Kinetics and Equilibrium Studies of the Removal of Blue Basic 41 and Methylene Blue from Aqueous Solution Using Rice Stems

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ABSTRACT: *Synthetic dyes are among the most common contaminants of the environment. Therefore, the aim of this study was investigation the removal of Basic Blue 41 (BB41) and Methylene Blue (MB) from industrial effluents by useing raw and modified rice stems. In this study raw and modified rice stems treated chemically with Citric Acid (CA) and were used to explore the potentiality of rice stems for removal of BB41 and MB dyes. Effect of various parameters including pH, contact time, adsorbent dose and initial dye concentration on the adsorption were studied. To characterize the adsorbents, Scanning Electron Microscope (SEM) was used. The adsorbent surface functional groups identified with Fourier Transform InfraRed (FT-IR) spectroscopy. The applicability of the adsorption data was explained by Langmuir, Freundlich, Temkin and BET isotherms. The results showed that increasing of contact time and adsorbent dose, dye removal increases for both raw and modified adsorbents. Dye adsorption on to adsorbent increased with increasing of pH. Also the results indicated that dye removal efficiency was increased by decreasing initial dye concentration. Among studied isotherms, data were fitted well by Langmuir model (R^2>0.98) for both raw and modified adsorbents. Also, adsorption kinetics were more fitted by pseudo second order model (R^2>0.99).The results of the present work showed that rice stem was a good, low cost and effective adsorbent for removal of BB14 and MB from industrial effluents.*

KEY WORDS: *MB, BB41; Adsorption; Isotherm; Kinetics; Rice stems.*

INTRODUCTION

Textile industry is the largest consumer of dyestuffs which produces millions of tons of colored effluents every day [1]. Direct discharge of dye containing effluents into aquatic environment cause decrease of light transmission through water and is harmful to marine life [2]. Dyes in addition to making the effluent highly colored and aesthetically unpleasant, also, containing toxic compounds and chemicals with aromatic rings which are stable and resistance to biodegradation [3,4]. Dyestuff industries produce millions of tons of colored effluents which cause

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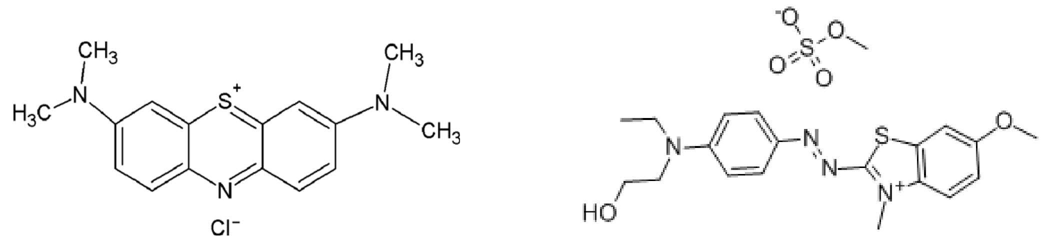

Fig. 1: Chemical structure of two dyes (left: MB, right: BB4).

adverse effects in the environment [5]. Methylene Blue (MB) is a heterocyclic aromatic chemical compound with dimethyl amino groups in its structure [6]. Azo dyes are the largest and the most common groups of synthetic commercial dyes. Basic Blue 41(BB41) is a cationic azo dye used in textile industry [7]. Basic dyes are typically cationic or positively charged. These dyes containing two aromatic rings with low degradation characteristics which can cause serious problems in the environment [8]. Due to presence of benzene ring in the structure of dyes [9], they lead to allergies, dermatitis, skin irritation, cancer [10] and are mutagen. (11). Therefore, the treatment of these effluents is necessary prior to discharge into the environment. Various methods have been reported to remove dyes from textile effluents including physical, physicochemical, biological and chemical methods [12]. Biological treatment[13], chemical oxidation[14], membrane processes[15], photochemical processes[16], zonation[17], adsorption onto activated carbon[18], chemical treatment methods[19], electrochemical processes such as electrocoagulation can be used to treat these effluents[20].

These methods have both advantages and limitations. Biological treatment methods require a long time to be efficient [21]. Disposal of activated carbon adsorption residues is expensive [22]. Advanced oxidation processes produce too much sludge which must finally disposed properly [23]. Therefore, use of cost effective natural adsorbents like chitosan [24], fly ash [25], pumice [26], saw dust [27] and charcoal [28] are being commonly used for treatment of textile effluents [29]. In the present work, rice stem, an abundant agricultural waste in Mazandaran province of Iran, has been used to remove dyes from textile effluents. The objective of this study was to remove MB and BB41 dyes from textile industry effluents by use of raw and modified rice stems as effective and inexpensive adsorbents.

EXPERIMENTAL SECTION

Materials and instruments

BB41 and MB dyes were provided from Alvansabet Hamadan Company(Iran). Citric acid, sulfuric acid and sodium hydroxide were purchased from Merck Co. (Germany).

Adsorbents preparation

The rice stems used in the present investigation were procured locally from Mazandaran province, Iran. The stems were washed with distillated water to remove dust like impurities; ground by use of mortar and the powder was sieved through a 30-40 mesh sieve. After that, the powder was dried in an oven at 90 °C for 2 h. The dried adsorbent was treated chemically using citric acid (0.5mol/L) at impregnation ratio of 1/12. Then, the mixture was stirred vigorously for 30 min and dried at 90 °C for 24 h. Again, for thermochemical reactions between acid and straw, heated at 120 °C for 90 min. After cooling in air, the modified adsorbent was washed with distilled water and filtered. The filtrate were soaked with NaOH (0.1 mol/L) and stirred for 60 min. To remove the remaining NaOH, adsorbents were washed with distillated water and dried at 50 ºC for 24 h in order to fix its weight and stored in desiccator for use [30, 31].

Adsorption experiments

Effect of contact time

Amount of dye removal with respect to contact time (10,20,30, 45,60, 90,120,180 and240 min) and constant conditions of 10 g per 100 mL adsorbent, initial dye concentration 10 mgL , pH 10, temperature 25 °C and stirring speed of150 rpm was investigated.

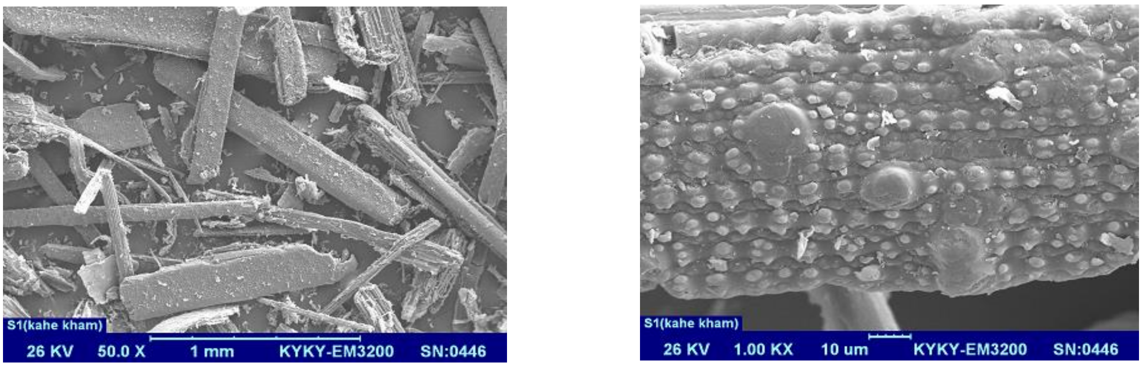

Fig. 2: SEM image of raw rice stems.

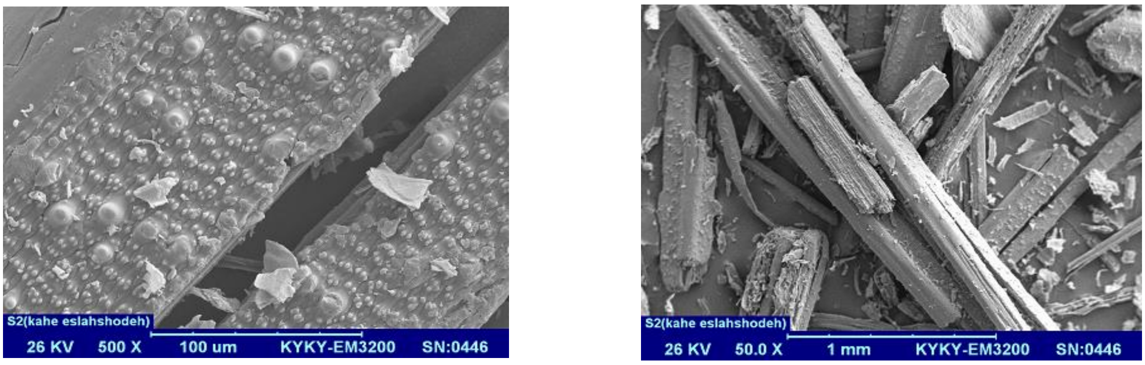

Fig. 3: SEM image of modified rice stems.

Effect of initial pH of dye solution

Effect of pH on dye removal at pH 2, 3, 4, 5, 6, 7, 8, 9 and 10, adsorbent dose of 10 g per 100 mL solution, initial dye concentration 10 mg/l, temperature 25 ^{o}C and stirring speed of 150 rpm was studied.

Effect of initial dye concentration

Effect of initial dye concentration on dye adsorption at different concentrations of 10, 20, 40, 80,100 and 200 mg/L, adsorbent dose 10 g per 100 mL of solution, temperature 25 ^{o}C and stirring speed of 150 rpm was investigated.

Effect of adsorbent dose

The removal percentage of dye with varying doses of adsorbent (2, 4,5,10,15,20,25 g/L), dye concentration 10 mg per 100 mL, temperature 25^{0}C and stirring rate (150 rpm) was investigated. The samples were centrifuged at 3600 rpm for 10 min. 1 N HClor1 N NaOH solutions were used for pH adjustment. These stages were repeated for determination of optimum pH, adsorbent dose and concentration of MB and BB41. Residual concentration of MB and BB41 was determined by using of spectrophotometer (Hack, DR 5000) at 665 and 617 nm, respectively. Data and correlation coefficients were analyzed by use of Excel software.

RESULTS AND DISCUSSION

The SEM images of raw and modified rice stem are shown in Figs. 2 and 3. As illustrated in Figs. 2 and 3, chemical modification has not changed structure of rice stem, and no considerable morphological differences in the structure of raw and modified rice stem could be seen. Also, FT-IR analysis was used for determination of the presence of specific functional groups on the adsorbents(Fig. 4). According to Fig. 4, peaks at 3400-3700, 2850-2970, 1690-1760, 1610-1680 and 1050-1300 (cm-1) correspond to functional groups of OH, C-H, C=O, C=C and C-O, respectively. As it’s clear from Fig. 4,

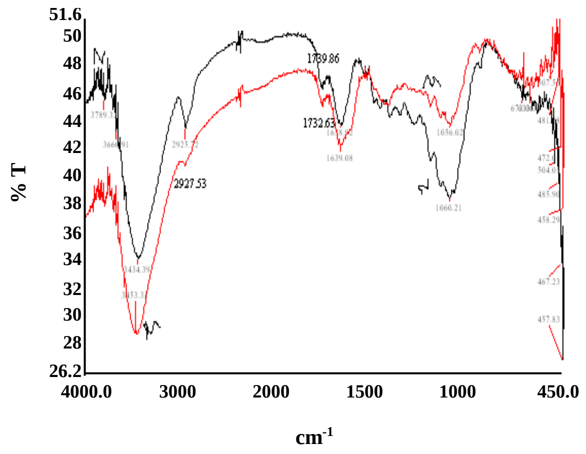

Fig 4: FT-IR spectra of raw and modified rice stems.

the sharp stretching vibration absorption peak of carboxyl group at 1732 cm^{-1} in FT-IR spectra of citric acid modified rice stem, demonstrates the citric acid esterification. These carboxyl groups on the surface of modified rice stems, at high pH values have negative charge which attract positively charged cationic dyes.

Effect of contact time on dye removal

The results of the experiments showed that adsorption rate increased sharply up to 90 min in which for this time the raw and modified rice stem were able to remove 80 and 98 percent of MB dye, and 75and 96 percentofBB41, respectively.

Effect of pH on dye removal

Fig. 6 shows the effect of pH on adsorption efficiency of rice stems. The optimum pH for removal of MB in raw and modified adsorbents was 10. Also, the experimental results clearly indicated that by increasing of pH, amount of adsorption increased in a linear form. Maximum amount of adsorption was observed at pH 10.

Effect of initial dye concentration on dye removal

Effect of initial dye concentration on dye removal efficiency is presented in Fig 7. The results showed that increasing initial dye concentration, adsorption capacity increased but dye removal efficiency decreased. At optimum conditions, the amount of dye adsorbed onto raw and modified rice stems was 80 and 98 % for MB, and 75 and 96 % for BB4, respectively.

Effect of adsorbent dose on dye removal

As Fig. 8 explains, the operational parameters such as adsorbent dose (2,4,5,10,15,20,25 g/L), pH(10), dye concentration(10 mg/L) and contact time (90 min) at constant dye concentration of 10 mg/L were studied.

These findings indicated that with an increase in adsorbent dose, adsorption efficiency increased. Under the optimum adsorption conditions at concentration of 2 g/L of MB and BB41 for modified adsorbent removal percentage was 74 and 65 percent and for raw adsorbent was 59 and 52 percent, respectively. But at adsorbent dose of 10 g/L, dye removal for raw and modified rice stem was above 95 and 82 percent.

Equilibrium and kinetic studies

Equilibrium studies were carried out in a 250 mL Erlenmeyer flask containing 100 mL solution with initial dye concentration range (10-200 mg/L), amount of adsorbent (10 g/L) at pH 7.4. In this study, adsorption equilibrium of MB and BB41 at various condition was investigated on rice stems and data were interpreted by use of Langmuir and Freundlich isotherms. Percentage removal of dye and amount of adsorbed dye per gram of adsorbent (*qe*) were calculated as follows:

$$R = (Co - Ce) \times 100 / Co$$

$$q_e = (Co - Ce) \times V / M$$

Where *R* is percentage removal, qe amount of adsorbed dye per gram of adsorbent (mg/g), C_o is the initial dye concentration (mg/L), *Ce* is the equilibrium concentration of dye (mg/L), *M* is the mass of the rice stem (g) and *V* is the volume of the solution [1,2].

Langmuir isotherm for description of adsorption data is given as:

Equilibrium parameter (R_L) depends on amount of *b* and q_m which is defined by [24, 25]:

$$R_L = 1/(1 + bc_o)$$

The value of R_L indicates the type of the isotherm to be either linear (R_L= 1), unfavorable (R_L> 1), favorable (0 <R_L< 1) or irreversible (R_L= 0) (26). The Freundlich isotherm is based on monolayer sorption on heterogeneous surface energies. Linear form of Freundlich isotherm is given in Table 1. K_f and *n* are constants related to the adsorption capacity and intensity of adsorption, respectively. The values of *1/n* in the range

Table 1: Isotherm equations and kinetics of MB and BB41 adsorption onto rice stems (32,33, 34).

Parameters	Isotherm equations	Isotherms
qe: amount adsorbed at equilibrium time (mg/g) kf: constant related to the adsorption capacity 1/n: intensity of adsorption	$q_e = k_f C_e^{1/n}$	Freundlich Isotherm
K_L= Langmuir adsorption constant (1/g) Ce: concentration in the solution at equilibrium (mg/L) qm: the maximum monolayer adsorption capacity(mg/g)	$q_e = \frac{K_L q_m C_e}{1+K_L C_e}$	Langmuir Isotherm
Xm:mg adsorption per g of adsorbent(mg/g) A: constant related to energy interaction Ci: saturation concentration in liquid(mg/L)	$\frac{C_e}{(C_i - C_e)q} = \frac{1}{A(X_m)} + \frac{A-1}{Axm}$	BET Isotherm
B_1 : constant related to the heat of adsorption Kt: equilibrium binding constant corresponding to the maximum binding energy	$qe = B_1 \ln (k_t) + B_1 \ln (Ce)$	Temkin Isotherm

Table 2: Isotherm constants and correlation coefficients of MB and BB41 dyes onto rice stems.

R^2	Isotherm constants		Adsorbent type	dye	Isotherm
0.97	1/n=1.39	KF=0.38	Raw	MB	Freundlich
0.992	1/n=1.37	KF=0.4	Modified	MB	
0.99	1/n=1.34	KF=0.55	Raw	BB41	
0.995	1/n=1.51	KF=0.6	Modified	BB41	
0.97	K_L =0.08	q_m=21.4	Raw	MB	Langmuir
0.96	K_L =0.11	q_m=18.3	Modified	MB	
0.94	K_L =0.09	q_m=17.7	Raw	BB41	
0.97	K_L =0.1	q_m=22.6	Modified	BB41	
0.91	A =14.8	X_m=0.19	Raw	MB	BET
0.9	A =17.6	X_m =0.12	Modified	MB	
0.94	A =21.5	X_m =0.17	Raw	BB41	
0.89	A =19.4	X_m =0.14	Modified	BB41	
0.93	B=25.9	k_t=1.6	Raw	MB	Temkin
0.918	B=24.3	k_t=2.3	Modified	MB	
0.94	B=31.2	k_t=1.9	Raw	BB41	
0.96	B=35.8	k_t=2.4	Modified	BB41	

of 0 to 1 represent non-uniformity of the adsorbent surfaces, becoming more non-uniform as its value gets closer to zero [26].

Adsorption kinetics

One of the main parameters influencing the design of adsorption processes prediction of adsorption rate. Most of adsorbents follow first and second order kinetic models. Equations related to the adsorption kinetics are given in Table 3. In these equations, *k*, *qe* and *qt* are rate constant, amount of dye removed at equilibrium and time *t*, respectively.

Discussion

Fig. 5 shows the effect of contact time and the time of attaining equilibrium. It was observed from the findings that the removal of MB and BB41 increases with increasing contact time. Dye removal efficiency increased sharply up to 45 min, after that, continued slightly and reached equilibrium at 90 min.

Table 3: Kinetic models of adsorption (pseudo first order and pseudo second order).

Pseudo second order model	Pseudo first order model
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_1 t$
K1:pseudo second order rate constant qe: amount of dye removed at equilibrium (mg/g)	K1:pseudo first order rate constant qe: amount of dye removed at equilibrium (mg/g) qt: amount of dye removed at time t (mg/g)

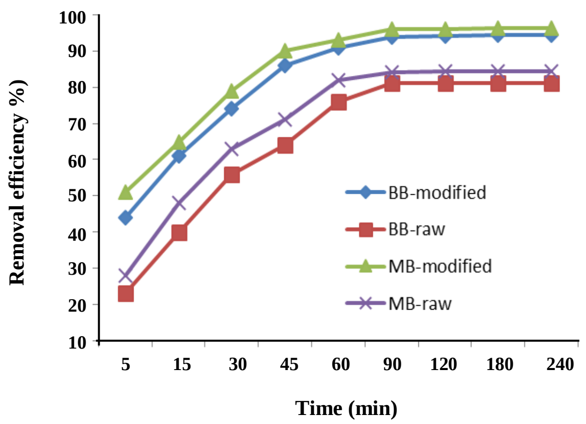

Fig. 5: Effect of contact time on percent removal (adsorbent dose10 g/L, initial dye concentration 10 mg/L, pH 10).

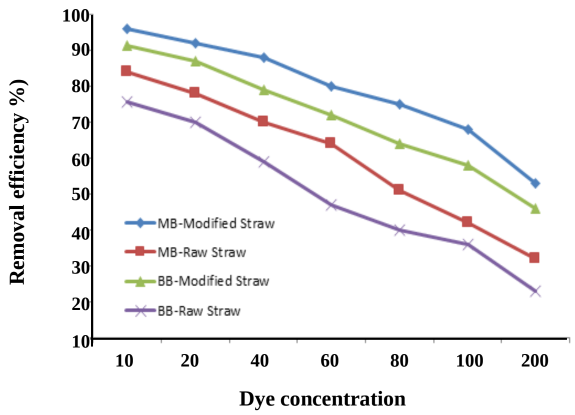

Fig. 7: Effect of initial concentration on percent removal (adsorbent dose10 g/L, contact time 90 min, pH 10).

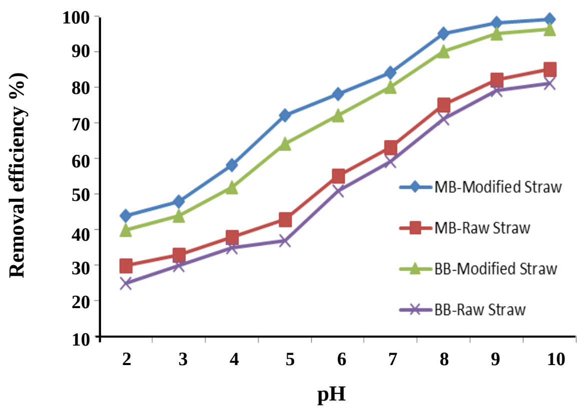

Fig. 6: Effect of pH on percent removal (adsorbent dose10 g/l, initial dye concentration 10 mg/L, contact time 90 min.

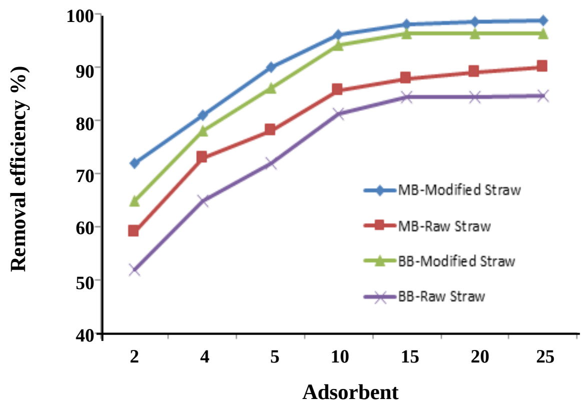

Fig. 8: Effect of adsorbent dose on percent removal (initial dye concentration 10 mg/L, contact time 90 min, pH 10).

The higher sorption rate at initial stage can be attributed to the availability of high numbers of vacant sites on the adsorbent surface. As the time passes, dye molecules occupy these sites. After that, Adsorption continues via active sites at the interior of the adsorbent particles [35, 36]. pH is an important parameter for adsorption which affects amount of adsorption. According to Fig. 6, dye removal increased by pH increase from 2 to 10, which was in a linear form. Maximum amount of dye removal was observed at pH 10. By changing the pH of solutions, positive or negative charges would be developed at the surface of medium. In the other word, in basic solutions, OH^- ion develops [37]. Thus, high numbers of OH^- ions would be available on the surface. Therefore, adsorbent surface tends to acquire negative charge, thereby resulting in increased affinity to exchange OH^- ion with cationic the solution. Also, electrostatic attraction between positively charged

Table 4: Isotherm constants and correlation coefficients of pseudo second order model for adsorption of MB and BB41 dyes onto rice stems.

pseudo second order	k_2 (g/mg min)	R^2
Raw stem by MB	0.12	0.999
Modified stem by MB	0.16	0.997
Raw stem by BB41	0.14	0.998
Modified stem by BB41	0.18	0.997

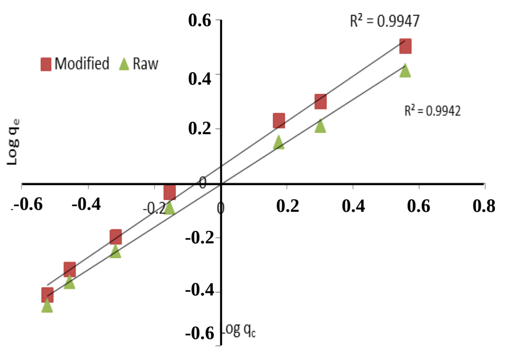

Fig. 9: Freundlich adsorption isotherm of BB41 onto rice stems.

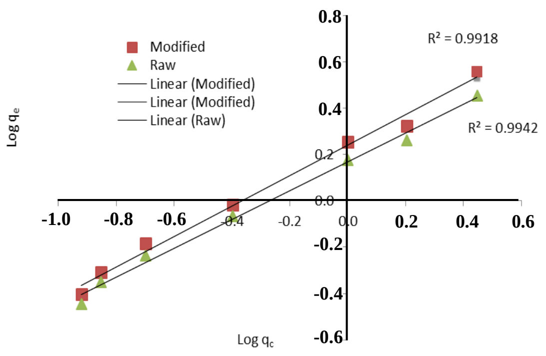

Fig. 10: Freundlich adsorption isotherm of MB onto rice stems.

dye molecules and negatively charged adsorbent result in higher dye removal efficiencies [25, 37]. The observed decrease in sorption may reasonably be due to the formation of soluble hydroxyl complexes. Another reason for decrease of MB removal at lower pH is the conversion of carboxylate group to carboxyl group. Therefore, amount of MB adsorption decreases in lower pH due to the conversion of carboxylate group to carboxyl group which cause accumulation of negative charges of pectin on the surface [7, 32]. By decreasing of pH, the number of surface sites with positive charges increases resulting in decrease of dye adsorption. This agrees with the findings of other studies (30, 31). As illustrated in Fig. 7, an increase in initial concentration of dye causes an increase in adsorption capacity, but removal efficiency decreases. In adsorption process as dye concentration increases, gradient concentration of adsorbate tends toward the adsorbent surface, which in general increases accumulation of dye particles onto the absorbent [27].

In lower concentrations, number of vacant binding sites on the adsorbent surface is high which decreases at higher dye concentrations [29]. Fig. 8 illustrates that by increasing of adsorbent dose, dye removal increases. An explanation for this behavior could be that, the increase of surface binding sites resulting in an increase in dyes removal [26, 27]. In low concentrations, there are many vacant binding sites available on the adsorbent, as the time passed, the sites were occupied and hence the rate of dye removal was slowed. Similar results were reported by other studies [29, 30]. By increase of adsorbent dose beyond 10 g/L, very little increase in adsorption efficiency was observed which using higher doses just increase the costs. This is because of remaining unsaturated surface sites on the adsorbent which result in a decrease in dye removal. Also, coverage of the active sites and accumulation of adsorbate onto surface occurs at high dye concentrations which result in decrease of migration of dye molecules onto adsorbent. Therefore, reduce the available sites and finally decrease amount of dye removal [29,30]. According to correlation coefficients, it is clear that equilibrium data follow more accurately by Freundlich model than Langmuir model for raw and

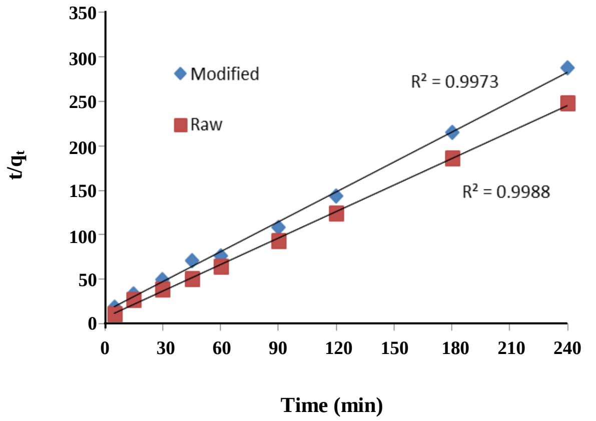

Fig. 11: Adsorption kinetic of pseudo first order of BB41 adsorption onto rice stems.

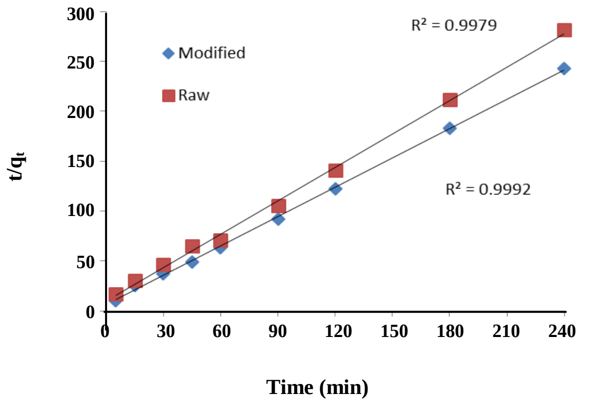

Fig. 12: Adsorption kinetic of pseudo first order of MB adsorption onto rice stems.

modified adsorbents. Values of R^2 forboth adsorbents are above 0.99. Adsorption kinetics data for both adsorbents were fitted well with pseudo second order model (R^2>0.99).

CONCLUSIONS

The results of this study showed that dye removal percentage depend on many parameters including contact time, initial dye concentration, adsorbent dose and initial ph. By increasing contact time and adsorbent dose, dye removal increases. When initial dye concentration increases, dye removal decreases. The highest efficiency was observed at pH 10. Raw and modified rice stems have many advantages such as high ability to remove dyes, local availability and low cost. Thus, it can be a good alternative to treat industrial effluents in comparison with artificial adsorbents. According to the values of correlation coefficients, it can be concluded that equilibrium data of both adsorbents (raw and modified) follow Freundlich model. The values of R^2 for both adsorbents were more than 0.98. Also, data demonstrate the applicability of pseudo second order model for dye removal by both adsorbents. The results of the present study have demonstrated that, rice stem could be used as an effective adsorbent for the removal of BB14 and MB from industrial effluents

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