

## Coconut husk as a biosorbent for methylene blue removal and its kinetics study

Shailesh R. Dave\*, Vaishali A. Dave and Devayani R. Tipre

Department of Microbiology and Biotechnology, School of Sciences, Gujarat University,  
Ahmedabad 380009, Gujarat, India

(Received August 13, 2012, Revised October 16, 2012, Accepted October 27, 2012)

**Abstract.** Biosorption of methylene blue (MB) from aqueous solution was studied with respect to the point of zero charge of coconut husk, dye concentration, particle size, pH, temperature, as well as adsorbent and NaCl concentration using coconut husk biomass. Amongst Langmuir and Freundlich adsorption isotherms studied, Langmuir adsorption isotherm showed better agreement. Pseudo second order kinetics model was found to be more suitable for data presentation as compared to pseudo first order kinetics model. Also, involvement of diffusion process was studied using intraparticle diffusion, external mass transfer and Boyd kinetic model. Involvement of intraparticle diffusion model was found to be more relevant (prominent) as compared to external mass transfer (in) for methylene blue biosorption by the coconut husk. Moreover, thermodynamic properties of MB biosorption by coconut husk were studied. Desorption of methylene blue from biomass was studied with different desorbing agents, and the highest desorption achieved was as low as 7.18% with acetone, which indicate stable immobilization. Under the experimental conditions MB sorption was not significantly affected by pH, temperature and adsorbent concentration but low sorption was observed at higher NaCl concentrations.

**Keywords:** methylene blue; biosorption; adsorption isotherm; coconut husk; kinetic models

---

### 1. Introduction

Dyes are mainly used in textile industries for colouration of fibers. Presence of less than 1 mg/L of dye in water, produce obvious colouration, that makes water undesirable (Alam 2004, Bhole *et al.* 2004). Dyes may affect photosynthetic activity in aquatic life. Depending on the exposure time and dye concentration, dyes have acute and/or chronic effects (Won *et al.* 2004, Daneshvar *et al.* 2007, Özera and Turabik 2010). As dyes are synthetic compounds with complex aromatic structures, they are very stable and difficult to degrade. Increasing concerns for pollution control has necessitated economic, affordable as well as effective pollution control methods (Aksu and Dönmez 2003, Fu and Viraraghavan 2003, Alam 2004, Bhole *et al.* 2004).

Various physical and chemical methods used for treatment of dye containing waste waters require considerable start up costs and cannot meet stringent effluent colour standards (Han *et al.* 2007, Vilar *et al.* 2007). Among basic dyes, methylene blue and rhodamine B, have been used as probe

---

\*Corresponding author, Professor, E-mail: [shaileshrdave@yahoo.co.in](mailto:shaileshrdave@yahoo.co.in)

molecules for the removal of dyestuffs (Fernandez *et al.* 2012). In biodegradation methods, nutrient requirements and growth conditions of involved microorganisms have to be maintained. Moreover, dyes are sometimes converted to more toxic compounds (Schliephake and Lonergan 1996). Thus, biosorption using waste biomass is an effective and economic option for dye removal (Mumin *et al.* 2007). Natural materials existing in large quantities, or certain waste products from industrial or agricultural operations, have been reported as potential biosorbents in lab studies (Gupta and Suhas 2009, Fernandez *et al.* 2012). Among these materials, agro-forest lignocellulosic residues have shown good biosorption capacities for some basic dyes (Fernandez *et al.* 2012). Large quantity of coconut husk is available as agro waste material in India.

In this context present study was aimed to determine and optimise the biosorption potential of coconut husk biomass as a biosorbent in the flask as well as lab scale column reactor for methylene blue - as a model basic dye.

## 2. Materials and methods

### 2.1 Biosorbent

Coconut husk biomass was collected, washed properly with distilled water and dried overnight in oven at 50°C. This dried biomass was crushed and sieved to get particle size < 595  $\mu\text{m}$ .

### 2.2 Dye

Basic dye Methylene blue (basic blue 9, C.I. 52015, M.W. 373.91 g/mol) of analytical grade obtained from ACS Chemicals, India, was used as biosorbate. Stock solution of 1000 mg/L (2.67 mmol/L) was prepared and diluted in distilled water as per requirement of experiments.

### 2.3 Biosorption study

If otherwise mentioned, biosorption batch experiments were conducted in triplicates in 100 mL Erlenmeyer flasks containing 25 mL sorbate solution having 40 mg/L MB and 0.1 g coconut husk as biosorbent. The system was kept at  $35 \pm 2^\circ\text{C}$  temperature agitating at 120 rpm in an environmental orbital shaker. Samples were withdrawn at regular time interval and was centrifuged at 5000 g for 10 min. To determine the sorbed dye, optical density was measured from the supernatant spectrophotometrically at 660 nm ( $\lambda_{\text{max}}$ ).

Point of zero charge (PZC) of coconut husk biomass was studied by adding 0.1 g biomass in 50 mL 1% w/v  $\text{KNO}_3$  solution with different initial pH ranging from 2-12 (pHi).

Effect of different physico-chemical parameters such as, MB concentration 10 to 200 mg/L in 25 mL system; pH 2 to 12; biomass concentration 0.1, 0.2, 0.4, 0.6 g in the system; temperature 10°C, 37°C and 55°C; and NaCl concentration 0 to 5% w/v were studied.

Laboratory scale column study was performed in a glass column of 40.0 cm height and 4.0 cm diameter filled with 20.0 g of biomass, to which 200 mL solution containing 100 mg/L MB concentration was passed with 1 h of residence time. The total volume of the column was 450 mL and working volume was kept 200 mL.

Different isotherms, kinetics and diffusion models studied are summarized in Table 1. Langmuir

Table 1 Detail of different isotherms, kinetics and diffusion models studied

Isotherm	Formulae	Constant
Langmuir	$q_e = \frac{Q_m b C_e}{1 + b C_e}$	$b$ is intercept of Langmuir isotherm plot
	$q_e$ = amount of adsorbed dye per unit weight of the biosorbent (mg/g); $C_e$ = unadsorbed dye concentration in solution at equilibrium (mg/L); $Q_m$ = maximum amount of dye per unit weight of biomass to form a complete monolayer on the surface ( $\mu\text{mol/g}$ )	
Freundlich	$q_e = K_F \cdot C_e^n$	$K_F$ and $n$ are slope and intercept of Freundlich adsorption isotherm
Kinetics		
Pseudo first order	$\log(q_e - q_t) = \log q_e + \frac{k_1}{2.303} t$	$k_1$ = Intercept of pseudo first order plot
	Where $q_t$ = amount of adsorbed dye per unit weight of the biosorbent at time $t$	
Pseudo second order	$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$k_2$ = Intercept of pseudo first order plot
Elovich model	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	$\alpha$ and $\beta$ slope and intercept of $\ln t$ versus $q_t$
Boyd model	$B_t = -0.498 - \ln\left(1 - \frac{q}{q_\infty}\right)$	
Diffusion process		
Mass transfer	$\left[\frac{dC/C_0}{dx}\right]_t = 0 = -\beta_L S$	$\beta_L S$ = Slope of $C/C_0$ versus time
Intraparticle diffusion	$\ln(1-\alpha) = -k_p t$ $\alpha$ = fractional attainment to equilibrium (FATE) given by $\alpha = [\text{dye}]_t / [\text{dye}]_e$ ; $k_p$ = intraparticle diffusion constant $q = K t^{1/2}$	$k_p$ = Slope of plot of $\alpha$ versus time  $K$ = Slope of plot of $q_t$ versus square root of time
	Where $q$ = amount of dye sorbed (mg/g) at time $t$ ; $K$ = intraparticle rate constant (mg/g/min)	

and Freundlich adsorption isotherms and sorption kinetics were derived from obtained data for MB sorption by the coconut husk. Mode of MB diffusion to coconut husk biomass was determined with the help of external mass transfer, intraparticle diffusion and Boyd kinetic model. Also thermodynamic properties of the sorption process were studied.

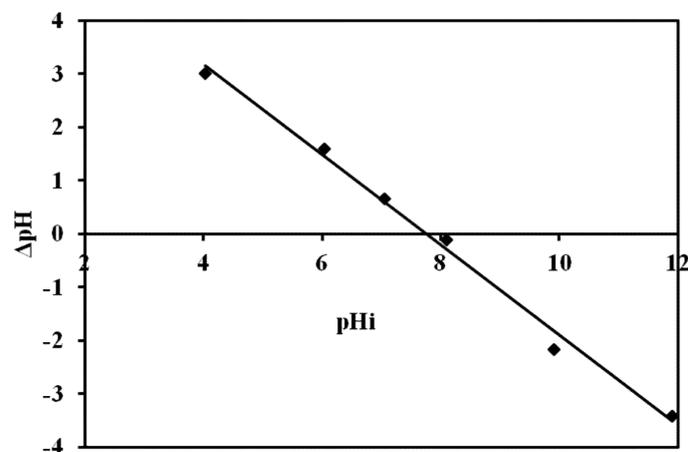


Fig. 1 Point of zero charge of coconut husk biosorbent

#### 2.4 Desorption and reuse study

Desorption of MB from biomass was tried with acetone, distilled water of pH 4 and pH 10, 0.1 N HCl, 0.1 N NaOH and 0.1 N EDTA. The potential of desorbed biomass for its reuse for dye sorption was checked by adding it to 25 mL of solution containing 10 mg/L MB.

### 3. Results and discussion

#### 3.1 Optimization of sorption process

PZC of coconut husk by solid addition method was found to be 7.8 (Fig. 1). PZC of biomass helps to explain the mechanism of biosorption because the net surface charge of the biosorbent depends on the system pH. Biosorption of cation is favoured at solution  $\text{pH} > \text{pH}_{\text{PZC}}$ , while anion biosorption is favoured at  $\text{pH} < \text{pH}_{\text{PZC}}$  (Ofomaja and Ho 2008). The MB being a potent cationic dye its sorption may be ideal when solution  $\text{pH} \geq \text{pH}_{\text{PZC}}$  as the net surface charge of the biosorbent is negative.

During biosorption equilibrium experiments, if the data are converted in terms of 1 g of biomass (in 250 mL of reaction system), it was observed that from 5, 10, 15, 20, 25, and 75 mg dye present in 250 mL the removal was 4.85, 9.77, 14.86, 19.85, 24.45 and 69.80 mg dye absorbed per 1 g of biomass respectively, which comes out to be more than 95% of dye sorbed within 30 min of contact time. Sorption capacity increased as dye concentration was increased (Fig. 2(a)). When 300 mg/L (0.8 mmol/L) MB solution was exposed to the biomass, the sorption capacity reached to as high as 69.8 and 74.0 mg/g biomass at 0.5 and 4 h of reaction time respectively. This could be due to increase in driving force of the concentration gradient with increasing dye concentration. Effect of dye concentration on sorption capacity was found to be similar as reported for sorption of basic dyes using sewage treatment plant biosolids, water hyacinth roots, *Hydrilla verticillata* and also for sorption of methylene blue by *Spirodela polyrrhiza* (Zhou and Zimmermann 1993, Benguella and Benaissa 2002, Alam 2004). Observed rapid uptake of dye suggests that the sorption process could be ion exchange in nature,

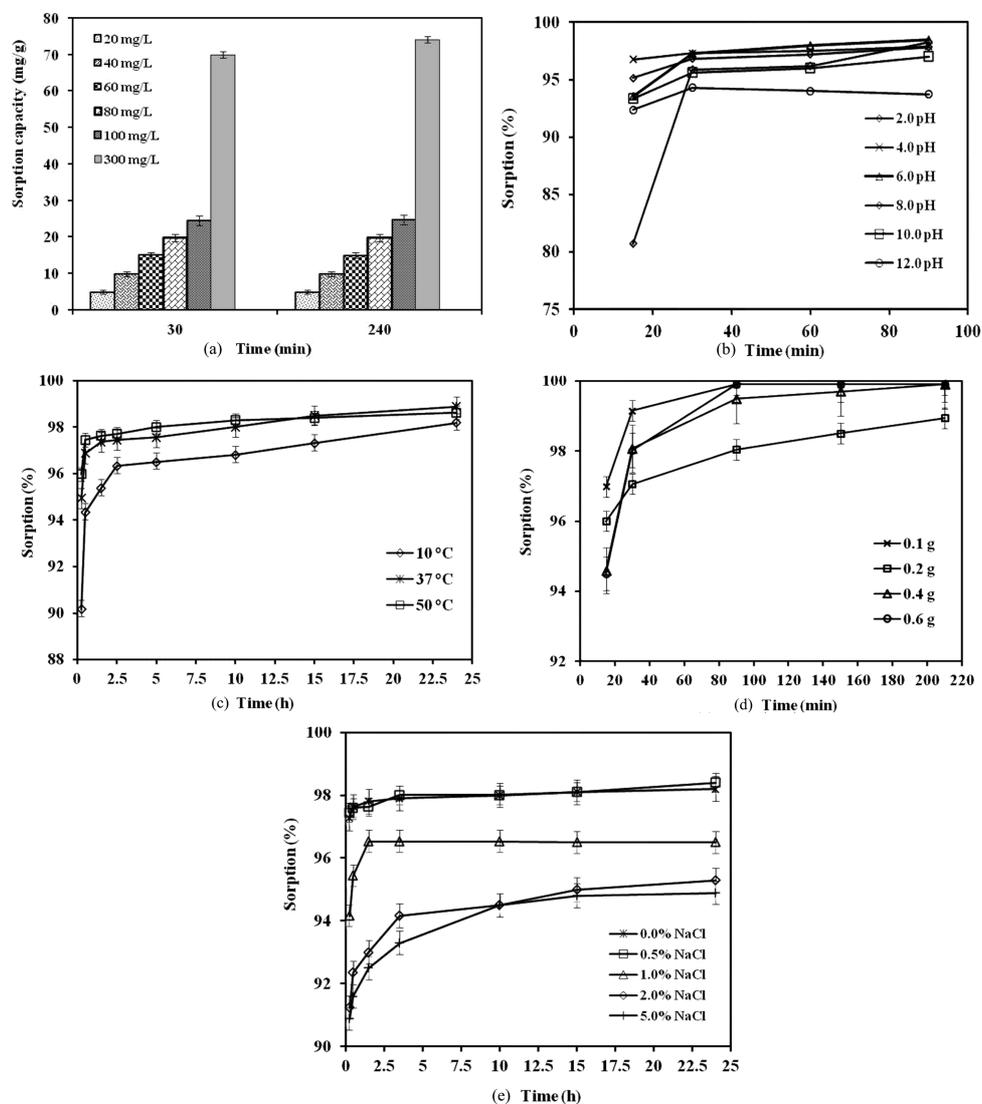


Fig. 2 Influence of various parameters on MB sorption (a) initial dye concentration (b) pH (c) reaction temperature (d) adsorbent concentration (e) NaCl concentrations

where the cationic dye molecules bind to the negatively charged organic functional groups present on the biomass surface (Zhou and Zimmermann 1993, Benguella and Benaissa 2002, Alam 2004, Ju *et al.* 2006).

The effect of particle size on MB was studied and data is shown in Table 2. Biosorbent of 500-595  $\mu\text{m}$  particle size showed ~5-6% higher sorption as compared to biosorbent of 595-707  $\mu\text{m}$  particle size. This may be due to the reason that smaller particle size provides more total surface area for binding of the dye. Thus, sorption was more and faster.

Both, colour of a dye as well as its sorption by a sorbent are affected by initial pH of a dye solution (Jaikumar and Ramamurthi 2009). Influence of pH on MB sorption was studied and the results are

Table 2 Effect of particle size on methylene blue sorption by coconut husk

Time (h)	Sorption %	
	Particle size < 595 $\mu\text{m}$	Particle size > 595 $\mu\text{m}$
0	0.00	0.00
0.25	51.65	45.78
0.50	65.06	61.43
1.00	70.59	64.23
1.50	74.15	66.88
2.00	76.66	70.17

shown in Fig. 2(b). In the range of pH 4-12, the highest sorption was observed at pH 4 and the lowest at pH 12. But there was only a marginal difference in the dye sorption between this pH range. This finding differs from the observation of Han *et al.* (2007). When 15 min contact time was considered, at pH 2 the lowest sorption was recorded may be due to the presence of an excess of  $\text{H}^+$  ions, which compete with the dye cation for biosorption sites (Fernandez *et al.* 2012). Even though at system pH 2.0 as high as 80.72% sorption was achieved after 15 min of contact time. The MB is a cationic dye, it should show more sorption at pH above the  $\text{pH}_{\text{PZC}}$  value of the biomass. However, no such difference was observed in this study. This indicates some other mechanism could be playing a significant role for the observed sorption.

Study of effect of temperature on the biosorption of dyes is important in application of biosorption at large level because textile and other effluents are produced at relatively high temperature (Jaikumar and Ramamurthi 2009). For the MB sorption on coconut fiber, the equilibrium uptake as a function of temperature is shown in Fig. 2(c). As it can be seen from the data, there was no significant difference in percent sorption at 37°C and 50°C reaction temperature beyond 1 h of contact time. The effect of temperature was clearly seen between 0 to 2.5 h of reaction time and sorption increased as the reaction temperature increased which may be attributed to increase in sorbent-sorbate interaction with increasing temperature. However, even at 10°C temperature after 15 min, the sorption was 90.1%, and at 50°C it was 94.9%, which indicate the possible utility of biomass in a wide range of temperature i.e., 10-50°C.

Range of biomass concentrations studied did not show much effect on MB sorption, however, highest 97% sorption was achieved with 0.1 g biomass containing 40 mg/L dye in 25 mL of system within 15 min of reaction time. This indicates that 0.1 g biomass was enough for 40 mg/L MB sorption and further increase in biomass concentration in the system caused particle aggregation and thus binding sites became unavailable to dye molecules (Fig. 2(d)).

The presence of 0.5% NaCl did not show any adverse effect on the MB sorption ability of the biomass. Beyond this NaCl concentration, there was a gradual decrease in sorption with an increase in NaCl concentration. Same observation was made by Han *et al.* (2007) for MB sorption by rice husk in the fixed bed column. It may be due to competition between MB cations and  $\text{Na}^+$  cations to bind with the biomass surface (Han *et al.* 2007). Even in the presence of 5% NaCl concentration after 1 h of incubation the difference in MB sorption was less than 6% as compared to control i.e., the system without any NaCl (Fig. 2(e)). This observation indicates that the biomass can be used even in the presence of 50 g/L NaCl in the system without significant loss in the MB removal ability of the biomass.

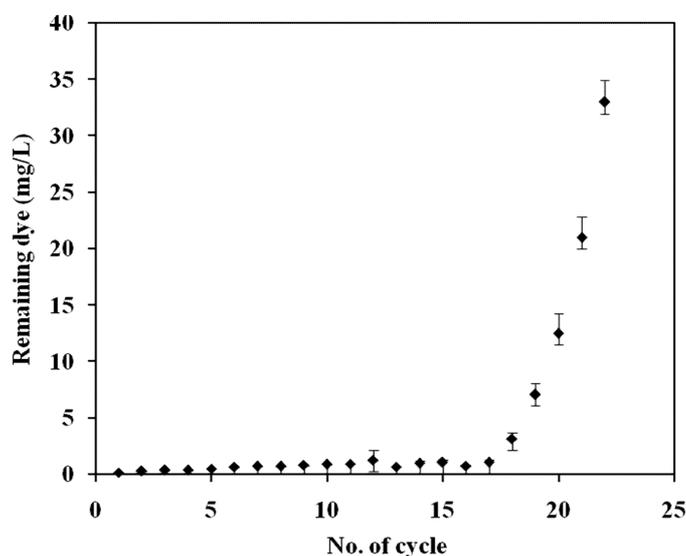


Fig. 3 Column study for MB removal by coconut husk

### 3.2 Development of column reactor

Laboratory scale column reactor study showed that coconut husk is an ecofriendly and efficient option for MB removal. Among the 22 cycles studied, with 200 mL dye solution having 100 mg/L concentration up to 18 cycles the unadsorbed MB in the effluent was less than 3.3 mg/L. Thereafter, the unadsorbed MB in the effluent increased and at 22nd cycle it reached to 12.5 mg/L (Fig. 3). In 18 cycles, the total MB sorbed was 350 mg, which leads to 17.5 mg sorption per g of biomass. When all the 22 cycles were considered, total sorption was 420 mg, which corresponds the sorption capacity of 21.0 mg/g of biomass in the column study.

### 3.3 Adsorption isotherms

Langmuir and Freundlich adsorption isotherms are commonly used for describing the adsorption equilibrium. The Langmuir isotherm assumes monolayer coverage and identical sites with the same adsorption energy on the sorbent surface while Freundlich adsorption isotherms assumes sorption onto heterogeneous solid surface and adsorption energy sites of exponential type. Furthermore, in Langmuir isotherm  $C_e/q_e$  versus  $C_e$  (Fig. 4(a)), the slope is adsorption capacity and intercept is adsorption equilibrium constant (Langmuir 1918, Staples and Geiselman 1988, Delle Site 2001, Ju *et al.* 2006). On the basis of comparison of  $R^2$  values, Freundlich adsorption isotherm (Fig. 4(b)) fitted better to the data as compared to Langmuir adsorption isotherm (Fig. 4(a)). Better agreement of Freundlich adsorption isotherm over Langmuir adsorption isotherm confirmed multilayer coverage of biosorbent molecule with available biosorbate. Values of various constants of Langmuir and Freundlich adsorption isotherm are shown in Table 3. Adsorption capacity can be calculated with the help of given formula (Freundlich 1926, Ju *et al.* 2006).

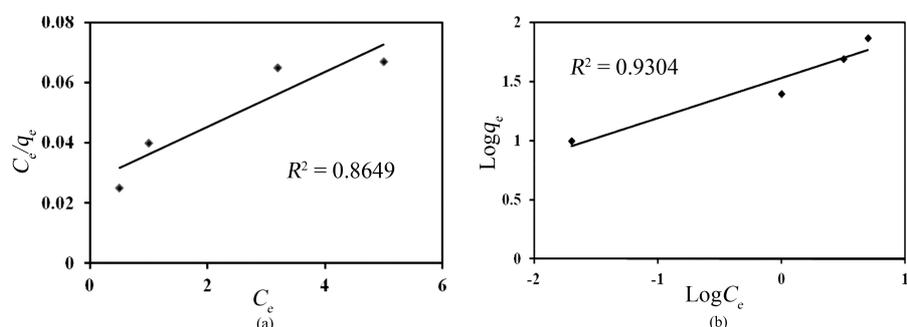


Fig. 4 Adsorption isotherms (a) Langmuir (b) Freundlich

Table 3 Langmuir and Freundlich isotherm constants for MB sorption by coconut husk

Isotherm						
Langmuir				Freundlich		
$q_e$ (mg/g)	$b$ (l/g)	$R_L$	$R^2$	$K_F$	$N$	$R^2$
11.91	13.00	0.004	0.996	1.528	0.34	0.930

$q_m = \frac{(C_0 - C_e)V}{M}$  where,  $q_m$  = adsorption capacity (mg/g);  $C_0$  and  $C_e$  = initial and equilibrium concentrations (mg/L);  $M$  = adsorbent dosage;  $V$  = solution volume.

### 3.4 Sorption kinetics

Study of adsorption kinetics provides information regarding the mechanism of sorption, which is important to know the efficiency of the process (Jaikumar and Ramamurthi 2009).

To investigate the sorption process of MB on coconut husk biomass, pseudo first order and pseudo second order kinetics were used and calculations were done using these equations (Table 1). A straight line of the plot of  $\log(q_e - q_t)$  versus  $t$  suggests the applicability of this kinetic model. In most cases, the first order equation of Lagergren does not provide a good fit over the whole range of contact time. Pseudo first order kinetic model for MB is shown in Fig. 5(a).

In pseudo second order kinetic model the initial biosorption rate  $h$  (mg/g.min) can be defined as,  $h = k_2 q_e^2$ .

The rate parameters  $k_2$  and  $q_e$  can be directly obtained from the plot of  $t/q_t$  against  $t$  (Fig. 5(b)). Values of  $k_1$ ,  $k_2$ ,  $q_e$ ,  $h$  and  $R^2$  for pseudo second order kinetic models are given in Table 4. The calculated correlation coefficients are closer to unity for pseudo second order kinetics than that for pseudo first order kinetic model. Therefore, the sorption can be approximated more appropriately by the pseudo second order kinetic model for the biosorption of MB by coconut husk.

The Elovich equation is given in Table 1. The constants  $\alpha$  and  $\beta$  can be obtained from the slope and the intercept of the linear plot of  $q_t$  versus  $\ln t$  (Alzaydien and Manasreh 2009). The Elovich kinetic model for MB sorption by coconut husk biomass is represented as the plot of  $\ln t$  versus  $q_t$  in Fig. 5(c). The correlation coefficients  $R^2$  and the constants  $\alpha$  and  $\beta$  are represented in Table 4. The correlation coefficient values obtained from an Elovich kinetic model are lower as compared to that

Table 4 First order, second order and Elovich kinetic constants for MB sorption by coconut husk

$C_0$ (mg/L)	First order kinetics			Second order kinetics				$C_0$ (mg/L)	Elovich kinetics model		
	$q_e$ (mg/g)	$k_1$ (l/min)	$R^2$	$q_e$ (mg/g)	$k_2$ (m/mg/min)	$H$ (mg/g.min)	$R^2$		$\alpha$ (m/mg/min)	$\beta$ (g/mg)	$R^2$
30	-0.006	0.5	0.8	7.35	0.017	0.918	1	20		10	0.85
50	0.013	-2.69	0.6	12.31	0.035	5.3	1	40	1.71	0.26	0.84
100	0.014	-2.85	0.6	24.68	0.071	43.24	1	60	1.17	0.21	0.9
200	0.008	-1.86	0.8	49.37	0.1	243.7	1	80	1.16	0.15	0.96

of pseudo second order model indicating that the experimental data generated for MB sorption by coconut husk biomass can be well represented by pseudo second order kinetic model.

### 3.5 Diffusion process

The absorption process of a sorbate on a sorbent includes 4 main steps: (1) transport of sorbate in the bulk of the solution; (2) diffusion of sorbate across the liquid film in its surrounding area; (3) diffusion within the pores of sorbent; and (4) sorption and desorption within the particle and the sorbent surface (Akkaya and Özer 2005, Ofomaja 2007).

The external mass transfer is critically involved in the initial phase of biosorption process (Akkaya and Özer 2005). For the biosorption of MB on coconut husk biomass plot of  $C/C_0$  versus  $T$  is shown in Fig. 6(a). The value of  $\beta_L S$  calculated for MB biosorption by coconut husk from the slope of the plot  $C/C_0$  versus  $T$ . The regression coefficient  $R^2$  and external mass transfer ( $\beta_L S$ ) calculated for MB sorption by

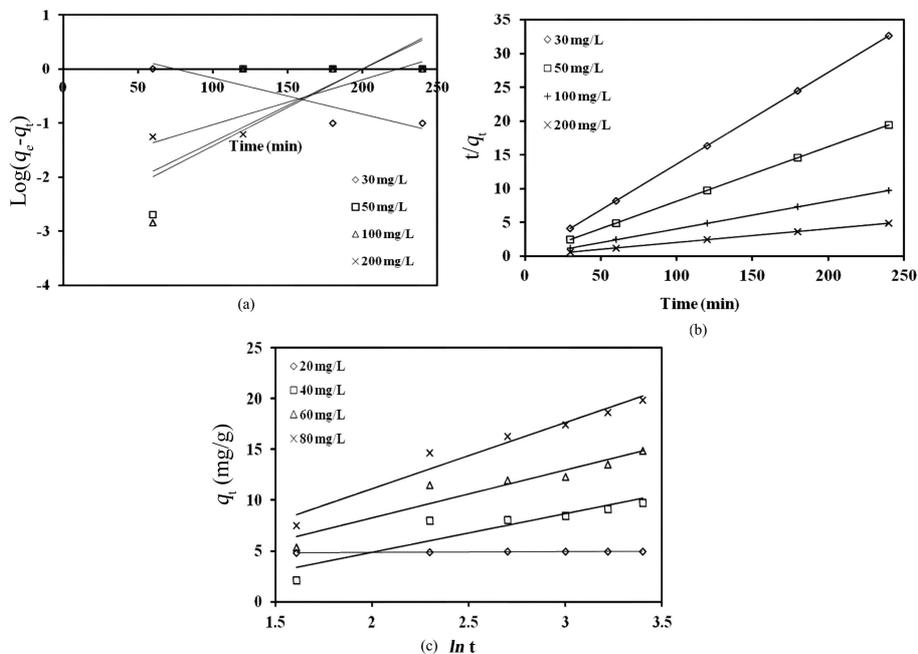


Fig. 5 Kinetics for MB sorption by coconut husk (a) Pseudo first order (b) Pseudo second order (c) Elovich

Table 5 External mass transfer and intraparticle diffusion constants for MB sorption by coconut husk

Dye concentration (mg/L)	External mass transfer constant ( $\beta_L S$ )	$R^2$	Intra particle diffusion constant ( $K$ )	$R^2$
20	0.013	0.63	0.019	0.85
40	0.024	0.66	0.78	0.89
60	0.02	0.77	1.4	0.88
80	0.021	0.82	2.21	0.99

coconut husk is given in Table 5.

Several models are available for intraparticle diffusion study of a biosorption process. The FATE (Fractional Attainment To Equilibrium) model is given by Okieimen and Okundaye (1989) and the equation is given in Table 1. The FATE plot (Fig. 6(b)) for MB describes how equilibrium was achieved by coconut husk biomass. As it is clear from the figure,  $\alpha$  value covers 1 for all dye concentrations showing that the sorption process has achieved equilibrium. Regression coefficient values  $R^2$  and intraparticle diffusion constant values are shown in Table 5.

Weber-Morris plot was also used for investigation of intraparticle diffusion mechanism for biosorption process and the equation for this model is given in Table 1. If the plot of  $q$  versus  $t^{1/2}$  is linear, intraparticle diffusion is involved in the sorption process and if the straight line passes through origin then intraparticle diffusion is the rate limiting step in the sorption process (Akkaya and Özer 2005). Weber-Morris model applied to experimental data is shown as Fig. 6(c). The value of intraparticle diffusion constant was obtained from the slope of the linear portion of the plot and shown in Table 5. An increase in  $K$  value was recorded with increasing initial dye concentration. Higher regression coefficient values ( $R^2 > 0.8$ ) were recorded for MB sorption by coconut husk. The involvement of external mass transfer and intraparticle diffusion in a sorption process can be differentiated with the help of Boyd kinetic model (Ofomaja 2007) that is shown in Table 1. The linearity of this plot of  $B_t$  versus time provides useful information to distinguish between external mass transfer and intraparticle diffusion (Ofomaja 2007). Boyd plot for MB sorption by coconut husk is expressed as Fig. 6(d). From Boyd plot it can be observed that 20 mg/L dye concentration line of the plot did not pass through the origin whereas, for all other dye concentrations under study, the plot moved towards the origin indicating that intraparticle diffusion is main rate controlling step for 40, 60, 80 mg/L dye concentrations. On the contrary external mass transfer played a critical role for 20 mg/L dye concentration.

### 3.6 Study of thermodynamic parameters

The equilibrium constants obtained from Langmuir adsorption isotherm for 10°C, 30°C and 50°C used to determine thermodynamic parameters like  $\Delta G$  (free energy change),  $\Delta H$  (enthalpy) and  $\Delta S$  (entropy change). These parameters are important to determine feasibility and the nature of the biosorption process.

$\ln k_d = \frac{\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R}$  where,  $k_d$  = sorption coefficient;  $R$  = ideal gas constant (8.314) Plot of  $\ln k$  versus  $1/T$  was used to find the values of  $\Delta H$  and  $\Delta S$  from the slop and intercept respectively. Standard free energy change  $\Delta G$  for specific adsorption was calculated using

$$\Delta G = \Delta H - T \Delta S$$

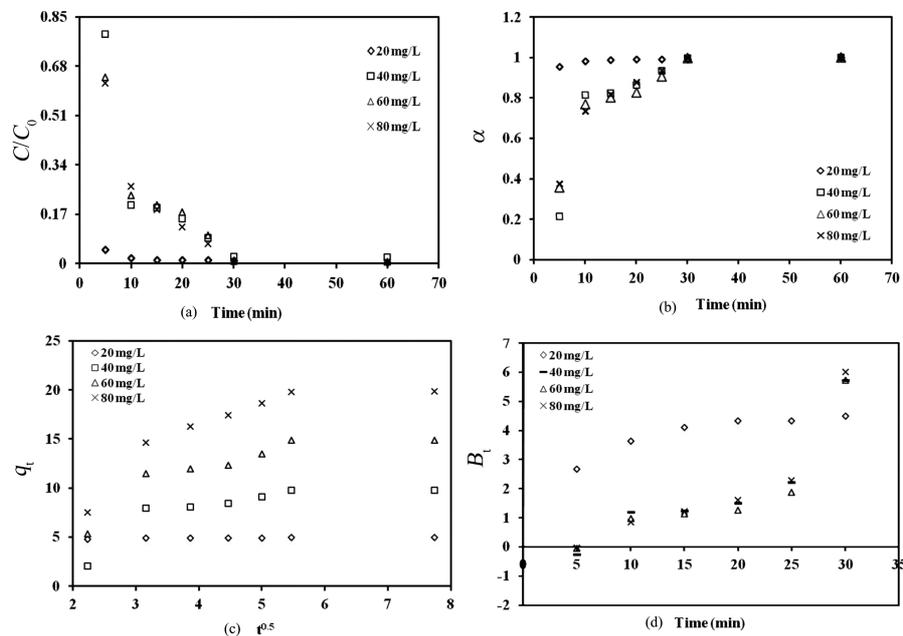


Fig. 6 (a) External mass transfer plot for MB sorption by coconut husk (b) Fractional attainment to equilibrium (FATE)  $\alpha$  against time for MB sorption by coconut husk (c) Intraparticle diffusion plot for MB sorption by coconut husk (d) Boyd plot for MB sorption by coconut husk

$\Delta H$  and  $\Delta S$  values obtained from Fig. 7 were found to be 1735 and -7.89 respectively.

Positive value of  $\Delta H$  indicated that MB sorption by coconut husk is an endothermic process indicating a strong interaction between MB and coconut husk. Moreover, the negative  $\Delta S$  value indicated decreases in randomness at solid liquid layer during the sorption process.  $\Delta G$  values calculated for 10, 30 and 50°C were found to be -499, -655.6 and -814.6 respectively, which shows the spontaneous nature of sorption process. The decrease  $\Delta G$  value with increasing temperature indicates a more efficient interface during adsorption.

### 3.7 Desorption and reuse

Among all desorbing agents studied, the highest desorption of MB achieved was only 7.18% by acetone (Table 6). Such a low desorption even with organic desorbing agents reduces chances of dye release from biomass and thus reduce chances of release of pollutants from biomass. This could provide almost complete long lasting immobilization of MB on coconut husk biomass. As high as 93% MB was sorbed in 3.5 h when desorbed biomass was recycled and reused (Table 5). This indicates that the biomass is not saturated and it can remove more MB.

## 4. Conclusions

Coconut husk was found to be an effective, ecofriendly and efficient sorbent for MB sorption. Point

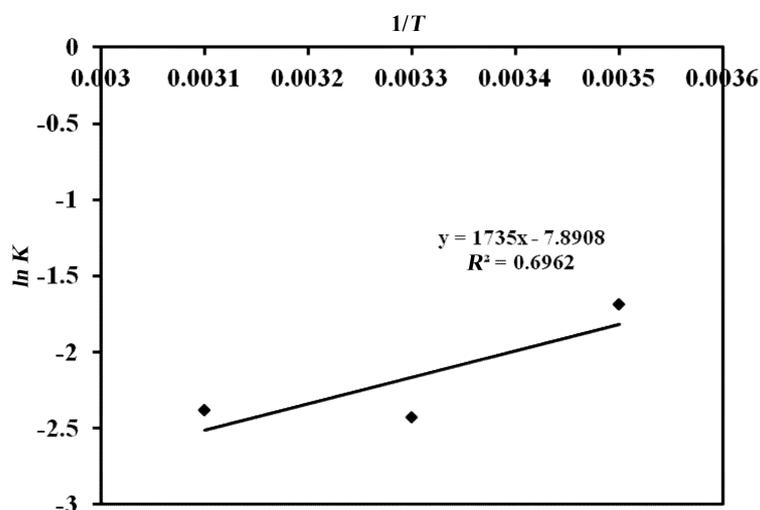


Fig. 7 Thermodynamic study for MB sorption by coconut husk

Table 6 Desorption of MB from biosorbent with different desorbing agents and resorption of the same by desorbed biomass

Desorption		Resorption	
Desorbing agent	Desorption (%)	Time (min)	Resorption (%)
Alkaline water	0.43	15	90.0
Distilled water	0.94	90	91.0
0.1 N HCl	3.29	210	93.0
0.1 N NaOH	4.68	1440	93.1
Acetone	7.18		
0.1 N EDTA	0.59		

of zero charge of MB was found to be 7.8. The studied biosorbent have sorption capacity as high as 74.0 mg/g of biomass under the experimental setup and it increased with increasing dye concentration. Temperature and pH did not have much effect on MB sorption but good sorption was achieved with smaller particle size. Higher NaCl concentration interferes with MB sorption. Biosorbent : biosorbate ratio of 1:1000 was found to be sufficient for optimum sorption. Increasing biomass concentration decreased per gram MB sorption. Out of all desorbing agents studied acetone was found to be the best. When desorbed biomass was reused, it also gave 92.83% sorption. Freundlich adsorption isotherm fitted better for MB sorption by coconut husk than Langmuir adsorption isotherm indicating multilayer covering of biomass by dye molecules. Pseudo second order kinetics model can express the process of MB biosorption by coconut husk more appropriately as compared to the pseudo first order kinetics and Elovich kinetic model. External mass transfer played important role in sorption for 20 mg/L MB concentration whereas, for all other dye concentrations intraparticle diffusion played significant role in sorption process. Study of thermodynamic parameters showed that MB sorption by the biomass is an endothermic and spontaneous process. Coconut husk is dumped as waste in many places and thus if

used as a biosorbent for dye removal could offer an economical and effective option for dye removal.

## References

- Akkaya, G. and Özer, A. (2005), "Biosorption of Acid Red 274 (AR 274) on *Dicranella varia*: determination of equilibrium and kinetic model parameters", *Process Biochem.*, **40**(11), 3559-3568.
- Aksu, Z. and Dönmez, G. (2003). "A comparative study on the biosorption characteristics of some yeasts for Remazol Blue reactive dye", *Chemosphere*, **50**(8), 1075-1083.
- Alam, M.Z. (2004), "Biosorption of basic dyes using sewage treatment plant biosolids", *Biotechnol.*, **3**(2), 200-204.
- Alzaydien, A.S. and Manasreh, W. (2009), "Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto activated phosphate rock", *Int. J. Phys. Sci.*, **4**(4), 172-181.
- Benguella, B. and Benaissa, H. (2002), "Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies", *Water Res.*, **36**(10), 2463-2474.
- Bhole, B.D., Ganguly, B., Madhuram, A., Deshpande, D. and Joshi, J. (2004), "Biosorption of methyl violet, basic fuchsin and their mixture using dead fungal biomass", *Curr. Sci. India*, **86**(12), 1641-1645.
- Daneshvar, N., Ayazloo, M., Khataee, A.R. and Pourhassan, M. (2007), "Biological decolourization of dye solution containing Malachite green by microalgae *Cosmarium* sp.", *Bioresour. Technol.*, **98**(6), 1176-1182.
- Delle Site, A. (2001), "Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review", *J. Phys. Chem. Ref. Data*, **30**(1), 187-439.
- Fernandez, M.E., Nunell, G.V., Bonelli, P.R. and Cukierman, A.L. (2012), "Batch and dynamic biosorption of basic dyes from binary solutions by alkaline-treated cypress cone chips", *Bioresour. Technol.*, **106**, 55-62.
- Freundlich, H. (1926), *Colloid and Capillary Chemistry*, Methuen and Co. Ltd., England.
- Fu, Y. and Viraraghavan, T. (2003), "Column studies for biosorption of dyes from aqueous solutions on immobilized *Aspergillus niger* fungal biomass", *Water SA*, **29**(4), 465-472.
- Gupta, V.K. and Suhas (2009), "Application of low-cost adsorbents for dye removal – a review", *J. Environ. Manage.*, **90**(8), 2313-2342.
- Han, R., Wang, Y., Yu, W., Zou, W., Shi, J. and Liu, H. (2007), "Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column", *J. Hazard. Mater.*, **141**(3), 713-718.
- Jaikumar, V. and Ramamurthi, V. (2009), "Biosorption of Acid Yellow by spent brewery grains in a batch system: Equilibrium and kinetic modelling", *Int. J. Biol.*, **1**(1), 21-29.
- Ju, D.J., Byun, I.G., Lee, C.H., An, G.H. and Park, T.J. (2006), "Biosorption characteristics of reactive dye into dried activated sludge", *Water Practice Technol.*, **1**(3), doi10.2166/wpt.2006.066 online.
- Langmuir, I. (1918), "The adsorption of gases on plane surfaces of glass, mica and platinum", *J. Am. Chem. Soc.*, **40**(9), 1361-1403.
- Mumin, M.A., Khan, M.M.R., Akhtar, K.F. and Uddin, M.J. (2007), "Potentiality of open burnt clay as an adsorbent for the removal of Congo red from aqueous solution", *Int. J. Environ. Sci. Tech.*, **4**(4), 525-532.
- Ofomaja, A.E. (2007), "Kinetics and mechanism of methylene blue sorption onto palm kernel fibre", *Process Biochem.*, **42**(1), 16-24.
- Ofomaja, A.E. and Ho, Y.S. (2008), "Effect of temperatures and pH on methyl violet biosorption by *Mansonia* wood sawdust", *Bioresour. Technol.*, **99**(13), 5411-5417.
- Okieimen, F.E. and Okundaye, J.N. (1989), "Removal of cadmium and copper ions from aqueous solutions with thiolated maize (*Zea mays*) cob meal", *Biological Wastes*, **30**(3), 225-230.
- Özera, A. and Turabik, M. (2010), "Competitive biosorption of acid dyes from binary solutions onto *Enteromorpha prolifera*: application of the first order derivative spectrophotometric analysis method", *Sep. Sci. Technol.*, **45**(3), 380-393.
- Schliephake, K. and Lonergan, G.T. (1996), "Laccase variation during dye decolourization in a 200 L packed-bed bioreactor", *Biotechnol. Lett.*, **18**(8), 881-886.
- Staples, C.A. and Geiselmann, S.J. (1988), "Cosolvent influences on organic solute retardation factors", *Ground Water*, **26**(2), 192-198.
- Vilar, V.J.P., Botelho, C.M.S. and Boaventura, R.A.R. (2007), "Methylene blue adsorption by algal biomass

- based materials: biosorbents characterization and process behaviour”, *J. Hazard. Mater.*, **147**(1-2), 120-132.
- Won, S.W., Choi, S.B., Chung, B.W., Park, D., Park, J.M. and Yun, Y.S. (2004), “Biosorptive decolorization of Reactive Orange 16 using the waste biomass of *Corynebacterium glutamicum*”, *Ind. Eng. Chem. Res.*, **43**(24), 7865-7869.
- Zhou, W. and Zimmermann, W. (1993), “Decolorization of industrial effluents containing reactive dyes by actinomycetes”, *FEMS Microbiol. Lett.*, **107**(2-3), 157-161.