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Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk

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ABSTRACT

Rice husk treated with NaOH was tested as a low cost adsorbent for the removal of malachite green from aqueous solution in batch adsorption procedure. The adsorption experiments were carried out as a function of solution pH, initial dye concentration, contact time and temperature. The adsorption was found to be strongly dependent on pH of the medium. The Freundlich isotherm model showed good fit to the equilibrium adsorption data. The mean free energy (E) estimated from the Dubinin–Radushkevich model indicated that the main mechanism governing the sorption process was chemical ion-exchange. The kinetics of adsorption followed the pseudo-second-order model and the rate constant increased with increase in temperature indicating endothermic nature of adsorption. The Arrhenius and Eyring equations were used to obtain the activation parameters such as activation energy (E_a), and enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$) and free energy ($\Delta G^{\#}$) of activation for the adsorption system. Thermodynamic studies suggested the spontaneous and endothermic nature of adsorption of malachite green by treated rice husk. The isosteric heat of adsorption (ΔH_X) was also determined from the equilibrium information using the Clausius–Clapeyron equation. ΔH_X increased with increase in surface loading indicating some lateral interactions between the adsorbed dye molecules.

1. Introduction

Synthetic dyes are widely used in various industries such as textile, leather, paper, printing, food, cosmetics, paint, pigments, petroleum, solvent, rubber, plastic, pesticide, wood preserving chemicals and pharmaceutical industry [1,2]. Over 10,000 of different commercial dyes and pigments exist and more than 7×10^5 tonnes are produced annually worldwide [3]. Approximately 12% of synthetic dyes are lost during manufacturing and processing operations and 20% of these lost dyes enter the industrial wastewaters [4]. Textile industries consume two thirds of the dyes manufactured. During textile processing, up to 50% of the dyes are lost after the dyeing process and about 10–15% of them are discharged in the effluents [5]. The textile manufacturing industry alone discharges about 146,000 tonnes of dyes per year along with its wastewater which ultimately finds its way into the environment [6]. Generally the wastewater contains dye concentrations ranging from 10 to 200 mg L^{-1} [7]. The discharge of dye containing effluents into the natural water bodies can pose hazardous effects on the living systems because of carcinogenic, mutagenic, allergenic and toxic nature of dyes [8]. Dyes impede light penetration, retard photosynthetic activity, inhibit the growth of biota and also have a tendency to chelate metal ions which result in micro-toxicity to fish and other organisms [9].

Malachite green (MG), an *N*-methyl diaminotriphenylmethane dye, is the most widely used for coloring purpose among all other dyes of its category [10]. It is an extensively used biocide in the aquaculture industry world-wide. It is also used as a food coloring agent, food additive, a medical disinfectant and anthelminthic as well as a dye in silk, wool, jute, leather, cotton, paper and acrylic industries [11–13]. However there are several reports describing its hazardous and carcinogenic effects [14]. It is known to be highly cytotoxic and carcinogenic to mammalian cells and acts as a liver tumor promoter. In humans, it may cause irritation to the respiratory tract if inhaled and causes irritation to the gastrointestinal tract upon ingestion. Contact to malachite green with skin causes irritation with redness and pain; upon contact with eye will lead to permanent injury of human eyes. It also affects the aquatic life and causes detrimental effects in liver, gill, kidney, intestine, gonads and pituitary gonadotrophic cells [15,16]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters.

The disposal of dye wastewater with proper treatment is a big challenge. This is mainly because synthetic dyes used in industries are designed to resist fading upon exposure to sweat, heat, light, water, many chemicals including oxidizing agents, and microbial attacks [17]. The traditional methods for color removal include reverse osmosis, electrodialysis, ultrafiltration, ion-exchange, chemical precipitation, etc. However, all these methods have disadvantages like

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incomplete removal, high reagent and energy generation of toxic sludge or other waste products that require careful disposal, high capital and operating costs, labor intensive, etc. In this light, adsorption has emerged as an efficient and cost-effective alternative to conventional contaminated water treatment facilities. It is defined as a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings [3]. Adsorption separation in the environmental engineering is now an aesthetic attention and consideration abroad the nations, owning to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions [18]. A large variety of natural materials or the wastes/by-products of industries has been employed as inexpensive adsorbents for dye removal [3]. The waste materials seem to be viable option for dye removal because of their economic and eco-friendly traits, availability in abundance, low cost, regeneration of the biosorbent and the possibility of dye recovery. In this connection, special attention have been given to agricultural wastes like orange peel, banana pith, banana peel, plum kernels, apple pomace, wheat straw, sawdust, coir pith, sugarcane bagasse, tea leaves, bamboo dust, etc [3].

In India, rice husk is an easily available agricultural waste material, produced in large quantities as a by-product of rice milling and create potential environmental problems. The annual generation of rice husk has been estimated to be 18–22 million tonnes [19]. Rice husk possesses a granular structure, is insoluble in water, has chemical stability, high mechanical strength and accounts for about 20% of the whole rice. It consists of about 32% cellulose, 21% hemicelluloses, 21% lignin, 20% silica and 3% crude protein [20,21]. It also contains abundant floristic fiber, and some functional groups such as carboxyl, hydroxyl and amidogen, etc, representing a favorable characteristic of rice husk to be a potential adsorbent material [19]. Silica present on the outer surface of rice husks in the form of silicon-cellulose membrane acts as a natural protective layer against termites and other microbial attack on the paddy. This component is however responsible for insufficient binding between accessible functional groups on rice husks' surfaces and various adsorbate ions/molecules. The inner surface of rice husk is smooth and may contain wax and natural fats that provide good shelter for the grain but the presence of these impurities on the inner surfaces of rice husks also affects the adsorption properties of rice husk chemically and physically [21]. Therefore, removal of silica and other surface impurities can be expected to improve the adsorption properties of rice husk. Chemical modification of rice husk surface is thus necessary to upgrade or improve the adsorption properties. Alkali treatment of rice husk with sodium hydroxide (NaOH) has been demonstrated to improve the adsorption properties [21]. NaOH removes natural fats, waxes and low molecular weight lignin compounds from the rice husk surface thus revealing chemically reactive functional groups like –OH. The removal of the surface impurities also improves the surface roughness of the fibers or particles thus opening more hydroxyl groups and other reactive functional groups on the surface. The aim of the present study was to investigate and explore the possibility of using alkali treated rice husk for adsorption of MG from aqueous solutions. The study includes an evaluation of the effects of various operational parameters such as initial dye concentration, contact time, temperature and pH on the dye adsorption process. The adsorption kinetic models, equilibrium isotherm models and thermodynamic parameters related with the process were also performed and reported.

2. Materials and methods

2.1. Adsorbate

Malachite green used in this study was of commercial quality (CI 42000, FW: 365, MF: $C_{23}H_{25}N_2Cl$, λ_{max}: 618 nm) and was used without further purification. The chemical structure is shown in Fig. 1. Stock solution (500 mg L^{-1}) was prepared by dissolving accurately weighed quantity of the dye in double-distilled water. Experimental dye solution of different concentrations was prepared by diluting the stock solution with suitable volume of double-distilled water.

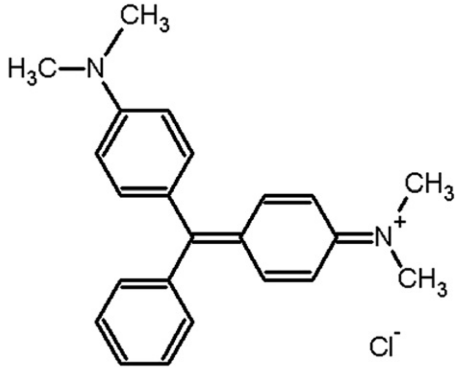

Fig. 1. Structure of malachite green.

2.2. Preparation of adsorbent

Rice husk used was obtained from a nearby rice mill of Durgapur, West Bengal, India. It was washed repeatedly with double-distilled water to remove dust and soluble impurities, and this was followed by drying at 343 K for 3 h. The dried rice husk was then suspended in 5% sodium hydroxide (NaOH) solution and the suspension was autoclaved at 10 psi for 15 min. The alkali solution was filtered off, and the rice husk was washed thoroughly with distilled water until the rice husk gave no color and the pH of the wash was close to neutral. The treated rice husk was then dried at 343 K for 6 h. After drying, the adsorbent was stored in sealed glass containers. The same adsorbent was used in all the experiments.

2.3. Scanning electron microscope (SEM) analysis

In order to characterize the surface structure and morphology of untreated and treated rice husk and treated rice husk after adsorption of MG, SEM analysis was carried out using a scanning electron microscope (Model Hitachi S-3000N) at an electron acceleration voltage of 20 kV. Prior to scanning, the samples were coated with a thin layer of gold using a sputter coater to make them conductive.

2.4. Batch adsorption experiments

The adsorption of MG on alkali treated rice husk was investigated in batch mode sorption equilibrium experiments. All batch experiments were carried out in 250 mL glass-stoppered, Erlenmeyer flasks containing a fixed amount of adsorbent with 100 mL dye solution at a known initial concentration. The flasks were agitated at a constant speed of 200 rpm for 2 h in an incubator shaker (Model Innova 42, New Brunswick Scientific, Canada) at 303 K. The influence of pH (2.0, 3.0, 4.0, 6.0, 7.0, 9.0), contact time (10, 30, 45, 60, 90, 120 min), initial dye concentration (10, 20, 50, 100 mg L^{-1}), and temperature (298, 303, 303, 313 K) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual dye concentration in the solution. The residual amount of dye in each flask was investigated using UV/VIS spectrophotometer (Model Hitachi-2800). The amount of dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according to a mass balance on the dye concentration using Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where C_i is the initial dye concentration (mg L^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), V is the volume of the solution (L), m is the weight of the treated rice husk in g. All the experiments were performed triplicate and the average value from results were taken.

In an adsorption study, it is necessary to fit the equilibrium adsorption data using different adsorption isotherm models and kinetic equations in order to analyze and design an adsorption process. Therefore, different theoretical models (Table 1) are applied to experimental data in order to find a model which adequately predicts kinetic and isotherm data. The validity of the models was evaluated by the coefficient of determination (r^2) and the chi-square test (χ^2) [18].

3. Results and discussion

3.1. Scanning electron microscope (SEM) analysis

SEM analysis is a useful tool for the analysis of the surface morphology of an adsorbent. SEM images of untreated and treated rice husks are shown in Fig. 2a–b. The micrographs in Fig. 2a and b represent an un-even surface and porous structure of both untreated and treated rice husk. However, as seen in Fig. 2b, the surface roughness of rice husk changed significantly after treatment with alkali. These include wearing of asperities and particle cracking. Pores and cavities of various dimensions are also clearly evident on the surface of treated rice husk. Further, the pores on the surface of the adsorbent are highly heterogeneous. The heterogeneous pores and cavities provided a large exposed surface area for the adsorption of MG. The presence of pores indicates that there was a good possibility for the dye molecules to be trapped and adsorbed onto the surface of the adsorbent. The mean size of surface cavities was measured on the image and the average diameter was less than 10 µm. These cavities are large enough to allow the dye molecules to penetrate into the lignocellulosic structure and interact therein with the surface groups.

Fig. 2c illustrates the SEM image of treated rice husk after adsorption of the dye. It is evident that the surface morphology of the treated rice husk is different before and after adsorption of the dye. The pores were completely filled after the adsorption of MG and the pores appear to be prominently swollen. This observation indicates that MG is adsorbed to the functional groups present inside the pores. The surface of the treated rice husk becomes smooth after adsorption of MG as shown in Fig. 2c. Smoothness of the surface is due to the adsorption of the dye. It may also be due to the decrease in surface heterogeneity.

3.2. Effect of pH

The pH of the aqueous solution has been recognized as one of the most important factors influencing any adsorption process. It influences not only the surface charge of the adsorbent, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry [10]. Thus the effect of pH on the removal efficiency of MG was studied at different pH ranging from 2.0 to 9.0. Results are shown in Fig. 3. It can be seen that adsorption of MG was strongly pH-dependent. The equilibrium uptake of dye increased notably with raising the pH from 2.0 to 4.0. Above these levels, the adsorption capacity did not change significantly up to pH 9.0. Similar trend was reported for adsorption of MG on treated ginger waste [38], maize cob powder [39], de-oiled soya [40] and coal [41]. The maximum sorption capacity takes place at pH 7; % removal of dye was 98.9%. Therefore further experiments were performed at pH 7. MG is a cationic dye, which exists in aqueous solution in the form of positively charged ions. As a charged species, the degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the

Table 1
Isotherm, kinetic and other equations used in this study.

Model/equation	Equation	Parameters	Ref.
Isotherm models			
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$	q_e (mg g^{-1}): equilibrium adsorption capacity q_m (mg g^{-1}): maximum adsorption capacity K_L (L mg^{-1}): Langmuir constant C_e (mg L^{-1}) : equilibrium adsorbate concentration in solution	[1,23]
Freundlich	$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$	K_F (mg g^{-1}) (L g^{-1})$^{1/n}$: Freundlich constant n : Heterogeneity factor	[8,22]
Temkin	$q_e = B_T \ln K_T + B_T \ln C_e$	K_T (L g^{-1}): Temkin adsorption potential B_T: Temkin constant	[24,25]
Dubinin–Radushkevich (D–R)	$\ln q_e = \ln q_m - \beta\varepsilon^2$ $\in = \mathrm{RT} \ln\left(1 + \frac{1}{C_e}\right)$	β ($mmol^2/J^2$): D–R constant $\in$ (Jm mol^{-1}): Polanyi potential R: universal gas constant (8.314 J mol^{-1} K^{-1}) T(K): temperature	[26,27]
Kinetic models			
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	q_t (mg g^{-1}): amount of adsorbate adsorbed at time t k_1 (min^{-1}): pseudo-first-order rate constant	[28–30]
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	k_2(g. mg^{-1} min^{-1}): pseudo-second-order rate constant	[30–32]
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	α (mg g^{-1} min^{-1}): initial sorption rate constant β (g mg^{-1}): desorption constant	[6,33]
Intraparticle-diffusion	$q_t = k_i t^{0.5}$	k_i (mg g^{-1} $min^{-0.5}$): intraparticle diffusion rate constant	[30,34]
Liquid film diffusion	$\ln(1 - F) = -k_{fd} t$	F: fractional attainment of equilibrium, equal to q_t/q_e	[35]
Activation parameters			
Arrhenius equation	$\ln k = \ln A - \frac{E_a}{RT}$	A: Arrhenius constant E_a (kJ mol^{-1}): activation energy R: universal gas constant (8.314 J mol^{-1} K^{-1}) T(K): temperature	[35,36]
Eyring equation	$\ln \frac{k}{T} = \left(\ln \frac{k_B}{h} + \frac{\Delta S}{R}\right) - \frac{\Delta H}{RT}$	k: rate constant k_B: Boltzman constant (1.3807×10^{-23} J K^{-1}) h: Plank constant (6.6261×10^{-34} Js)	[35,37]

solution pH. At low pH values, the protonation of the functional groups present on the adsorbent surface easily takes place, and thereby restrict the approach of positively charged dye cations to the surface of the adsorbent resulting in low adsorption of dye in acidic solution. With decrease in acidity of the solution, the functional groups on the adsorbent surface become de-protonated resulting in an increase in the negative charge density on the adsorbent surface and facilitate the binding of dye cations. The increase in dye removal capacity at higher pH may also be attributed to the reduction of H^+ ions which compete with dye cations at lower pH for appropriate sites on the adsorbent surface. However with increasing pH, this competition weakens and dye cations replace H^+ ions bound to the adsorbent surface resulting in increased dye uptake.

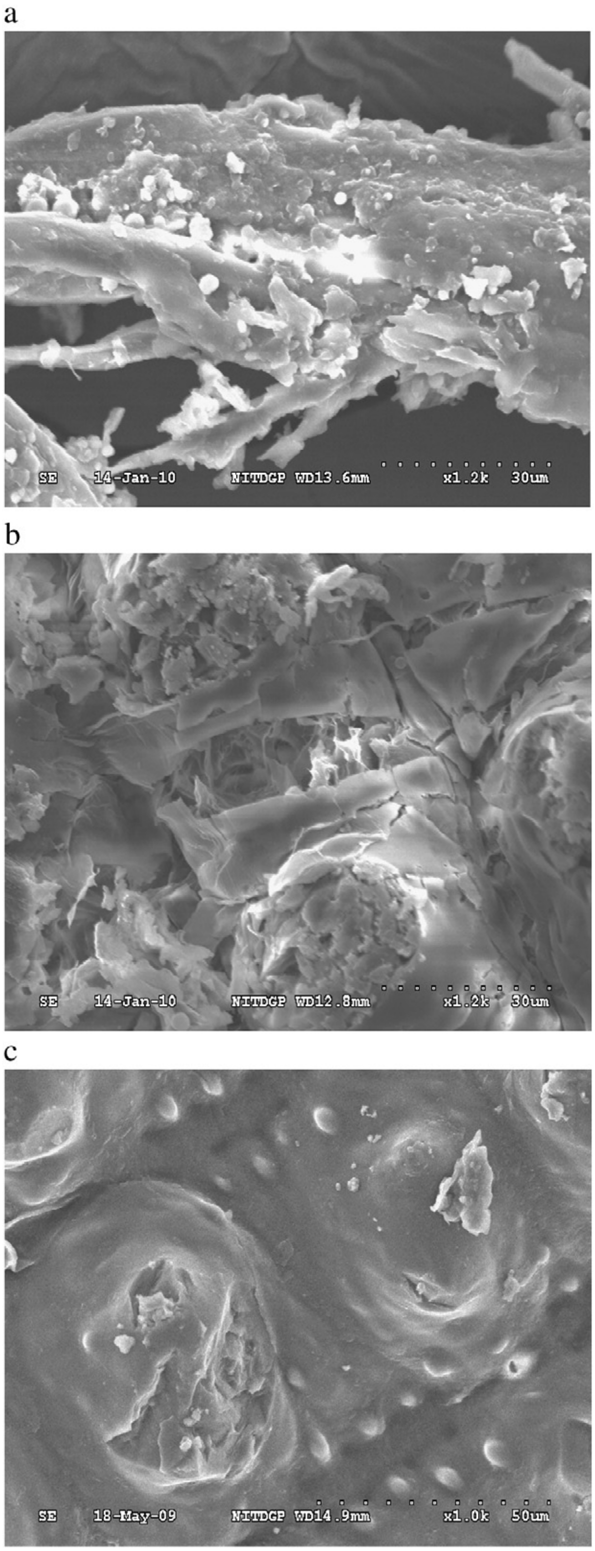

Fig. 2. Scanning electron micrograph of (a) untreated rice husk, (b) treated rice husk, (c) treated rice husk after adsorption of MG.

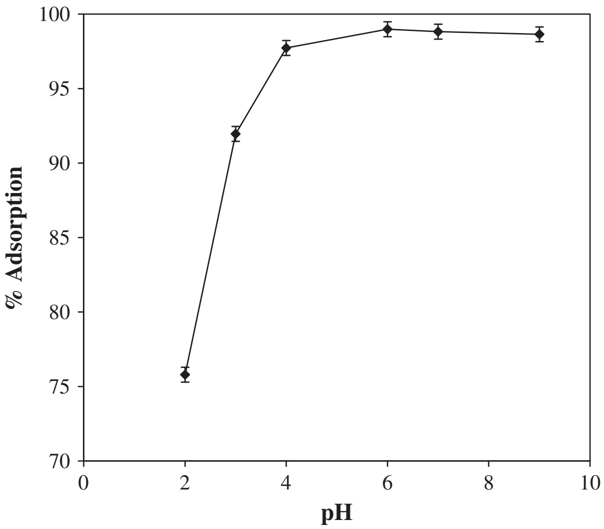

Fig. 3. Effect of pH on adsorption of MG using treated rice husk (conditions: weight of adsorbent = 1.0 g L^{-1}, agitation speed = 200 rpm, contact time = 180 min, temperature = 298 K).

3.3. Effect of contact time and initial concentration

It is essential to evaluate the effect of contact time required to reach equilibrium for designing batch adsorption experiments. Therefore the effect of contact time on adsorption of MG was investigated. Fig. 4a shows the adsorption of MG by treated rice husk as a function of contact time at different initial concentrations. It is seen that the adsorption of MG increased with rise in contact time up to 20 min. Further increase in contact time did not enhance the adsorption. Initially, the rate of adsorption was rapid due to the adsorption of dye molecules onto the exterior surface. After that the molecules enter into pores (interior surface), a relatively slow process. The initial faster rates of adsorption may also be attributed to the presence of large number of binding sites for adsorption and the slower adsorption rates at the end is due to the saturation of the binding sites and attainment of equilibrium. Similar conclusions have been proposed by Khattri and Singh [42] for adsorption of MG by neem sawdust. The adsorption reached equilibrium within 60 min and was independent of the initial dye concentration.

The rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important factor to be considered for effective adsorption. Fig. 4b depicts the effect of initial dye concentration on the adsorption of MG using treated rice husk. It was observed that as the initial dye concentration increased from 10 mg L^{-1} to 100 mg L^{-1}, the adsorption capacity of the treated rice husk increased (not shown in Fig. 4b). As a rule, increasing the initial dye concentration results in an increase in the adsorption capacity because it provides a driving force to overcome all mass transfer resistances of dyes between the aqueous and solid phase. However as shown in Fig. 4b, the sorption percentage decreased from 97.16% to about 89.13%. It can be explained that the adsorbent has a limited number of active sites, which becomes saturated at a certain concentration. This indicates that the adsorption capacity will increase with the increase of initial dye concentration mainly due to the rise in the mass transfer from the concentration gradient.

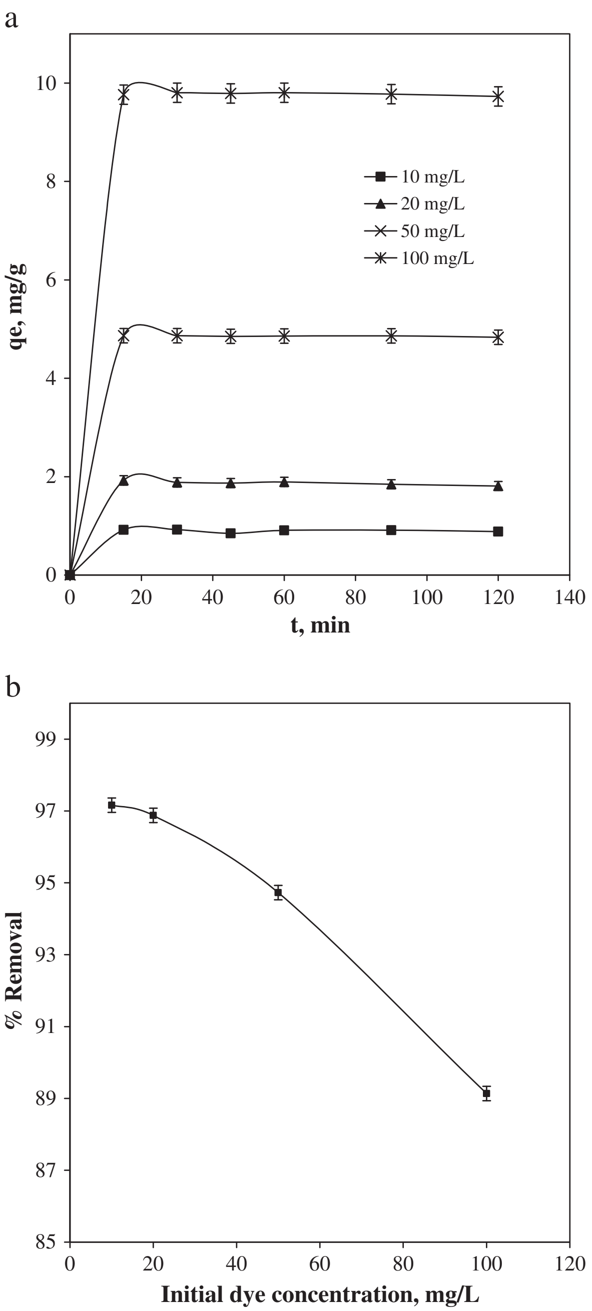

Fig. 4. (a) Effect of contact time on MG adsorption onto treated rice husk at different initial dye concentrations (conditions: weight of adsorbent = 1.0 g L^{-1}, agitation speed = 200 rpm, temperature = 298 K). (b) Effect of initial dye concentration on adsorption of MG using treated rice husk (conditions: weight of adsorbent = 1.0 g L^{-1}, agitation speed = 200 rpm, contact time = 120 min, temperature = 298 K, pH 7).

However, the concentration will inversely impact on the adsorption frequency because of the limited adsorption sites available for the uptake of cationic dye. Similar observations have been reported by Baek et al. [43] and Zhang et al. [44].

3.4. Effect of temperature

Fig. 5 illustrates the variation of solid phase dye concentrations with time at different temperatures. From the figure it is seen that temperature remarkably influenced the equilibrium dye uptake. The adsorption of dye increased with increase in temperature indicating that a high temperature favored MG removal by adsorption onto chemically modified rice husk. The enhancement in adsorption with rise in temperature may be attributed to increase in the number of active surface sites available for adsorption, increase in the porosity and in the pore volume of the adsorbent. An increase of temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer and within the internal pores of the adsorbent particle, due to decrease in the viscosity of the solution. The enhancement in adsorption may also be a result of an increase in the mobility of the dye molecules with an increase in their kinetic energy. The finding is in agreement with the observations of Daneshvar et al [45] on the biosorption of MG on *Cosmarium* species. The increase of the equilibrium uptake with increase in temperature means that the dye adsorption process is controlled by an endothermic process. This phenomenon is characteristic of a chemical reaction or bonding being involved in the adsorption process [37]. So it is suggested that sorption of MG by chemically modified rice husk may be a chemical sorption.

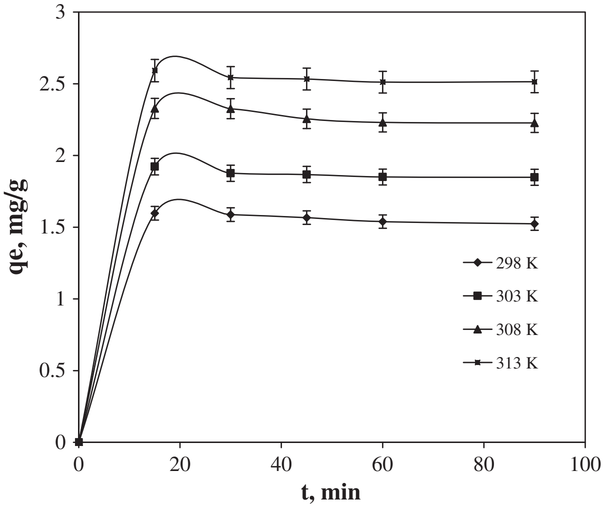

Fig. 5. Effect of temperature on the adsorption of MG using treated rice husk (conditions: weight of adsorbent = 1.0 g L^{-1}, agitation speed = 200 rpm, contact time = 120 min, pH 7).

3.5. Adsorption isotherms

In the present study four isotherm equations namely, Freundlich, Langmuir, Temkin and Dubinin–Radushkevich (D–R) (Table 1) were

Table 2
Isotherm parameters for adsorption of MG onto chemically modified rice husk.

Isotherm	Parameters	T(K)			
		298	303	308	313
Langmuir	q_m(mg g^{-1})	12.16	15.49	17.76	17.98
	K_L(L mg^{-1})	0.1597	0.4124	0.6410	1.077
	r^2	0.975	0.979	0.972	0.966
	χ^2	0.105	0.108	1.470	0.703
Freundlich	K_F(mg g^{-1}) (L $mg^{-1})^{1/n}$	4.088	5.139	6.527	7.395
	$1/n$	0.722	0.636	0.560	0.522
	r^2	0.998	0.986	0.992	0.993
	χ^2	0.064	0.299	0.989	0.060
Temkin	K_T(L mg^{-1})	9.44	11.20	14.21	15.47
	B_T	1.095	2.057	3.649	4.163
	r^2	0.954	0.963	0.923	0.956
	χ^2	0.119	0.825	2.987	1.113
Dubinin–Radushkevich	q_m(mg g^{-1})	9.22	11.53	13.38	16.62
	β ($mmol^2 J^{-2}$)	6.15×10^{-9}	5.98×10^{-9}	5.39×10^{-9}	4.92×10^{-9}
	E(kJ mol^{-1})	9.012	9.143	9.625	10.071
	r^2	0.863	0.838	0.762	0.803
	χ^2	0.493	2.216	4.879	1.025

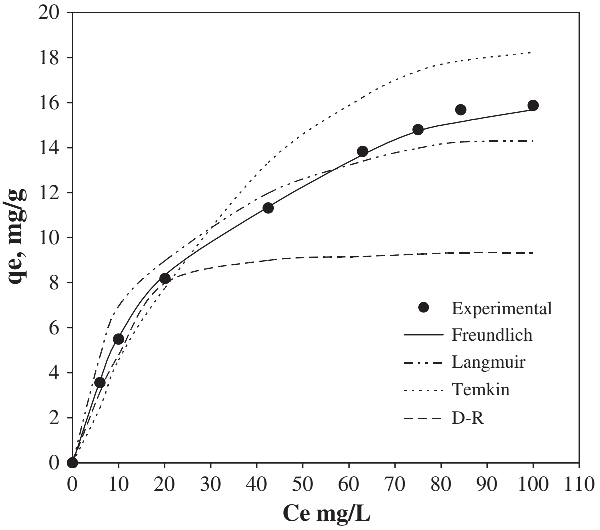

Fig. 6. Comparison between the measured and modelled isotherms profiles for the adsorption of MG by treated rice husk (weight of adsorbent = 1.0 g L^{-1}, agitation speed = 200 rpm, contact time = 120 min, pH 7, temperature: 298 K).

fitted to the experimental equilibrium data for MG at different temperatures. The results are shown in Table 2 and the modelled isotherms are plotted in Fig. 6. The Langmuir isotherm constants K_L and q_m were calculated from the slope and intercept of the plot between C_e/q_e and C_e. The values of K_L increased with increase in temperature, which accounts for the endothermic nature of the adsorption process.

The equilibrium data were further analyzed using the Freundlich model. The Freundlich constants K_F and $1/n$ were calculated from the intercept and slope of the straight line of the plot log q_e versus log C_e. The magnitude of $1/n$ gives a measure of favorability of adsorption. The values of $1/n$ less than 1 represent a favorable sorption. For the present study the value of $1/n$ also presented the same trend representing a beneficial sorption. The increase of Freundlich constants with increase of temperature confirmed that adsorption was favorable at high temperatures and the process was endothermic in nature.

The Temkin equation was also fitted to the experimental data. The constants K_T and B_T were determined from the intercept and slope of the plot between q_e andln C_e. Smaller values of the Temkin constant B_T for alkali treated rice husk suggest that adsorption of MG on this adsorbent was favorable. As seen from Table 2, B_T increased with increasing temperature, indicating endothermic adsorption.

The Dubinin–Radushkevich (D–R) model, which does not assume a homogeneous surface or a constant biosorption potential as the Langmuir model, was further used to test the experimental data. The plots between $\ln q_e$ and ε^2 gave straight lines at all temperatures; the values of constants q_m and β thus obtained are given in Table 2. The constant β gives an idea about the mean sorption energy, E, which is defined as the free energy transfer of 1 mol of solute from infinity of the surface of the sorbent and can be calculated using the relationship [35,46]:

$$E = \frac{1}{\sqrt{2\beta}} \tag{2}$$

The parameter gives information about the type of adsorption mechanism as chemical ion-exchange or physical adsorption. If the magnitude of E is between 8 and 16 kJ mol−1, the sorption process is supposed to proceed via chemisorption, while for values of $E < 8$ kJ mol^{-1}, the sorption process is of physical nature [35,46]. The magnitude of E were higher than 8 kJ/mol for all studied temperatures indicating that the adsorption mechanism was chemical ion-exchange.

Table 3
Freundlich parameters for adsorption of MG by various low cost adsorbents.

Adsorbent	Temp (K)	K_F	1/*n*	Ref.
Hen feathers	303	1.000	0.096	[47]
	313	1.000	0.099	
	323	1.000	0.104	
Sand	–	0.694	0.956	[48]
Commercially available powdered activated carbon	303	127.73	0.194	[9]
Groundnut shell based powdered activated carbon	303	143.45	0.128	
Treated ginger waste	303	1.14	1.075	[38]
	313	1.11	1.030	
	323	1.04	0.993	
Bagasse fly ash	303	25.149	0.423	[49]
Activated carbon (commercial grade)	303	1.189	0.411	
Activated carbon (laboratory grade)	303	5.629	0.449	
Caulerpa racemosa var. *cylindracea*	298	13.10	2.631	[50]
	308	8.43	1.923	
	318	12.03	1.851	
Cellulose powder	298	0.74	0.25	[51]
Jute fiber carbon	303	32.290	0.285	[52]
De-oiled soya	303	2.357×10^{-4}	34.482	[40]
	313	2.666×10^{-4}	32.258	
	323	2.960×10^{-4}	30.303	
Bentonite clay	298	1.72×10^{-3}	0.724	[53]
	308	9.91×10^{-4}	0.657	
	318	8.10×10^{-4}	0.625	
	328	4.36×10^{-4}	0.512	
Degreased coffee bean	298	2.03	1.956	[43]
	308	0.079	3.484	
	318	0.007	4.761	
Epicarp of *Ricinus communis*	300 ± 2	2.3046	0.2613	[54]
Maize cob powder	300	11.040	1.0434	[39]
Rice bran	–	8.2553	0.595	[55]
Wheat bran		2.3664	0.637	
NaOH treated rice husk	298	4.088	0.722	Present study
	303	5.139	0.636	
	308	6.527	0.560	
	313	7.395	0.522	

The correlation coefficient (r^2) and chi-square (χ^2) values of the four isotherms are also listed in Table 2. Based on the error function values, the applicability of the isotherms was compared. It could be concluded that the adsorption of MG onto chemically modified rice husk, best fitted to the Freundlich isotherm equation under the temperature range studied. The fitness of the adsorption data to the Freundlich isotherm implies that that adsorption of MG onto treated rice husk was multilayer adsorption applicable to heterogeneous surfaces. A list showing the Freundlich parameters of different low cost adsorbents for the sorption of MG from its aqueous solutions is given in Table 3. A direct comparison is difficult due to the varying experimental conditions employed in those studies. However, from Table 3, it can be concluded that chemically modified rice husk is an excellent adsorbent for MG.

3.6. Adsorption kinetics

In order to investigate the mechanism of adsorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models are exploited to test the experimental data. In this study, the experimental equilibrium data of MG onto chemically modified rice husk was first analyzed by the pseudo-first-order and pseudo-second-order kinetic models (Table 1). Table 4 present the results of fitting experimental data with pseudo-first-order and pseudo-second-order models using correlation coefficient (R^2), coefficient of determination (r^2), and

Table 4
Comparison of regression coefficient (R^2), coefficients of determination (r^2) and chi-square test (χ^2) for pseudo-first order and pseudo-second-order kinetic models.

C_i(mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
	R^2	r^2	χ^2	R^2	r^2	χ^2
5	0.854	0.821	3.739	0.996	0.996	0.0320
10	0.897	0.878	2.377	0.998	0.996	0.0229
20	0.889	0.864	2.598	0.999	0.998	0.0237
50	0.954	0.934	1.765	1.000	0.999	0.0115
100	0.910	0.899	2.279	1.000	0.999.	0.0111

Table 5
Kinetic parameters for adsorption of MG onto chemically modified rice husk.

Kinetic model	Parameters	T(K)			
		298	303	308	313
Pseudo-second-order	$q_{e,exp}$ (mg g^{-1})	21.32	22.16	23.50	24.92
	$q_{e,cal}$ (mg g^{-1})	21.55	22.25	23.71	25.07
	k_2 (g mg^{-1} min^{-1})	0.0329	0.0466	0.0804	0.1187
	h (mg g^{-1} min^{-1})	15.27	23.06	45.19	74.60
	R^2	0.999	1.000	1.000	1.000
Elovich	α(mg g^{-1} min^{-1})	1.234	1.951	2.824	3.164
	β (mg g^{-1})	3.092	4.216	5.768	5.495
	R^2	0.9891	0.9969	0.9915	0.9803
Intraparticle diffusion	Intercept	1.668	2.892	3.208	3.825
	k_i(mg g^{-1} min$^{-0.5}$)	0.0138	0.0215	0.0283	0.0344
	R^2	0.9210	0.9625	0.9468	0.9431
Liquid film diffusion	Intercept	-1.54	-1.80	-2.02	-2.34
	k_{fd}(min^{-1})	-0.0107	-0.0135	-0.0169	-0.0182
	R^2	0.9815	0.9233	0.9366	0.9733

also the chi-square test (χ^2). From Table 4, a comparison of the error functions indicate that the pseudo-first-order equation cannot provide an accurate fit of the experimental data. The results suggest that pseudo-second-order kinetic model, in contrast to the pseudo-first-order model, provided a good correlation for the adsorption of MG on treated rice husk. The plots of t/q_t versus t gives straight line relation for all the initial dye concentrations studied (Fig. 7a), and all the R^2 values are close to 1 (Table 4), confirming the applicability of the pseudo-second-order equation. On the other hand, the plots of t/q_t versus t at different temperatures (figure not shown) showed good linearity; implying that the adsorption system studied follows the pseudo-second-order kinetic model. The q_e and k_2 values were calculated from slope and intercept of this plots, respectively and are listed in Table 5. It is observed from Table 5 that rate constant, k_2 increases as the temperature increases indicating that adsorption of MG on treated rice husk was an endothermic process. In addition, there is only a small difference between the $q_{e,exp}$ and $q_{e,cal}$, reinforcing the applicability of the pseudo-second-order model. From, the pseudo-second-order kinetic parameters, the initial adsorption rate, h(mg g^{-1} min^{-1}) at different temperatures was calculated using Eq. (3) [56] and are given in Table 5.

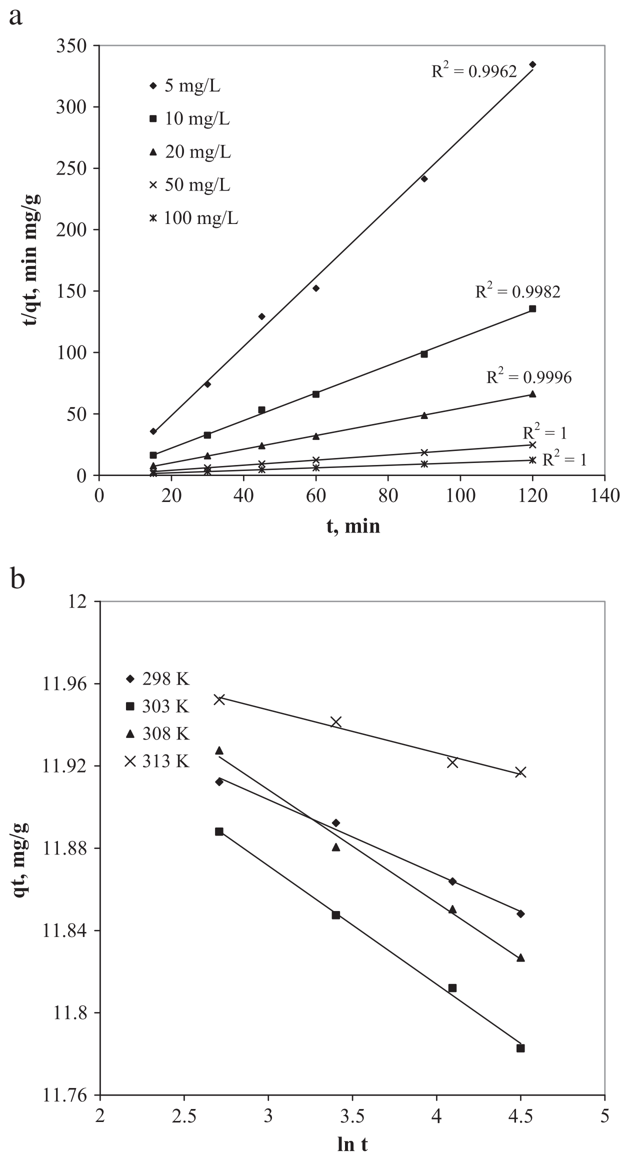

Fig. 7. (a) Pseudo-second-order kinetics for adsorption of MG at different initial concentration using treated rice husk. (b) Elovich kinetic plots for adsorption of MG onto treated rice husk at different temperatures.

$$h = k_2 q_e^2 \tag{3}$$

It can be seen in Table 4 that, the value of h increases with increase in temperature indicating higher temperature favors the adsorption process by increasing adsorption rate and capacity. The pseudo-second-order kinetic model provides an accurate description of sorption kinetics of MG onto treated rice husk for the studied cases and conditions, and thus supports the assumption behind the model that the adsorption is due to chemisorption. Similar results were previously reported for adsorption of MG onto esterified soybean hull [57], activated carbon developed from *R. communis* [54], cyclodextrin-based adsorbent [10] and chlorella-based biomass [58].

Further the kinetic data was fitted to the Elovich equation (Table 1). The Elovich equation assumes that the solid surface active sites are heterogeneous in nature and therefore, exhibit different activation energies for chemisorptions [59]. The Elovich plot (q_t vs. ln t) at different temperatures is shown in Fig. 7b. The values of the coefficients α and β are listed in Table 5. The correlation coefficients (R^2) determined from these plots reveal a linear characteristic ($R^2 = 0.9969–0.9803$). In Elovich model, α is related to rate of chemisorption (initial adsorption rate) and β is related to surface coverage (desorption constant). With the increase in temperature, the constants α and β increased showing that both the rate of chemisorption and the available adsorption surface would increase.

In many adsorption processes, the adsorbate species are most probably transported from the bulk of the solution into the solid phase through intraparticle diffusion/transport. So the intraparticle diffusion is another kinetic model which should be used to study the rate of MG adsorption onto treated rice husk. The possibility of intraparticle diffusion was explored by plotting q_t versus $t^{0.5}$. The plots of q_t versus $t^{0.5}$ were linear (figure not shown) and the R^2 values were between 0.9210 and 0.9625. It can be generally stated that adsorption process tends to follow intraparticle diffusion. However, if the intraparticle diffusion is the sole rate-limiting step, it is essential for the q_t versus $t^{0.5}$ plots to pass through the origin. As the plots did not have a zero intercept, it may be concluded that surface adsorption and intraparticle diffusion were concurrently operating during interaction of MG with treated rice husk.

The diffusion of the adsorbate from the bulk liquid phase to the surface of the adsorbent might also play an important role in determining the rate of an adsorption process. Therefore the kinetic data were analyzed by the liquid film diffusion model (Table 1). The plots of $\ln(1-F)$versus t with zero intercept would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbents. The plots of $\ln(1-F)$ versus t (figure not shown) were found to be linear ($R^2 = 0.9233$–0.9815) with intercepts in the range of –1.54 to –2.34. The rate constant, k_{fd}, had values ranging from –0.0107 to –0.0182 min^{-1} (Table 5). The linear plots did not pass through the origin suggesting limited applicability of the liquid film diffusion model in the present adsorption system.

3.7. Activation parameters

From the pseudo-second-order rate constant k_2 (Table 5), the activation energy E_a for adsorption of MG onto treated rice husk was determined using the Arrhenius equation (Table 1). By plotting $\ln k_2$ versus $1/T$ (figure not shown), E_a was obtained from the slope of the linear plot. The value of E_a was 68.12 kJ mol^{-1}. The magnitude of E_a may give an idea about the type of adsorption. According to literature [36], the process may be an activated chemical adsorption process. The Eyring equation was used to calculate the standard enthalpy ($\Delta H^{\#}$), and entropy of activation ($\Delta S^{\#}$) were calculated using the Eyring equation (Table 1). The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were calculated from the slope and intercept of the plot of $\ln(k_2/T)$ versus $1/T$ (figure not shown). The free energy of activation ($\Delta G^{\#}$) was obtained from: $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$. The values of $\Delta G^{\#}$ were found to be (75.76, 77.93, 78.10, 80.27) kJ mol^{-1} at T = (298, 303, 308 and 313) K respectively. The large positive values of $\Delta G^{\#}$ suggests that energy was required in the adsorption reaction to convert reactants into products. The positive value of $\Delta H^{\#}$ (65.53 kJ mol^{-1}) indicates endothermic process. The negative value of $\Delta S^{\#}$ (−124.34 J mol^{-1} K^{-1}) suggests that MG adsorption onto chemically modified rice is an associative mechanism [37].

3.8. Thermodynamic parameters

The thermodynamic parameters such as Gibbs free energy change (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated using the following equations [36]:

$$\Delta G^0 = -RT\ln K_C \tag{4}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{5}$$

where K_C is the distribution coefficient for adsorption and is determined as:

$$K_C = \frac{C_a}{C_e} \tag{6}$$

where C_a is the equilibrium dye concentration on the adsorbent (mg L^{-1}) and C_e is the equilibrium dye concentration in solution (mg L^{-1}).

The Gibb's free energy (ΔG^0) for adsorption of MG onto treated rice husk obtained at all temperatures are listed in Table 6. ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of ΔG^0 versus T (figure not shown) and are also tabulated in Table 6. The values of ΔG^0 were negative at all temperatures and the negative values confirm the feasibility of the process and the spontaneous nature of MG adsorption onto treated rice husk. The increase of the absolute value of ΔG^0 as temperature rises indicates that the affinity of MG on alkali treated rice husk was higher at high temperature. The positive value of ΔH^0 (63.76 kJ mol^{-1}) confirms that the adsorption reaction is endothermic. The positive value of ΔS^0 (234.4 J mol^{-1} K^{-1}) reflects the affinity of the treated rice husk for MG and an increased randomness at the solid-solution interface during adsorption [60].

Table 6
Thermodynamic parameters and isosteric heat of adsorption of MG onto chemically modified rice husk.

Thermodynamic parameters

Sl. No	Temperature (K)	ΔG^0 (kJ mol^{-1})	ΔH^0(kJ mol^{-1})	ΔS^0(J mol^{-1} K^{-1})
1	298	−6.18	63.76	234.4
2	303	−7.09		
3	308	−8.40		
4	313	−9.65		

Isosteric heat of adsorption

Sl. No	q_e(mg g^{-1})	ΔH_X(kJ mol^{-1})	R^2
1	2	78.630	0.9614
2	4	79.699	0.9685
3	6	81.264	0.9555
4	8	83.848	0.9638
5	10	89.132	0.9465

3.9. Isosteric heat of adsorption

Isosteric heat of adsorption (ΔH_X, kJ mol^{-1}) defined as the heat of adsorption determined at constant amount of adsorbate adsorbed is one of the basic requirements for the characterization and optimization of an adsorption process. Knowledge of the heats of sorption is very important for equipment and process design. The isosteric heat of adsorption at constant surface coverage ($q_e = 2, 4, 6, 8, 10$ mg g^{-1}) was calculated using the Clausius–Clapeyron equation [36,61]:

$$\frac{d(\ln Ce)}{dT} = -\frac{\Delta H_X}{RT^2} \tag{7}$$

For this purpose, the equilibrium concentration (C_e) at constant amount of dye adsorbed was obtained from the isotherm data at different temperatures. The values of ΔH_X were obtained from the slope of a plot of $\ln C_e$ versus $1/T$ for different amounts of adsorbate onto adsorbent. The plots of $\ln C_e$ versus t were found to be linear (Fig. 8a). The values of ΔH_X were determined from the slope of the plots. The R^2 values of the isosteres and the corresponding ΔH_X values are listed in Table 6. For physical adsorption ΔH_X should be below 80 kJ mol^{-1} and for chemical adsorption it ranges between 80 and 400 kJ mol^{-1} [62]. In the present system, the values of ΔH_X were between 78.63 and 89.13 kJ mol^{-1} indicating that the adsorption of MG onto treated rice husk was a chemical process involving ion exchange. The variation of ΔH_X with surface loading is presented in Fig. 8b. It is observed that the ΔH_X values increased steadily with an increase in q_e indicating that chemically modified rice husk was having heterogeneous surfaces. The dependence of ΔH_X on surface coverage can be due to adsorbate-adsorbate interaction followed by adsorbate-adsorbent interaction. Initially, at lower q_e values, adsorbate-adsorbate interaction takes place resulting in low ΔH_X values. As q_e increases, adsorbate-adsorbent interaction occurs resulting in high heats of adsorption. Variation in ΔH_X with surface loading can also be attributed to the possibility of having lateral interactions between the adsorbed dye molecules.

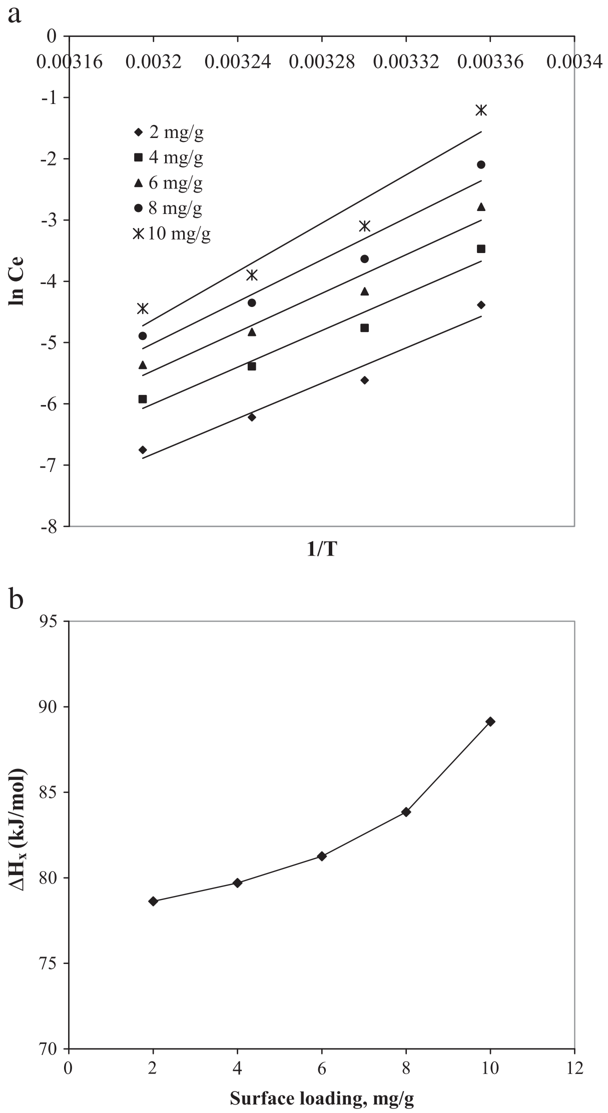

Fig. 8. (a) Plots of ln C_e against 1/T for adsorption of MG onto treated rice husk. (b) Plot of isosteric heat of adsorption against surface loading for adsorption of MG onto treated rice husk.

3.10. Adsorption mechanism

The major challenge in an adsorption study is to elucidate the adsorption mechanism. However, before understanding the adsorption mechanism it is necessary to consider to two points: firstly the structure of the adsorbate; and secondly the adsorbent surface properties. In this connection, it must be pointed out that MG is a cationic dye having two amino groups. On the other hand, rice husk consists of cellulose, hemicelluloses, lignin and silica as its main components, besides other minor constituents such as crude protein, fats, waxes etc [19,20]. Both cellulose and hemicellulose contain majority of oxygen functional groups which are present in lignocellulosic materials such as hydroxyl, ether, and carbonyl, while lignin is a complex, systematically polymerized, highly aromatic substance, and acts as a cementing matrix that holds between and within both cellulose and hemicelluloses units. Silica is present on the outer surface of rice husk in the form of silicon-cellulose membrane and acts as a natural protective layer [21]. Chemical modification of rice husk with sodium hydroxide removes silica, lignin and other impurities from the rice husk surface thus revealing chemically reactive functional groups like –OH.

In this study, the removal of MG by adsorption on chemically modified rice husk was found to be rapid at the initial period of contact time and then to become slow and stagnate with the increase in contact time (Fig. 4a). The adsorption was strongly pH-dependent (Fig. 3). MG was adequately adsorbed for pH between 4.0 and 9.0. It was also observed that the modeling of intraparticle diffusion showed a contribution of film diffusion on the control of sorption kinetics; however intraparticle diffusion was not the dominating mechanism. The pseudo-second-order kinetic model provides best correlation with the experimental data for the adsorption of MG onto chemically modified rice husk.

According to the experimental findings of the present study, and based on the structure of the adsorbate and adsorbent surface properties, the mechanism for the removal of MG by adsorption on treated rice husk may be assumed to involve the following steps:

- Migration of dye from bulk of the solution to the surface of the adsorbent
- Diffusion of dye through the boundary layer to the surface of the adsorbent
- Adsorption of dye on the surface of treated rice husk, which may be due to the formation of surface hydrogen bonds between the hydroxyl groups on the rice husk surface and the nitrogen atoms of MG as suggested in Fig. 9 or through a possible mechanism of a dye–hydrogen ion exchange process as shown below:

$$\text{Rice Husk—OH} \rightleftharpoons \text{Rice Husk—O}^- + \text{H}^+$$

$$\text{Rice Husk—O}^- + \text{MG}^+ \rightleftharpoons \text{Rice Husk—O—MG} + \text{H}^+$$

- Intraparticle diffusion of dye into the interior pores of the adsorbent

In order to confirm this mechanism, more experiments need to be carried out using other cationic dyes.

3.11. Cost analysis

Adsorbent cost is an important parameter for comparing the industrial application of adsorbent materials; however it is seldom reported in the literature [3]. The overall cost of the adsorbent

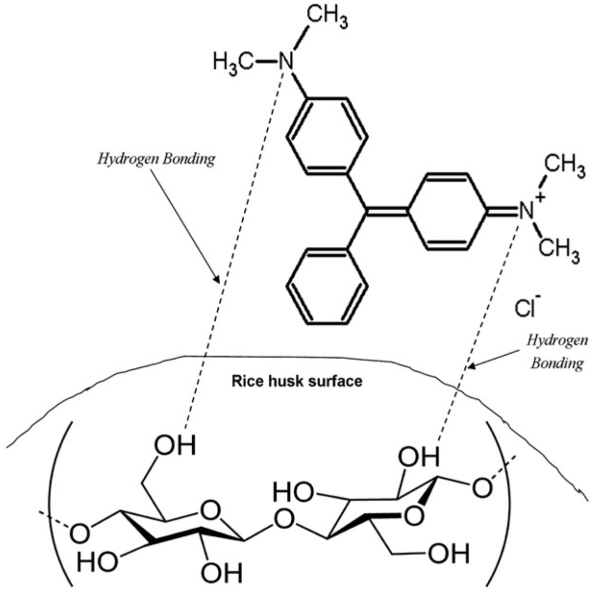

Fig. 9. Schematic representation of hydrogen bonding between nitrogen atoms of MG and hydroxyl groups on the treated rice husk surface, cellulose unit.

Table 7
Total cost for preparing 1 kg of the adsorbent.

Sl. no	Material	Unit cost, INR	Amount used	Net price, INR
1	Sodium hydroxide	188.00 kg^{-1}	50 g	9.40
2	Cost of autoclaving	2.50 kWh^{-1}	0.75 kWh (10 psi: 15 min)	1.87
3	Cost of drying	2.50 kWh^{-1}	7.20 kWh (343 K: 9 h)	18.00
4	Net cost			29.27
5	Other overhead costs (10% of net cost)			2.92
	Total cost			32.19

material is governed by several factors which include its availability (whether it is natural, industrial/agricultural/domestic wastes or by-products or synthesized products), the processing required and reuse [3]. Rice husk is available in abundance as a waste from the rice mills at no cost. The modification method of rice husk is very simple and is performed by treatment with sodium hydroxide. However, the modification process adds to the cost of the adsorbent. The breakdown of the cost of each step of the modification process is presented in Table 7. The total cost for the preparation of 1 kg of rice husk is estimated as 32.19 INR. The total cost of the adsorbent can however be reduced to 12.39 INR by drying the adsorbent naturally at room temperature.

The most popular commercial adsorbent of the present time for the removal of basic and reactive dyes is activated charcoal. In India the cheapest variety of the commercial activated charcoal costs around 1000 INR per kg [40]. Compared to activated charcoal, rice husk modified with sodium hydroxide is quite a cheap material. The MG loaded rice husk can be dried and used as a fuel in boilers/incinerators, or can be used for the production of fire briquettes. The ash may be used to make fire-bricks, thus disposing of MG through chemical fixation. This approach of adsorbent disposal entails energy recovery from the treated rice husk and the safe disposal of the adsorbed MG. Thus the use of chemically modified rice husk as an adsorbent is a thoughtful and economic attempt for its valuable, necessitous and needy utilization for wastewater treatment processes.

4. Conclusion

The study shows that chemically modified rice husk, can be used as an adsorbent for removal of MG from aqueous solutions. The adsorption characteristics of MG in aqueous solution were shown to be influenced by several factors. The adsorption process was highly pH dependent and the optimum pH for maximum adsorption was found to be at pH 7.0. The isotherms exhibited the Freundlich behavior at all temperatures, which indicates a heterogeneous surface binding. The adsorption data showed good agreement with the pseudo-second-order kinetic model for different sorbent concentration. The rate constant increased with increase in temperature indicating endothermic nature of adsorption. The values of E_a, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ were estimated using the Arrhenius and Eyring equations. Based on these values, the adsorption of MG onto chemically modified rice husk was diffusion controlled and an associative mechanism. The adsorption capacity increased with the rise in temperature indicating that the adsorption was a spontaneous, endothermic process. This was also supported by the thermodynamic parameters calculated at different temperatures. The isosteric heats of adsorption were calculated by applying the Clausius–Clapeyron equation. The isosteric heat of adsorption increased with increase in surface loading indicating that chemically modified rice husk is having energetically heterogeneous surface and there may be some lateral interactions between the adsorbed dye molecules Taking into consideration all the above obtained results, it can be concluded that chemically modified rice husk can be an alternative economic material to more costly adsorbents used for dye removal in wastewater treatment processes.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.desal.2010.07.047.

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