order kinetics may be expressed in a linear form as [48,49]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

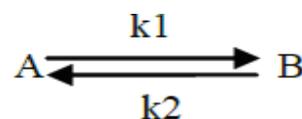
Where the equilibrium adsorption capacity ( $q_e$ ), and the second order constant  $k_2$  (g/mg min) can be determined experimentally from the slope and intercept of plot  $t/q_t$  versus  $t$  (Fig. 10). The  $k_2$  and  $q_e$  determined from the model are presented in Table 4 along with the corresponding correlation coefficients.

The values of the calculated and experimental  $q_e$  are represented in Table 4. It can be seen that there is an agreement between  $q_e$  experimental and  $q_e$  calculated values for the pseudo-second-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics. Similar phenomenon has been observed in the adsorption of methylene blue by hazelnut shells and wood sawdust [50].



**Fig. 10.** Pseudo-second-order sorption kinetics for methylene blue sorption onto rice husk

Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time or sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In this study, the kinetics of the methylene blue dye removal was carried out to understand the behavior of this low-cost adsorbent. The adsorption of methylene blue dye from an aqueous solution follows reversible second-order kinetics, when a single species is considered on a heterogeneous surface. The heterogeneous equilibrium between the methylene blue dye solution and the rice husk was represented in the following equation.



Where  $k_1$  is the forward rate constant and  $k_2$  is the backward rate constant.  $A$  represents the methylene blue remaining in the aqueous solution and  $B$  represents the methylene blue adsorbed on the surface of the rice husk. [51,24].

Another study of methylene blue onto rice husk showed that Equilibrium data fitted well into the Langmuir isotherm equation.

The sorption kinetics was found to follow a pseudo-second-order kinetic model [4]. A comparative case study of two models (Thomas model and bed-depth/service time analysis model) has shown that these models are suitable for describing the biosorption process of the dynamic behavior of removal methylene blue with the rice husk. All the results suggested that rice husk as adsorbent to removal methylene blue from solution be efficient, and the rate of biosorption process be rapid [5].

**Table 4.** Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental  $q_e$  values obtained at different initial methylene blue concentrations

Kinetic model	Parameters
Pseudo-first-order	
$q_{e,cal}$ (mg.g <sup>-1</sup> )	0.169
$k_1$ (min <sup>-1</sup> )	0.02
$R^2$	0.984
Pseudo-second-order	
$k_2$ (g. mg <sup>-1</sup> .min <sup>-1</sup> )	0.474
$q_{e,cal}$ (mg.g <sup>-1</sup> )	1.135
$h$ ( mg.min <sup>-1</sup> .g <sup>-1</sup> )	0.610
$R^2$	0.999
$q_{e,exp}$ (mg.g <sup>-1</sup> )	1.123

The value of  $q_m$  in the present work is compared with number of recently reported adsorbents used for the adsorption of methylene blue in Table 5. It is evident from Table 5 that the value of adsorption capacity in the present work (13.63 mg/g) is higher than some of adsorbents but lower than the activated carbon obtained from rice husk.

#### 4. Conclusion

The present investigation showed that rice husk can be effectively used as adsorbent. The amount of dye sorbed was found to vary with initial solution pH, adsorbent dose, temperature and contact time. Methylene blue adsorption onto rice husk is increased with the rise in initial pH. The maximum monolayer adsorption capacity,  $q_{max}$ , at 25 °C of Methylene blue onto rice husk was found to be 13.63. The kinetics studies indicated that the adsorption kinetics of dye on rice husk followed the pseudo-second order. The equilibrium data have been analyzed. The results showed that the methylene blue followed Freundlich isotherm model. Thermodynamic studies indicated that the dye adsorption onto rice husk was a spontaneous, endothermic and physical reaction. Rice husk is economically

**Table 5.** Comparison of adsorption capacity of various adsorbents reported in literature and rice husk

Adsorbents	$q_m$ (mg/g)	References
Rice husk (grinded to powder)	40.58	4
Neem leaf (powder)	8.76-1961	53
Eggshell and eggshell membrane	0.8-0.24	54
Fly ash	13.42	55
Wheat shells (grinded to powder)	16.56	56
Activated date pits (500°C)	12.9	57
Activated date pits (900°C)	17.3	57
Banana peel (washed and dried)	20.8	58
Pumpkin seed hull (crushed)	141.29	59
Rice Husk (washed and dried)	4.41	60
Rice Husk's activated carbon	441.52	61
<b>Present work</b>	<b>13.63</b>	

cheap and so regeneration is not necessary. Furthermore, being an agriculture waste, the rice husk is easily available and a cheap material in agricultural countries such as Iran, so it can be used as potential adsorbent for the removal of MB. Given the facts that rice husk necessitates no pretreatment; it is eco-friendly and low-cost, and that it has a satisfying biosorption capacity.

## References

- [1] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresour. Technol.* 77 (2001) 247–255.
- [2] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, *Process Biochem.* 40 (2005) 997–1026.
- [3] S. Wang, Z.H. Zhu, A. Coomes, F. Haghseresht, G.Q. Lu, The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater, *J. Colloid Interf. Sci.* 284 (2005) 440–446.
- [4] V. Vadivelan, K.V. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, *J. Colloid Interf. Sci.* 286 (2005) 90–100.
- [5] R. Han, et al., Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column. *J. Hazard. Mater.* 141(3) (2007) 713–718.
- [6] R.P. Han, Y.F. Wang, P. Han, J. Shi, J. Yang, Y.S. Lu, Removal of methylene blue from aqueous solution by chaff in batch mode, *J. Hazard. Mater.* 137(2006) 550–557.
- [7] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*), *Environ. Pollut.* 125 (2003) 385–392.
- [8] V.K. Garg, M. Amita, R. Kumar, R. Gupta, Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian rose-wood sawdust: a timber industry waste, *Dyes. Pigm.* 63 (2004) 243–250.
- [9] G. McKay, J.F. Porter and G.R. Prasad, The removal of dyecolors from aqueous solutions by adsorption on low-cost materials, *Water, Air, Soil Pollut.*, 114 (1999) 423–438.
- [10] G.M. Walker and L.R. Weatherley, Adsorption of acid dyes onto granular activated carbon in fixed beds, *Water Res.*, 31(1997) 2093–2101.
- [11] F.C. Wu, R.L. Tseng and R.S. Juang, Comparative adsorption of metal and dye on flake- and bead-types of chitosans prepared from fishery wastes, *J. Hazard. Mater.*, 73 (2000) 63–75.
- [12] V. Golob and A. Ojstrs, Removal of vat and disperse dyes from residual pad liquors. *Dyes. Pigm.*, 64 (2005) 57–61.
- [13] J. Sarasa, M.P. Roche, M.P. Ormad, E. Gimeno, A. Puig and J.L. Ovelleiro, Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation, *Water Res.*, 32 (1998) 2721–2727.
- [14] P.K. Malik, S.K. Sanyal, Kinetics of decolourisation of azo dyes in wastewater by UV/H<sub>2</sub>O<sub>2</sub> process, *Sep. Purif. Technol.*, 36(2004) 167–175.
- [15] P.K. Malik and S.K. Saha, Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Sep. Purif. Technol.*, 31 (2003) 241–250.
- [16] G. Ciardelli, L. Corsi and M. Marucci, Membrane separation for wastewater reuse in the textile industry, *Resour. Conserv. Recycl.*, 31 (2000) 189–197.
- [17] A. Aguedacha, S. Brosillonb, J. Morvanb and E. Lhadi, Photocatalytic degradation of azo-dyes reactive black 5 and reactive yellow 145 in water over a newly deposited titanium dioxide, *Appl. Catal. B*, 57 (2005) 55–62.
- [18] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard and J.M. Herrmann, Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo red, Methylene Blue) in water by UV-irradiated titanium, *Appl. Catal. B*, 39 (2002) 75–90.
- [19] A. Sakalis, K. Mpoulmpasakos, U. Nickel, K. Fytianos and A. Voulgaropoulos, Evaluation of a novel electrochemical pilot plant process for azo dye removal from textile wastewater, *Chem. Eng. J.*, 111 (2005) 63–70.
- [20] A. Lopes, S. Martins, A. Morão, M. Magrinho and I. Gonçalves, Degradation of a Textile Dye C. I. Direct Red 80 by Electrochemical Processes, *Port. Electrochim. Acta*, 22 (2004) 279–294.
- [21] C. Namasivayam, R. Radhika and S. Suba, Uptake of dyes by a promising locally available agricultural solid waste: coir pith, *Waste Manage.*, 21 (2001) 381–387.
- [22] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresour. technology*, 97(2006) 104–109.
- [23] W. S. Wan Ngah, M. A. K. M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresour. technology*, (2008) 99, 3935–3948.
- [24] T. G. Chuah, A. Jumariah, I. Azni, S. Katayon, S. Y. Thomas Choong, S. Y. Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview. *Desalination*, 175 (2005) 305–316.
- [25] A. H. Mahvi, A. Maleki, A. Eslami, (2004). Potential of Rice Husk and Rice Husk Ash for Phenol Removal in Aqueous Systems. *Am. J. Appl. Sci.* 1 (2007) 321–326.
- [26] B. S. Ndazi, S. Karlsson, S. Chemical and physical

- modifications of rice husks for use as composite panels. *Composites: Part A*, 38 (2007) 925-935.
- [27] S. B. Daffalla, H. Mukhtar, M. S. Shaharun, Removal of Phenol from Aqueous Solutions using Rice Husk Ash. *Casp. J. Appl. Sci. Res.* 2(2013) 36-49.
- [28] Metcalf & Eddy, Inc., 2003, "Wastewater Engineering treatment and reuse", McGraw-Hill Higher Education, U.S.A.
- [29] M. Bansal, U. Garg, D. Singh, V.K. Garg, Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: A case study of rice husk. *J. Hazard. Mater.* 162 (2009) 312-320.
- [30] V. C. Srivastava, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *J. Hazard. Mater.* B134 (2006) 257-267.
- [31] C. H. Lai, Chen C.Y. (2001), Removal of metal ions and humic acid from water by iron-coated filter media, *Chemosphere*, 44(2001) 1177-1184.
- [32] V. J. P. Poots, G. McKay, J. J. Healy JJ. The removal of acid dye from effluent using natural adsorbents-I, *Peat. Water Res.* 10(1976) 1061-66.
- [33] S. Boutemedjet, O. Hamdaoui, Sorption of malachite green by eucalyptus bark as a non-conventional low-cost biosorbent, *Desal. Water treat.* 8 (2009) 201-210.
- [34] S. Senthikumar, P. Kalaamani, C. V. Subburaam, Liquid phase adsorption of Crystal violet onto activated carbons derived from male flowers of coconut tree, *J. Hazard. Mater.* B 136 (2006) 800-808.
- [35] T. Robinson, B. Chandran and P. Nigam, Effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption, *Bioresour. Technol.*, 85 (2002) 119-124.
- [36] R.M. Gong, Y. Ding, M. Li, C. Yang, H.J. Liu and Y.Z. Sun, Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution, *Dyes Pigm.*, 64 (2005) 187-192.
- [37] A., Ozcan, E. M., Oncu, A.S., Ozcan, Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite, *Colloids Sur. A: Physchem. Eng. Aspects*, 277 (2006) 90-97.
- [38] J. Eastoe, J.S. Dalton, Dynamic surface tension and adsorption mechanisms of surfactants at the air water interface, *Adv. J. Colloid Interface Sci.* 85(2000) 103-144.
- [39] J.W. Lee, T.W. Kwon and I.S. Moon, Adsorption of monosaccharides, disaccharides and malt oligosaccharides on activated carbon for separation of maltpentose, *Carbon*, 42 (2004) 371-380.
- [40] Z. Al-Qodah, Adsorption of dyes using shale oil ash, *Water Res.*, 34 (2000) 4295-4303.
- [41] M. Dogan, M. Alkan and Y. Onganer, Adsorption of methylene blue from aqueous solution onto perlite, *Water Air Soil Pollut.*, 120 (2000) 229-248.
- [42] D. Mohan, K.P. Singh, G. Singh and K. Kumar, Removal of dyes from wastewater using flyash, a low-cost biosorbent. *Ind. Eng. Chem. Res.*, 41 (2002) 3688-3695.
- [43] I. Langmuir I. The Constitution and Fundamental Properties of Solids and Liquids. *J. Am. Chem. Soc.* 38 (1916) 2221-2295.
- [44] T. W. Weber, R.K. Chakravorti, Pore and Solid Diffusion Models for Fixed Bed Adsorbents. *Am. Inst. Chem. Eng. J.* 20 (1974) 228-232.
- [45] H. Freundlich, Über die adsorption in lösungen (adsorption in solution), *Z. Phys. Chem.* 57 (1906) 384-470.
- [46] S. Lagergren, Zur theorie der sorption, *Sven. Vetenskapsakad., Handl.* 24 (1898) 1-39.
- [47] Y.S. Ho, G. McKay, The sorption of lead(II) ions on peat, *Water Res.* 33(1999) 578-584.
- [48] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115-124.
- [49] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.* 34 (2000) 735-742.
- [50] F. Ferrero, Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust, *J. Hazard. Mater.* 142 (2007) 144-152.
- [51] A. Özer, G. Dursun G, Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon. *J. Hazard. Materials.* 146(2007) 262-269
- [52] S. Wang S, Y. Boyjoo, A. Choueib, Comparative study of dye removal using fly ash treated by different methods. *Chemosphere.* 60(2005) 1401-1407.
- [53] K.G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder, *Dyes Pigm.* 65 (2005) 51-59.
- [54] W.T. Tsai, J.M. Yang, C.W. Lai, Y.H. Cheng, C.C. Lin, C.W. Yeh, Characterization and adsorption properties of eggshells and eggshell membrane, *Bioresour. Technol.* 97 (2006) 488-493.
- [55] S. Wang, Y. Boyjoo, A. Choueib, A comparative study of dye removal using fly ash treated by different methods, *Chemosphere* 60 (2005) 1401-1407.
- [56] Y. Bulut, H. Aydın, Kinetics and thermodynamics study of methylene blue adsorption on wheat shells, *Desalination* 194 (2006) 259-267.
- [57] F. Banat, S. Al-Asheh, L. Al-Makhadmeh, Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, *Process Biochem.* 39 (2003) 193-202.
- [58] G. Annadurai, R. Juang, D. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *J. Hazard. Mater.* 92 (2002) 263-274.
- [59] B.H. Hameed, M.I. El-Khairay, Removal of basic dye from aqueous medium using a novel agricultural waste material: Pumpkin seed hull, *J. Hazard. Mater.* 155 (2008) 601-609.

- [60] R. Han, Y. Wang, W. Yu, W. Zou, J. Shi, H. Liu, Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column, *J. Hazard. Mater.* 141 (2007) 713–718.
- [61] K.Y. Foo, B.H. Hameed, Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K<sub>2</sub>CO<sub>3</sub> activation, *Bioresour. Technol.* 102 (2011) 9814–9817.