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Adsorption of methylene blue dye from aqueous solution by sugar extracted spent rice biomass

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ABSTRACT

This study was aimed at using sugar extracted spent rice biomass (SRB) as a potential adsorbent to remove methylene blue (MB) dye from aqueous solution. The SRB was used without any modification. A three factor full factorial experimental design (2^3) was employed to investigate the effect of factors (adsorbent dose, dye concentration, temperature) and their interaction on the adsorption capacity and color removal. Two levels for each factor were used; adsorbent dose (0.25–0.5 g/100 mL), dye concentration (25–50 mg/L), and temperature (25–45 °C). Initial dye concentration and adsorbent dosage were found as significant factors for the adsorption of MB dye. Langmuir isotherm ($R^2 > 0.998$) best explained the equilibrium of MB adsorption on SRB with monolayer adsorption capacity of 8.13 mg/g. The pseudo-second order model ($R^2 > 0.999$) was best fitted to explain the adsorption kinetics. Thermodynamic investigation revealed that the adsorption process was spontaneous, endothermic, and was feasible to treat dyeing wastewater.

1. Introduction

Global economy is confronted with the biggest challenges of energy insecurity and the consequences of environmental pollution. Lignocellulosic bioethanol (LCB) has emerged as an environment friendly and sustainable renewable fuel (Alvira, Tomás-Pejó, Ballesteros, & Negro, 2010). Besides its various advantages and cheap feedstock, the production of LCB is limited due to many technical and financial obstacles (Agbor, Cicek, Sparling, Berlin, & Levin, 2011; Lynd et al., 2008). The extraction of fermentable sugars from lignocellulosic biomass is hindered by its recalcitrant structure and the arrangement of polysaccharides (Geddes, Nieves, & Ingram, 2011). Several pretreatment techniques have been investigated to extract reducing sugars to be fermented into bioethanol. These pretreatments disrupt the biomass structure and make polysaccharides accessible for the subsequent hydrolysis step (Alvira et al., 2010). A substantial amount of biomass, however, is produced as waste after sugar extraction and/or fermentation. These biomass wastes require additional cost for their appropriate disposal. This disposal poses an additional financial liability for LCB industry which already faces market competitiveness against cheap fossil fuels. Thus, it is extremely important for any LCB facility to find out some economical and viable alternatives for the disposal of residual waste.

Wastewater treatment is a costly yet important task for process industries due to the straighten regulations in most of the countries. Various process industries use more than 10,000 synthetic dyes for different kind of applications (Ahmad & Rahman, 2011). These industries generate a huge volume of colored effluent carrying residual dyes which cannot be released without prior treatment due to its toxicity (Deng, Lu, Li, Zhang, & Wang, 2011). Several treatment approaches involving biological, physiochemical, membrane filtration, and advanced oxidation (Ma et al., 2011; Madaeni, Jamali, & Islami, 2011; Verma, Dash, & Bhunia, 2012; Whang, Hsieh, & Chen, 2012) have been investigated to treat dye containing wastewater. However, performance of these treatments is constrained due to their operations, cost and production of sludge (Al-Anber, Al-Anber, Matouq, Al-Ayed, & Omari, 2011). Adsorption process has emerged as a feasible alternative for the treatment of such colored wastewater due to its simplicity and performance (Asgher & Bhatti, 2012; Mona, Kaushik, & Kaushik, 2011). Different kinds of adsorbents have already been investigated for their application in colored wastewater treatment. Activated carbon, derived from various renewable and nonrenewable resources, has been found the most successful material for this task (Pavan, Lima, Dias, & Mazzocato, 2008). Although commercial activated carbon is highly efficient yet it is an expensive technology. Thus, a lot of studies have been carried out to search for low cost adsorbents especially renewable biomass (Ahmed & Dhedan, 2012; Dutta, Bhattacharyya, Ganguly, Gupta, & Basu, 2011). Lignocellulosic biomass is a cheap and frequently available adsorbent; however, it inherits low efficiency when used without any

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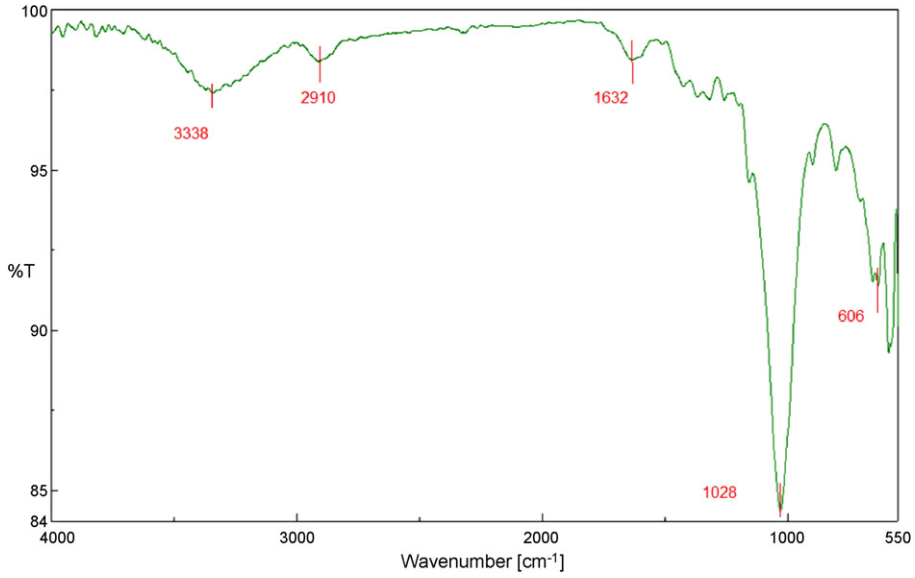

Fig. 1. FTIR spectra of spent rice biomass.

pretreatment (Chowdhury, Misra, Kushwaha, & Das, 2011; Low, Teng, Ahmad, Morad, & Wong, 2011). The spent lignocellulosic biomass from LCB facility may offer several advantages as an adsorbent. It does not require any pretreatment and furthermore, it will economically manage the disposal of residue.

The objective of present study was to investigate the feasibility of sugar extracted spent rice biomass (SRB) as an adsorbent to remove methylene blue (MB) dye from the aqueous solution. MB is a cationic dye which is extensively used in dyeing industry. MB is a toxic dye and causes several health risks in humans upon exposure such as nausea, vomiting, eye injury, and methemoglobinemia (Al-Anber et al., 2011; Dutta et al., 2011; Vucurovic, Razmovski, & Tekic, 2012). A three factor full factorial experimental design was used for this investigation in order to evaluate the influence of operating factors (biosorbent dose, dye concentration, temperature). Adsorption dynamics, kinetics and thermodynamics of the adsorption process were also studied.

2. Materials and methods

2.1. Preparation and characterization of adsorbent

The spent rice biomass, used in this study, was obtained from our research group. The biomass was pretreated and enzymatically hydrolyzed for sugar extraction. Raw rice biomass was ground using lab scale grinder, and was sieved to obtain a particle size of less than 3 mm. The ground biomass was dried at 50 °C for 24 h in an oven. The dried biomass was subjected to alkali pretreatment under such conditions; alkali concentration (1–4%), temperature (60–100 °C) and pretreatment time (30–90 min), which yielded a glucose recovery of 254.5 ± 1.2 g/kg. Spent rice biomass obtained from this experiment was dried in oven for 24 h. SRB was ground prior to be used in adsorption studies. No further physical/chemical treatment was applied to SRB to find its effectiveness as a residue.

The SRB was characterized using the Fourier transform infra-red spectrophotometer before the adsorption of MB dye (Fig. 1). The peak around 3338 cm^{-1} represented the O—H stretching vibration that showed the presence of free hydroxyl group on the surface of SRB. This vibration corresponded to inter and intra molecular hydrogen bonding among the constituents of biomass (Nasuha & Hameed, 2011; Nasuha, Hameed, & Din, 2010; Sharma, Uma, & Upadhyay, 2011). The peak at 2910 cm^{-1} represented symmetric and asymmetric C—H stretching due to the presence of —CH and CH groups present in the lignin of SRB (Reddy, Sivaramakrishna, & Reddy, 2012; Safa & Bhatti, 2011). The peaks at 1632 cm^{-1} and 1028 cm^{-1} were assigned to the stretching vibrations of C=O (Nasuha & Hameed, 2011; Reddy et al., 2012; Sharma et al., 2011). The zeta potential, Brunauer, Emmett, Teller (BET) surface area, and molecular cross sectional area were measured to be −14.28 mV, 0.4703 m^2/g, and 0.162 nm^2, respectively.

2.2. Preparation of dye solutions

Methylene blue was used as a model cationic dye for this experiment. MB dye was purchased from local supplier, and was used without further purification. The stock solution (500 ppm) of MB dye was prepared by dissolving 0.5 g of MB in 1 L of distilled water. The experimental solutions of desired concentration were prepared by diluting stock solution with distilled water. The concentration of MB dye was measured at λ_{max} = 668 nm (Nasuha & Hameed, 2011) using UV–visible spectrophotometer (Hach DR 5000).

2.3. Adsorption studies

Adsorption experiments were carried out with 100 mL experimental volume of the dye solution in 250 mL flasks. The solution pH was kept at its original value (5.2), and was not controlled during the experiment. Adsorption equilibrium experiments were conducted according to a three factor factorial experimental design (2^3) described in the subsequent section. Adsorbent dose (g/100 mL), dye concentration (mg/L) and temperature (°C) were selected as experimental factors. The desired SRB dose was mixed with dye solution, and was then agitated at a rate of 200 rpm in a shaking incubator. Adsorption kinetics and thermodynamic experiments were carried out using initial dye concentration (25–50 mg/L) at the equilibrium experimental conditions whereas dye samples were withdrawn at regular time intervals for their residual dye analysis.

The adsorption capacity (q_e) and color removal efficiency (R) were calculated using following Eqs. (1) and (2), respectively.

$$q_e\ (\mathrm{mg/g}) = \frac{(C_0 - C_t)V}{M} \quad (1)$$

$$R(\%) = \frac{(C_0 - C_t)100}{C_0} \quad (2)$$

Table 1
Factorial design matrix for investigated factors with actual and predicted response values for adsorption capacity and color removal.

Coded factor			Actual factor level			q_e (mg/g)	$q_{e\,pred}$	R (%)	R_{pred}
A	B	C	Adsorbent dose (g/100 mL)	Dye conc. (ppm)	Temperature (°C)				
−1	1	−1	0.25	50	25	8.58	8.47	85.8	85.1
1	1	1	0.5	50	45	8.98	8.86	89.8	89.1
−1	−1	1	0.25	25	45	4.57	4.46	91.4	90.7
−1	−1	−1	0.25	25	25	4.64	4.75	92.7	93.4
1	−1	−1	0.5	25	25	4.37	4.27	93.0	92.3
−1	1	1	0.25	50	45	7.86	7.98	78.6	79.3
1	1	−1	0.5	50	25	8.40	8.51	89.3	90.0
1	−1	1	0.5	25	45	4.70	4.82	94.0	94.7

where C_0 is the initial dye concentration (mg/L), C_t is the residual dye concentration (mg/L) at time t, V is the volume (L) of aqueous solution, and M is the mass of the adsorbent (g).

2.4. Experimental design and analysis

A two level (2^3) full factorial experimental design was employed in this work with three main factors; adsorbent dose (A), dye concentration (B) and temperature (C) as suggested in literature (Abdel-Ghani, Hegazy, El-Chaghaby, & Lima, 2009). The investigated factor levels are given in Table 1. The demarcation of experimental design space for each factor was fixed based upon our previous lab studies. The experimental design and statistical significance of investigated factors and their combinations were carried out using Design Expert Trial (8.0.1.7, Stat-Ease Inc., Minneapolis, USA). A multiple regression analysis was conducted based on the first-order response function as given in Eq. (3):

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_i X_i X_j + \varepsilon \quad (3)$$

where β_0, β_i, β_{ij} are regression coefficients for the intercept, linear and interactions among factors, respectively, y is the response vector for q_e and R, whereas X_i and X_j are the independent factors in coded units, and ε is the error term (Chang, Teng, & Ismail, 2011). The fitness of regression model was evaluated by calculating coefficient of determination (R^2).

3. Results and discussion

3.1. Screening factors for decolorization and adsorption

The experimental design matrix, measured and predicted response of color removal (%R) and adsorption capacity (q_e) are given in Table 1. A randomized experimental sequence was followed in order to minimize the experimental noise of uncontrolled factors. The values for adsorption capacity and color removal were found in the range of 4.3–9.0 mg/g and 78–94%, respectively. Statistical significance of experimental factors was evaluated using normal probability plots and Pareto charts at 95% significance level. The effects of main factors and their interactions on adsorption capacity and color removal are presented in Fig. 2. The factors and their interactions, affecting the response vectors insignificantly, followed a normal distribution along a straight line. Contrary to non-significant terms, significant factors and combinations deviated from the normally distributed terms (Chang et al., 2011). Dye concentration was the most significant factor in terms of adsorption capacity whereas adsorbent dose and dye concentration appeared significant factors for color removal. These outcomes from probability plots were further verified employing Pareto charts (Fig. 3). The horizontal line in the charts specified the least significant effect level for factors and their interactions for a significance level ($p < 0.05$). The vertical column height showed the significance of each effect. Pareto chart verified that the factor B (dye concentration) showed a significant positive effect on the adsorption capacity of SRB. However, adsorbent dose (positive) and dye concentration (negative) displayed leading effects on color removal compared with rest of the factors and their interactions. The second-order codified polynomial regression models which correlate q_e and %R with each factor and its second-order interactions are given by the following equations:

$$q_e\,(\mathrm{mg/g}) = +6.51 + 0.10A + 1.94B + 0.015C + 0.13AB + 0.21\,AC - 0.050BC \quad (4)$$

$$R\,(\%) = +89.33 + 2.20A - 3.45B - 0.88C + 1.48AB + 1.25AC - 0.80BC \quad (5)$$

where A, B, C are the coded values of experimental factors; adsorbent dose, dye concentration and temperature, whereas AB, AC and BC represent interactions between the respective factors. The factors with positive values for their coefficients can improve the respective response vector for an increase in the level of those factors, whereas negative value of the coefficients suggests their inverse relationship with the response vectors. It was noticed from above equations that the adsorption capacity could be increased by increasing SRB dose, dye concentration and temperature, however, color removal appeared a function of adsorbent dosage only. These facts were in agreement with the findings of normal probability plots and Pareto charts. The coefficient of determination (R^2) and adjusted R^2 for the model were found in close agreement (0.996, 0.976). The closeness of two values implied that there was a negligible likelihood of including insignificant terms in the regression models (Chang et al., 2011). This fact was further verified by the closeness of experimental values of q_e and R aginst their respective predicted values as given in Table 1. The predicted values were normally distributed along their mean value which verified the adequacy of the regression models to describe adsorption capacity and color removal according to Eqs. (4) and (5).

The significance effect of initial dye concentration on adsorption capacity and color removal had also been discussed in literature. Safa and Bhatti (2011) have argued that the initial dye concentration is a driving force that can overcome mass transfer resistance present between the dye molecules in aqueous solution and adsorbent particles. Thus, the number of dye molecules competing for adsorption on the adsorbent surface increases at higher initial dye concentration leading to higher adsorption capacity. Nasuha et al. (2010) reported an increase in the adsorption capacity of tea waste from 18.6 to 134 mg/g against an increase in the concentration of MB dye from 50 to 500 mg/L. Similarly, Reddy et al. (2012) showed that adsorption capacity increases from 10.47 to 34.67 mg/g when initial dye concentration was increased from 25 to 100 mg/L. Although the adsorption capacity obtained in this study was lower compared with reported values in literature (Nasuha et al., 2010) yet it is higher or at least comparable with those of

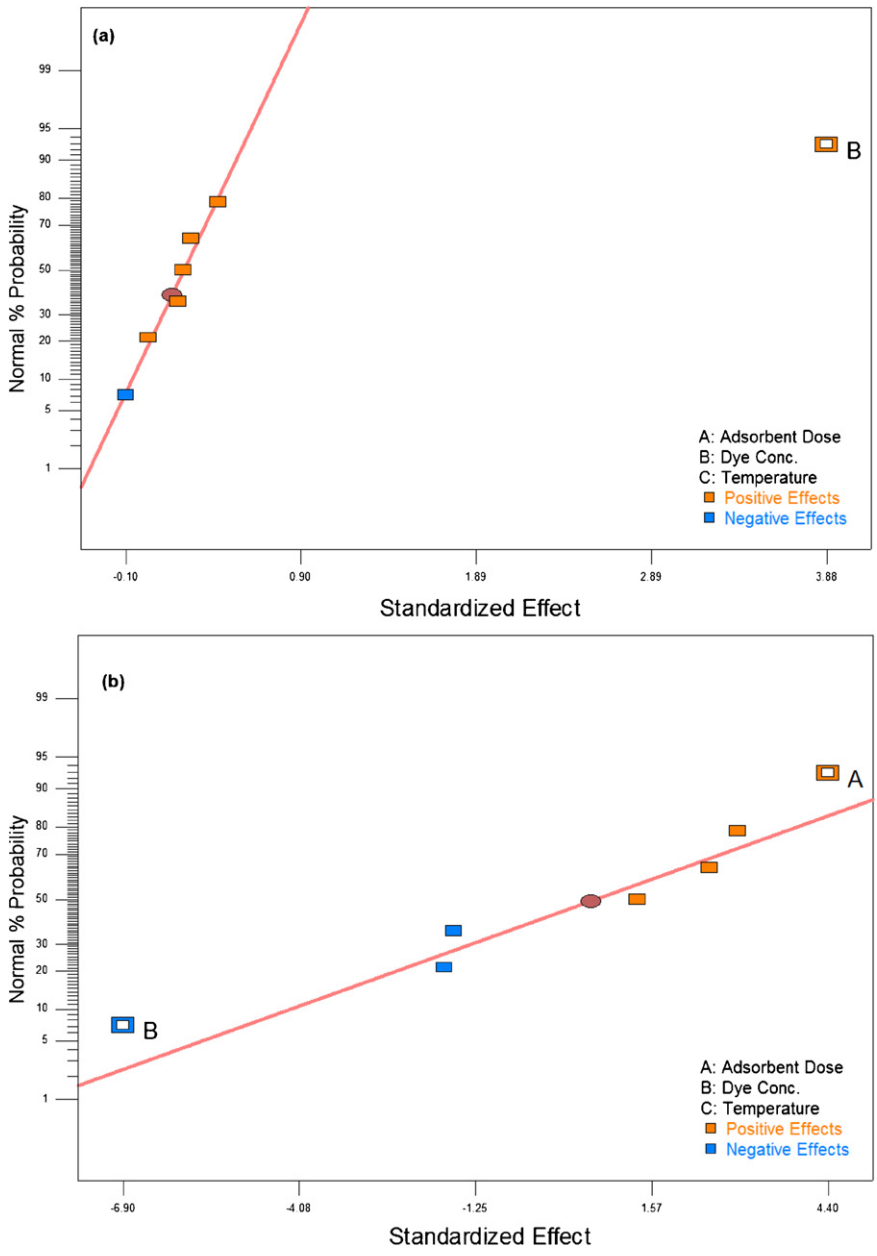

Fig. 2. Normal probability plot for standardized effects for (a) adsorption capacity and (b) color removal.

other lignocellulosic biomasses (Chowdhury et al., 2011; Low et al., 2011; Rafatullah, Sulaiman, Hashim, & Ahmad, 2010). The comparison of adsorption capacities of various materials is given in Table 2. Although q_e value is lower for SRB yet it is advantageous because it can be used without any costly treatment that makes it an economical option than other low cost adsorbents.

3.2. Adsorption dynamics

Adsorption isotherm studies are carried out in order to correlate adsorption capacity and residual concentration of adsorbate present in the aqueous solution. Several isotherm models (Langmuir, Freundlich) are applied to search for such correlations.

Table 2
Comparison of the monolayer adsorption capacities of MB dye on various biomass based adsorbents.

Adsorbent	Adsorption capacity (mg/g)	Reference
Cashew nut shell	5.31	Kumar et al. (2011)
Neem leaf powder	8.76	Bhattacharyya and Sharma (2005)
Activated carbon of rice husk	9.73	Sharma et al. (2011)
Natural rice husk	19.77	Zou, Li, Bai, Shi, and Han (2011)
Oxalic acid modified rice husk	53.21	Zou et al. (2011)
Peanut husk	72.13	Song, Zou, Bian, Su, and Han (2011)
Pine cone biomass	109.89	Sen et al. (2011)
Spent rice Biomass	8.30	This study

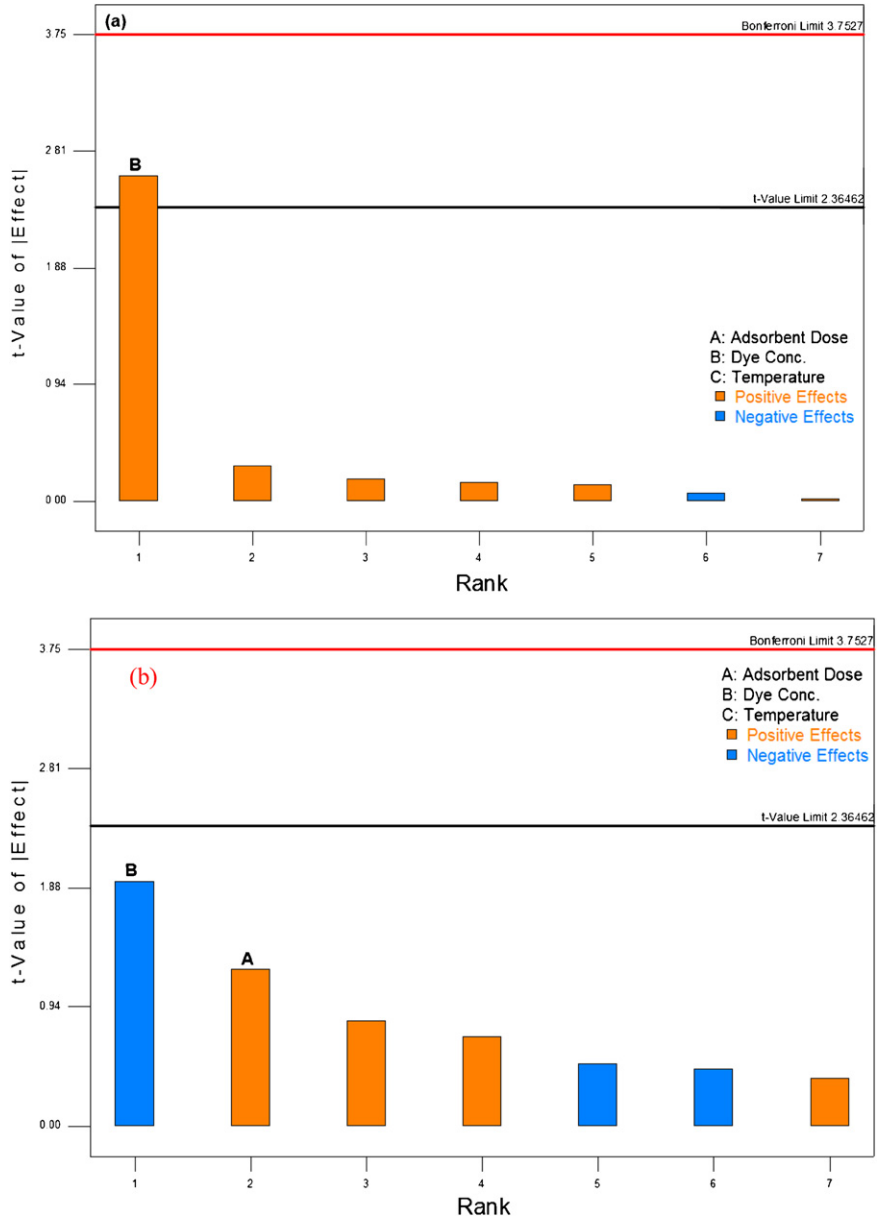

Fig. 3. Pareto charts of standardized effects for (a) adsorption capacity and (b) color removal.

However, only Langmuir isotherm model (Langmuir, 1916) is described in this study due to its adequacy (data for other models are not shown), and is presented in Eq. (6)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_{aqm}} \tag{6}$$

where q_m is the maximum adsorption capacity in monolayer adsorption, K_a is the adsorption equilibrium constant (L/mg) related to free energy of adsorption. The Langmuir isotherm model and its parameters have been presented in Fig. 4a. A linear relationship was found ($R^2 > 0.999$) that showed the fitness of model to describe the equilibrium of adsorption process. The closeness of q_m and experimental adsorption capacity further verified the validity of this model. Langmuir model was successfully applied and reported in the literature (Low et al., 2011; Nasuha et al., 2010; Reddy et al., 2012; Safa & Bhatti, 2011; Samarghandi, Hadi, Moayedi, & Askari, 2009). The validity of Langmuir model to the experimental data proposed that the adsorption of MB dye on SRB was mainly governed by chemisorption in the form of monolayer adsorption (Safa & Bhatti, 2011). Besides mechanistic description, this model also provided information about the feasibility of adsorption process through a dimensionless constant; separation factor; R_L (Hall, Eagleton, Acrivos, & Vermeule, 1966) which is given in Eq. (7).

$$R_L = \frac{1}{(1 + K_a C_0)} \tag{7}$$

Adsorption of any contaminant is regarded feasible and favorable if R_L values fulfill following condition; $0 < R_L < 1$. Furthermore, $R_L > 1$ (unfavorable), $R_L = 1$ (linear), $R_L = 0$ (irreversible). R_L values in this study were found in the range of 0–1 thus showing the feasibility of MB dye biosorption by SBR. A reduction in R_L value was also observed with the increase in the initial dye concentration. This observation proposed that the adsorption of MB dye was more favorable at higher initial dye concentration (Ahmad & Rahman, 2011), and the treatment of a wastewater with relatively higher

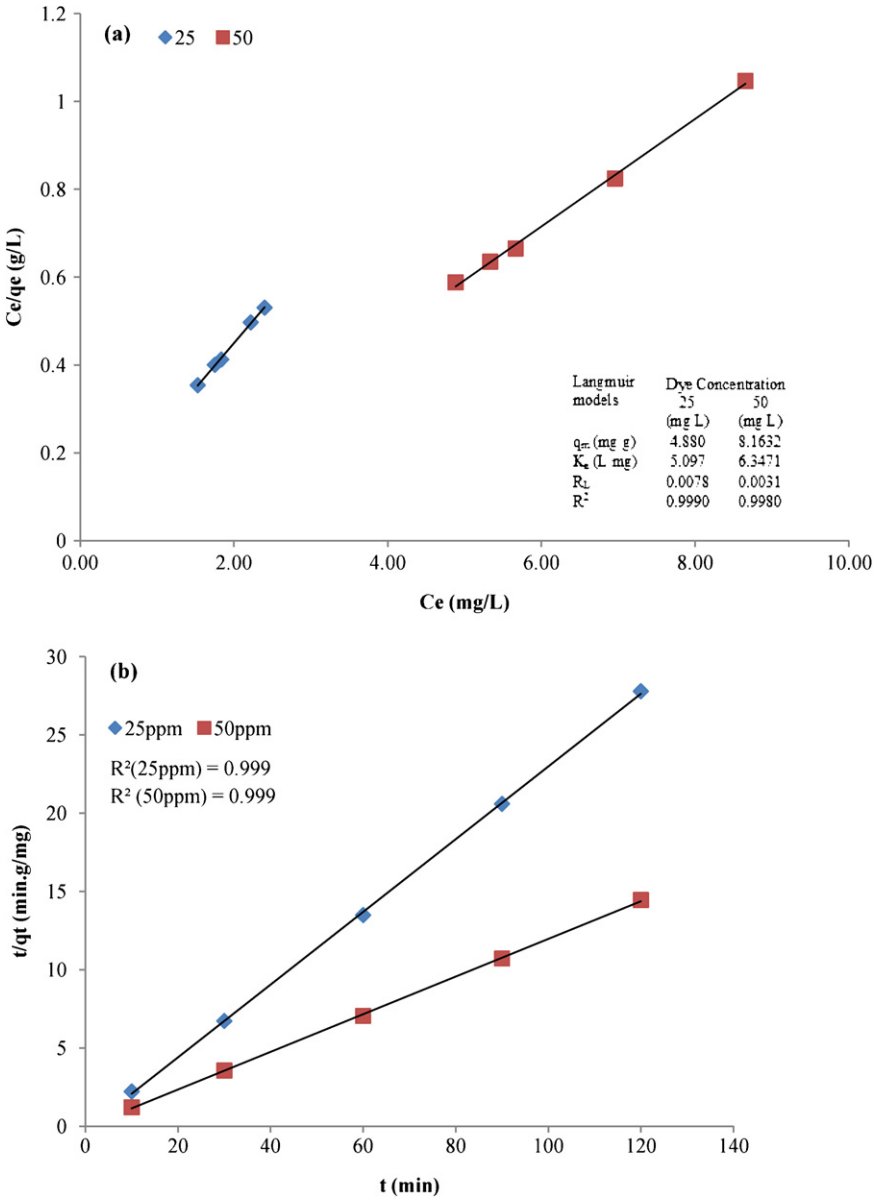

Fig. 4. Biosorption dynamics: (a) Langmuir isotherm plot and (b) pseudo second-order kinetic plot, for the adsorption of MB dye on SRB for 25–50 mg/L initial dye concentrations.

initial dye concentration could be possible. This fact provided the evidence of commercial scale application of SRB.

3.3. Adsorption kinetics

The dynamics and mechanism of adsorption process can be understood by evaluating the kinetic data (Ma et al., 2012; Silva et al., 2011). Adsorbate molecules undergo several stages during adsorption process which include migration of adsorbate molecules to the external surface of adsorbent particles, molecular and pore diffusion (Berrios, Martın, & Martin, 2012). Any adsorption process of dye molecules may involve either one single step or combinations of these steps depending on various factors (Ma et al., 2012; Safa & Bhatti, 2011).

Three kinetic models; pseudo first and second order and intra particle diffusion, are mostly used to describe the adsorption kinetics (Chen et al., 2012; Hu, Chen, Ji, & Yuan, 2010; Silva et al., 2011). However, it was noticed that the pseudo first order and intra particle diffusion models did not fit well to this study (data not shown) in agreement with literature (Ahmad & Rahman, 2011; Hu et al., 2010; Low et al., 2011; Vucurovic et al., 2012). Thus, kinetic data was best explained by pseudo-second order model (Ho & McKay, 1998) as shown in Fig. 4b. This model is given as under by Eq. (8).

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \tag{8}$$

where q_t is the adsorption capacity (mg/g) at any time t, and k_2 (g/mg min) is the second order rate constant. Pseudo second order model was applied by plotting t/q_t vs. t, and model parameters; rate constant (k_2) and initial adsorption rate ($h = k_2 q_e^2$), were calculated from the intercept of plot. These parameters are given in Table 3. The values of R^2 for two dye concentration levels were calculated as 0.999 which showed the adequacy of this model to describe kinetic data. The fitness of this model was further verified by calculating

Table 3
Pseudo second order kinetic parameters for the biosorption of MB dye onto spent rice biomass.

Dye conc	q_{exp}	$q_{e\,calc}$	k_2	h (mg/g min)	R^2	Δq (%)
25	4.32	4.30	0.218	16.83	0.999	3.6
50	8.30	8.31	0.244	4.04	0.999	1.5

normalized standard deviation (Δq), as used in literature (Nasuha & Hameed, 2011; Nasuha et al., 2010) given in Eq. (9).

$$\Delta q(\%) = \sqrt{\frac{\sum[(q_t, \exp - q_t, \text{calc})/q_t, \exp]^2}{n-1}} \times 100 \quad (9)$$

where $q_{t,exp}$ and $q_{t,calc}$ represent experimental and calculated values of q and n is the total number of data points. Higher values of R^2 and lower values of Δq suggested the fitness of kinetic model. Both the parameters ($R^2 = 0.999$, $\Delta q < 3.6\%$) exhibited the validity of pseudo second order model for the adsorption of MB dye (Nasuha & Hameed, 2011; Zhang et al., 2011; Dural, Cavas, Papageorgiou, & Katsaros, 2011). Vucurovic et al. (2012) have reported that the validity of pseudo second order model suggests chemisorption as the rate controlling step. Besides pseudo second order model, intra particle diffusion model (Weber & Morris, 1963) was also investigated (data not shown) to search for possible adsorption mechanism. The model is given as under

$$q_t = K_{pi} t^{1/2} + C_i \quad (10)$$

where q_t (mg/g) is the adsorption capacity at any time t, K_{pi} (mg/g min$^{1/2}$) is the intra-particle diffusion rate constant, and C_i is the boundary layer thickness. The plot for intra particle diffusion model did not pass through the origin implying that the intra particle diffusion was not the rate controlling factor. Although intra particle diffusion model was not fitted well to the kinetic data but it followed two distinct linear trends as reported in literature (Ma et al., 2012). These two trends described two possible mechanistic phases of adsorption process. The first phase represented rapid adsorption due to the mass transfer from the MB dye solution to the external surface of SRB. Rapid adsorption during first phase was followed by a slower phase of intra-particle diffusion (Vadivelan & Kumar, 2005). Thus, combination of mechanisms was involved in the adsorption of MB dye on SRB. Similar results have been reported in the literature (Gusmão, Gurgel, Melo, & Gil, 2012; Hameed, Mahmoud, & Ahmad, 2008; Ma et al., 2012; Safa & Bhatti, 2011; Vadivelan & Kumar, 2005; Vucurovic et al., 2012).

3.4. Adsorption thermodynamics

Temperature presents a notable effect on the adsorption process that is explained by means of thermodynamic parameters (Hu et al., 2010). Thermodynamic parameters such as change in standard free energy (ΔG°), change in standard enthalpy (ΔH°), and change in standard entropy (ΔS°), are calculated using following equations (Smith and Van Ness, 1987).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (12)$$

where R is the ideal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin, $K_D = C_s/C_e$, is the distribution coefficient, and C_s (mg/L) is the equilibrium concentration of MB dye adsorbed on cattail biomass (Hu et al., 2010). The overall ΔG° values were negative (−1314, −1508 J/mol) for temperature levels of 25–50 °C which established that the biosorption process was spontaneous. Positive value of ΔH° (1568 J/mol) indicated endothermic nature of the biosorption process (Nasuha & Hameed, 2011). This fact was confirmed by the removal higher dye concentration from the aqueous phase (>45 mg/L) at 45 °C. The positive value of ΔS° (9.67 J/mol k) exhibited an increase in the randomness at dye–SRB interface which could possibly remove some of the adsorbed water molecules from the rice biomass surface (Malkoc & Nuhoglu, 2007) leading to higher dye removal. Similar finding has been reported by Safa and Bhatti (2011) and Nasuha and Hameed (2011) where MB dye was adsorbed on rice husk and tea waste, respectively.

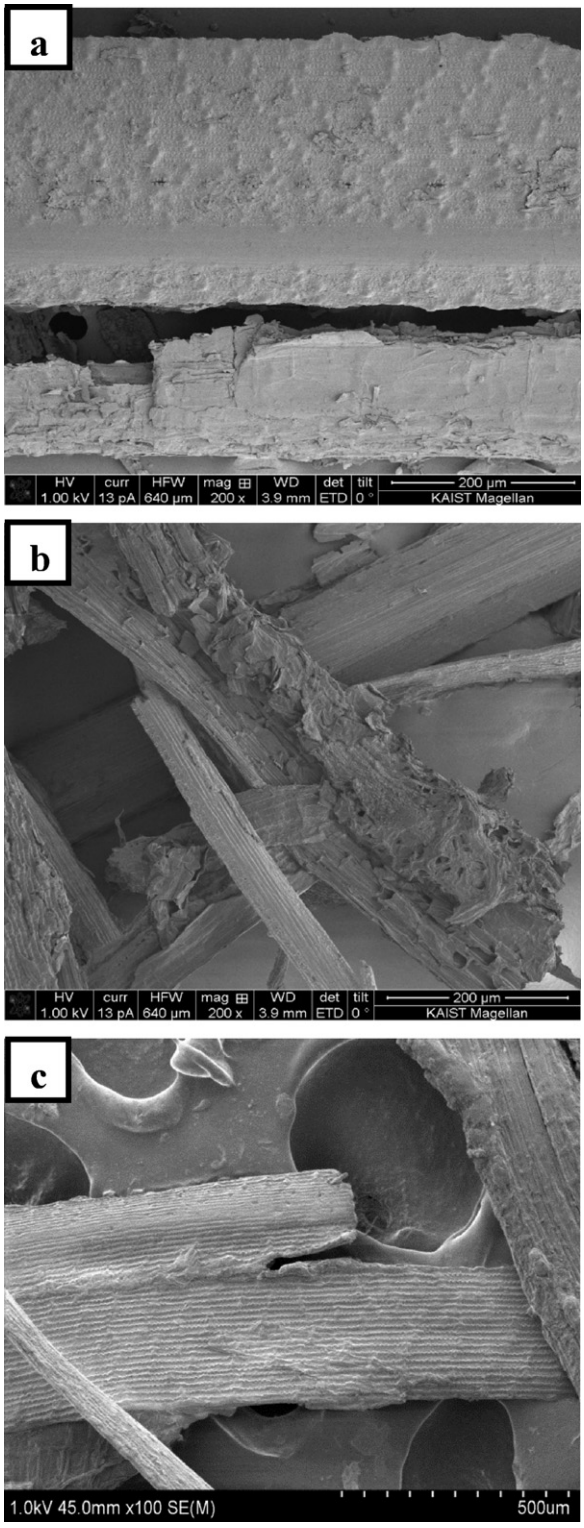

Fig. 5. SEM micrograph of (a) raw rice biomass, (b) sugar extracted rice biomass and (c) MB dye loaded SRB.

3.5. Scanning electron microscopy

The morphology and structure of adsorbent surface are characterized using scanning electron microscopy (SEM). Adsorbent surface without and with adsorption of MB dye is given in Fig. 5. It is clear from these micrographs that a monolayer has adsorbed on the surface of SRB. This finding has been confirmed by the fitness of Langmuir biosorption isotherm model.

4. Conclusion

This study was mainly focused to establish the feasibility of using spent rice biomass waste after sugar extraction as a low cost adsorbent for dyeing wastewater. The sugar extracted biomass from a cellulosic bioethanol facility required proper waste disposal which could add financial burden on the industry. The utilization of such biomass if used as adsorbent cannot only minimize its disposal cost but can also remove organic dyes from aqueous solutions. Adsorption was investigated using the statistical design of experiment to investigate the effects of experimental factors. Dye concentration appeared the most critical factor in terms of adsorption capacity and color removal. Kinetic, equilibrium and thermodynamic investigations verified the feasibility of spent rice biomass for its application as an adsorbent.

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