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ORIGINAL ARTICLE

Biosorption of methylene blue from aqueous solutions by a waste biomaterial: hen feathers

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Abstract Biosorption potential of hen feathers (HFs) to remove methylene blue (MB) from aqueous solutions was investigated. Batch experiments were carried out as function of different process parameters such as pH, initial dye concentration, biosorbent dose and temperature. The optimum conditions for removal of MB were found to be pH 7.0, biosorbent dose = 1.0 g, and initial dye concentration = 50 mg L^{-1}. The temperature had a strong influence on the biosorption process. Experimental biosorption data were modeled by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms with the Langmuir isotherm showing the best fit at all temperatures studied. The maximum monolayer sorption capacity was determined as 134.76 mg g^{-1} at 303 K. According to the mean free energy values of sorption (E) calculated using the D–R isotherm model, biosorption of MB onto HFs was chemisorption. Kinetic studies showed that the biosorption of MB followed pseudo second-order kinetics. The activation energy (E_a) determined using the Arrhenius equation confirmed that the biosorption involved chemical ion-exchange. Thermodynamic studies showed that the biosorption process was spontaneous and exothermic. To conclude, HFs is a promising biosorbent for MB removal from aqueous solutions.

Keywords Biosorption · Hen feathers · Methylene blue · Equilibrium · Kinetics · Thermodynamics

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Introduction

The contamination of water bodies by synthetic dyes has created a serious environmental problem worldwide. A considerable amount of dyes is released into the aquatic ecosystems through the wastewater streams of industries such as textile, carpet, leather, paper, printing, food, cosmetics, paint, pigments, petroleum, solvent, rubber, plastic, pesticide etc. (Chowdhury et al. 2011a; Chowdhury and Saha 2010a). Dye residues affect photosynthetic activity by preventing light penetration in aquatic life and produce toxic chemicals of aromatics, metals, amines and chlorides, having a detrimental effect on flora, fauna and human beings.

Methylene blue (MB), a thiazine (cationic) dye, is commonly used for dyeing of silk, leather, plastics, paper, cotton mordanted with tannin, and also in manufacturing of paints and printing inks (Nasuha et al. 2010). It finds application in aquaculture as an alternative to malachite green for the treatment of fungal infections. In the dairy industry, it is used to determine the microbial load in the milk (Bapat et al. 2006). Although MB is not hazardous compared to other commercial dyes, acute exposure to MB can cause increased heart rate, vomiting, diarrhea, nausea and shock (Nasuha et al. 2010; ALzaydien 2009). It can cause eye burns which may lead to permanent injury to the eyes of human and animals (Rafatullah et al. 2010). On inhalation, it can give rise to short periods of rapid or difficult breathing (dyspnea), while ingestion through mouth produces a burning sensation (Rafatullah et al. 2010; Tan et al. 2008). Potential exposure to MB can also cause hypertension, pre-cordial pain, dizziness, headache, fever, fecal discoloration, profuse sweating, mental confusion, methemoglobinemia and hemolytic anemia (Saha 2009; Saha and Datta 2009; Ghosh and Bhattacharyya 2002;). Hence, there is a necessity for the treatment

of effluents containing such dye due to its harmful impacts on receiving waters.

In recent years, biosorption has been strongly recommended as an economically viable sustainable technology for the treatment of wastewater streams (Chowdhury et al. 2011b). The importance and usefulness of biosorption in wastewater treatment is well established (Chowdhury et al. 2011b). Biosorption in environmental engineering is now an aesthetic attention and consideration in all nations, owing to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions (Foo and Hameed 2010). A huge number of low-cost biosorbents based on natural materials or agro-industrial wastes such as rice husk (Saha 2009), tamarind fruit shell (Saha 2010), wheat shell (Bulut and Aydin 2006), orange peel (Annadurai et al. 2002), banana peel (Annadurai et al. 2002), pineapple leaves (Weng et al. 2009), pineapple stem (Hameed et al. 2009), peanut hull (Gong et al. 2005), garlic peel (Hameed and Ahmad 2009), rejected tea (Nasuha et al. 2010), *Luffa cylindrical* fibers (Demir et al. 2008), yellow passion fruit waste (Pavan et al. 2008), neem leaf powder (Bhattacharyya and Sharma 2005) etc. have been investigated intensively by researchers worldwide for the removal of MB from aqueous solutions. In recent years, researchers have focused on the application of biomaterials that are capable of biosorbing dyes from wastewaters. Biological materials such as peat, chitosan, yeast, fungi and bacterial biomass, have been used as biosorbents to concentrate and remove dyes from solutions (Srinivasan and Viraraghavan 2010). In this paper, we report the biosorption characteristics of hen feathers (HFs)—a waste biomaterial for the removal of MB from aqueous solution.

Feathers (chicken/hen) are generated in huge quantities as waste product at commercial poultry processing plants. Worldwide, nearly 8.5 billion tonnes of feathers are generated annually as waste by poultry-processing industries, of which India's contribution alone is 350 million tonnes (Agrahari and Wadhwa 2010). The feathers are either used as animal feed supplement in the form of feather meal, for land filling, incinerated or buried, which involves storage, handling, emission control and ash disposal problems (Taskin and Kurbanoglu 2011; Agrahari and Wadhwa 2010). Feathers are composed mainly of keratin, a kind of self organized protein with high mechanical stability (Zaghloul et al. 2011). Keratin has a high content of the amino acids glycine, alanine, serine, cysteine and valine (Taskin and Kurbanoglu 2011). These amino acids are responsible for the presence of a number of functional groups (carboxyl, hydroxyl and amine-groups) both on the backbone and the side chain of the polypeptide molecule, thereby rendering it an interesting physicochemical property for the sorption of organic/inorganic compounds (Aguayo-Villarreal et al. 2011). Till date, few studies have proved feathers to be effective and economically feasible to remove several pollutants including dyes from aqueous solutions (Mittal et al. 2007). However, to the best of our knowledge, no study has been reported on the removal of MB using hen feathers. Thus, our primary aim was to investigate and explore the possibility of using HFs as biosorbent for the removal of MB from aqueous solutions. The study includes an evaluation of the effect of various operational parameters such as solution pH, initial dye concentration, biosorbent dose and reaction temperature on the dye biosorption process with special focus on biosorption isotherms, kinetics and thermodynamics.

Materials and methods

Dye

MB (C.I. 52015, FW: 319.86, MF: $C_{16}H_{18}N_3SCl$) used in this study was of commercial purity and used without further purification. Stock dye solution (500 mg L^{-1}) was prepared by dissolving 0.5 g of the dye in 1 L of distilled water. Experimental dye solution of desired concentration was prepared by further dilution of the stock solution with suitable volume of distilled water. The initial solution pH was adjusted with 0.1 M HCl and 0.1 M NaOH solutions using a digital pH meter (LI 127, ELICO, India) calibrated with standard buffer solutions.

Biosorbent

Hen feathers used in this study were collected from a local poultry in Durgapur, West Bengal, India. The feathers were first washed with detergent and rinsed thoroughly with distilled water to remove adhering dirt and any unwanted particles. They were then washed with aqueous ethanol (20 % v/v) to remove organic residues, and then rinsed again with distilled water. The washed feathers were then air dried and the barbs were cut into about 0.5 cm length with the help of scissors, discarding the hard middle rachis. Finally, the prepared biosorbent was stored in sterile, air tight glass bottles and used without any further treatment for dye biosorption.

Biosorbent characterization

Specific surface area (S_{sp}, m^2 g^{-1}) of the biosorbent was determined by Brunauer, Emmett, Teller (BET) method using a surface area and porosity analyzer (NOVA 2200, Quantachrome Corporations, USA). A gas mixture of 22.9 mol% nitrogen and 77.1 mol% helium was used for this purpose. The surface structure of the biosorbent was

analyzed by a scanning electron microscope (S-3000 N, Hitachi, Japan) at an electron acceleration voltage of 15 kV. Prior to scanning, the biosorbent was mounted on a stainless steel stab with double stick tape and coated with a thin layer of gold in a high vacuum condition. An XRD spectrum of the biosorbent was also recorded using Miniflex X-ray diffraction spectrometer with a CuKα radiation source (used at 30 kV and 15 mA, diffraction angle ranged from 60° to 5° with a scan speed of 5°/min).

Batch biosorption

Batch mode biosorption experiments were performed in 250 mL glass-stoppered, Erlenmeyer flasks with 100 mL of dye solution of known initial concentration (50 mg L^{-1}). A weighed amount (1 g) of biosorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm for 3 h in an incubator shaker (Model Innova 42, New Brunswick Scientific, Canada) at 303 ± 1 K. The influence of pH (2.0–10.0), initial dye concentration (20–100 mg L^{-1}), biosorbent dose (0.5–5 g) and temperature (303–323 K) were evaluated during the present study. Samples were collected from the flasks at regular time intervals and the residual dye concentration in the solution was analyzed by monitoring the change in absorbance values at maximum wavelength (λ_{max}) of 663 nm using UV/Vis spectrophotometer (U-2800, Hitachi, Japan).

Control experiments were conducted in two ways: (1) without biosorbent, to check for the retention of the dye at the glassware surface and other possible losses, and (2) without the dye (in double distilled water), to verify if any colored species present in the feathers were water soluble and would contribute to the color of water, masking in the results. Dye loses at the glassware surface was negligible and no significant color effect could be accounted to the feathers.

Calculations

The amount of dye adsorbed per unit biosorbent (mg dye/g of biosorbent) was calculated according to a mass balance on the dye concentration using Eq. (1):

$$q_e = \frac{(C_0 - C_e)\,V}{m} \quad (1)$$

where C_0 is the initial dye concentration (mg L^{-1}), C_e the equilibrium dye concentration in solution (mg L^{-1}), V the volume of the solution (L), and m is the mass of the biosorbent in g. The percent removal (%) of dyes was calculated using the following equation:

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

Statistical analysis

In order to ensure the accuracy, reliability, and reproducibility of the collected data, all biosorption experiments were performed in triplicate, and the mean values were used in data analysis. Relative standard deviations were found to be within ±3 %. Microsoft Excel 2007 program was employed for data processing.

In a biosorption study, it is necessary to fit the equilibrium biosorption data using different biosorption isotherm models and kinetic equations in order to analyze and design a biosorption process. Therefore, different theoretical models (Table 1) were applied to the experimental data. Non-linear regression analysis using Origin Pro 8.0 software was employed to determine the isotherm parameters and kinetic constants.

Results and discussion

Biosorbent characterization

The specific surface area of the biosorbent (S_{sp}, $m^2\ g^{-1}$) as obtained by BET measurements was 557.9 $m^2\ g^{-1}$. SEM micrograph of the biosorbent material (Fig. 1) shows a very large surface area that could possibly facilitate the entrapment and subsequent biosorption of MB by the surface functional groups. Figure 2 shows the diffraction pattern of HFs. Two distinct peaks are observed at $2\theta = 9.3°$ and 19.2° respectively, both indicative of semi-crystalline keratin. The peak at $2\theta = 9.3°$ can be attributed to α-helix conformation of the protein molecule, while the peak at $2\theta = 19.2°$ is due to the presence of stranded β-sheet structure. The results of XRD analysis are in accordance with those reported previously by Aguayo-Villarreal et al. 2011 for chicken feathers.

Effect of pH

Solution pH is an important monitoring parameter influencing the sorption behavior of adsorbate onto biosorbent surface due to its impact on both the surface binding-sites of the biosorbent and the dye solution chemistry. In the present study, the effect of pH on biosorption of MB onto HFs was studied over a pH range of 2–10. Results are shown in Fig. 3. The amount of dye removed at equilibrium increases with increasing pH, appreciably up to pH 6.0. With further increase in pH, there is no significant increase in the amount of dye removed. Maximum removal is observed at pH 7.0. Hence, all further experiments were carried out at pH 7.0.

Table 1 Isotherm and kinetic models used in this study

Model	Equation	Parameters	Reference
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 sorption capacity q_m (mg g^{-1}): maximum sorption capacity K_L (L mg^{-1}): Langmuir constant C_e (mg L^{-1}): equilibrium adsorbate concentration in solution	Langmuir 1916
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	Freundlich 1906
Dubinin-Radushkevich (D-R)	$\ln q_e = \ln q_m - \beta\varepsilon^2$ $\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$	β (mmol^2 J^{-2}): D–R constant ϵ (J $mmol^{-1}$): Polanyi potential R: universal gas constant (8.314 J mol^{-1} K^{-1}) T (K): temperature	Dubinin and Radushkevich 1947
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	Lagergren 1898
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	Blanchard et al. 1984

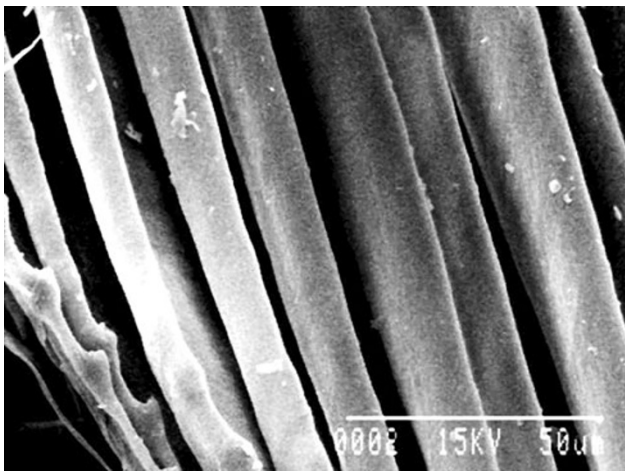

Fig. 1 SEM micrograph of HF (magnification: 1,000×)

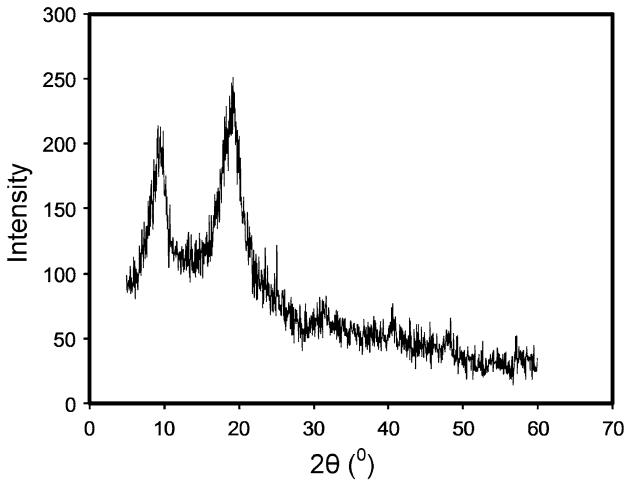

Fig. 2 XRD spectrum of HF

The pH of the aqueous solution affects both the surface charge of the biosorbent material as well as the degree of ionization of the dye molecule. Feathers mainly contain N–H, C=O and C–H functional groups on their surface (Aguayo-Villarreal et al. 2011). Protonation of these functional groups at low pH values renders a net negative charge to the biosorbent surface while deprotonation of the functional groups at high pH values render it positively charged. The pK_a of MB is 0.04 (Weng et al. 2009); hence, it is completely ionized at pH >0.04 and exists as cationic species. At low pH values, there exists a strong electro-negative repulsion between the positively charged dye ions and the negatively charged HF surface resulting in low dye uptake capacity. On the contrary, as the pH of the dye solution increases, a considerable increase in adsorptive removal of dye is observed due to strong electrostatic attraction between negatively charged sites on the biosorbent and the dye cations. Similar results were previously reported for biosorption of MB from aqueous solution onto garlic peel (Hameed and Ahmad 2009), neem leaf powder (Bhattacharyya and Sharma 2005) and yellow passion fruit peel (Pavan et al. 2008).

Effect of biosorbent dose

Biosorbent dose is an important parameter influencing the biosorption process since it determines the biosorption

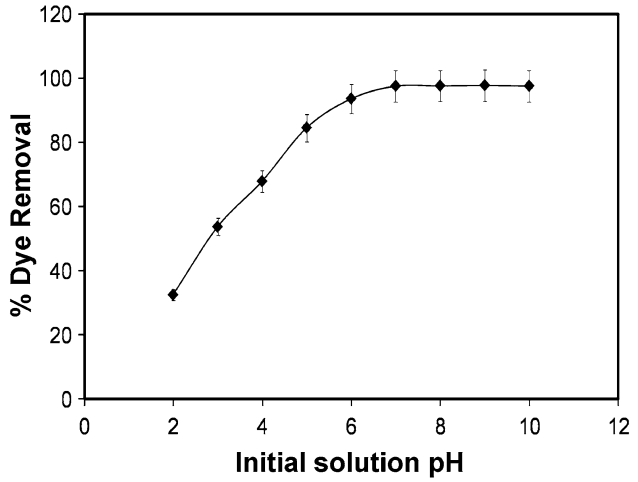

Fig. 3 Effect of pH on biosorption of MB by HFs (experimental conditions: initial MB concentration = 50 mg L^{-1}, biosorbent dose = 1 g/0.1 L^{-1}, agitation speed = 150 rpm, contact time = 3 h, temp. = 303 K, *error bars* represent the standard deviation at $n = 3$)

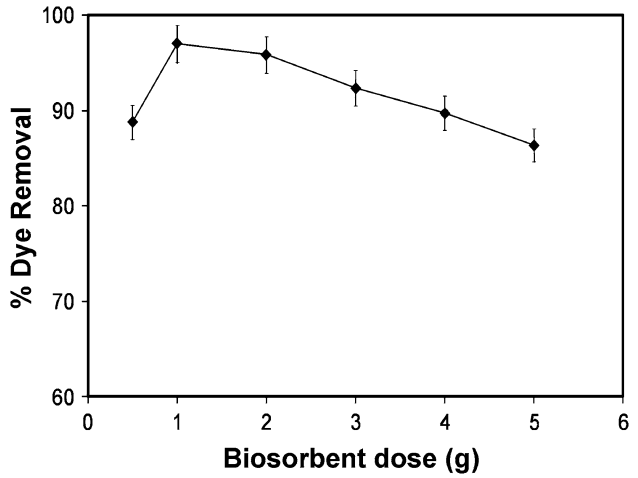

Fig. 4 Effect of biosorbent dose on biosorption of MB by HFs (experimental conditions: initial MB concentration = 50 mg L^{-1}, pH 7.0, agitation speed = 150 rpm, contact time = 3 h, temp. = 303 K, *error bars* represent the standard deviation at $n = 3$)

capacity of a biosorbent for a given initial concentration of the adsorbate under the operating conditions. Therefore, the effect of biosorbent dose on biosorption of MB by HFs was investigated. The amount of biosorbent was varied from 0.50 to 5.00 g in 100 mL dye solution, while all the other variables such as pH, agitation speed, contact time, and temperature were kept constant. Data obtained from the experiments are presented in Fig. 4. With increase in biosorbent dose from 0.5 to 1 g, the dye removal efficiency increases from 85.76 to 97.02 %, which is probably due to an increase in the number of binding sites available for biosorption (Saeed et al. 2010; Ahmad 2009). Further increase in biosorbent dose reduces the percentage removal

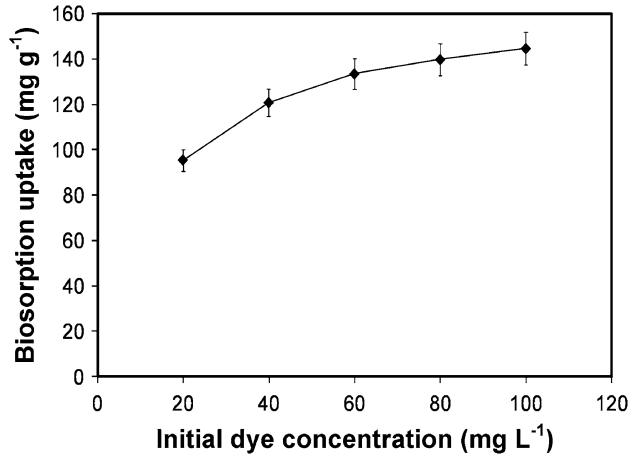

Fig. 5 Effect of initial dye concentration on biosorption of MB by HFs (experimental conditions: pH 7.0, biosorbent dose = 1 g/0.1 L^{-1}, agitation speed = 150 rpm, contact time = 3 h, temp. = 303 K, *error bars* represent the standard deviation at $n = 3$)

of MB. Such behavior can be attributed to saturation of the dye binding sites due to particulate interaction such as aggregation (Aksakal and Ucun 2010). Therefore, in the following experiments, the biosorbent dose was fixed at 1 g. These observations are in agreement with those reported previously by other researchers for the sorption of dyes by different sorbent materials (Aksakal and Ucun 2010; Crini et al. 2007).

Effect of initial dye concentration

Biosorption of MB onto HFs was also carried out at different initial dye concentrations (20, 40, 60, 80, and 100 mg L^{-1}) and the results are shown in Fig. 5. It is clearly evident from the figure that the biosorption capacity increases with increasing initial dye concentration. Initial dye concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases (Chowdhury and Saha 2010a). Hence, a higher initial dye concentration of dye will enhance the biosorption process. A similar trend has been reported by Yao et al. (2009) for biosorption of MB by *Xanthoceras sorbifolia* seed coat.

Effect of temperature

Temperature has pronounced effect on the sorption removal of dyes from aqueous solutions. As such, the effect of temperature on the biosorption process of MB was studied in the range of 303–323 K and the results are depicted in Fig. 6. The figure shows that the dye uptake capacity decreases with increasing temperature. This finding suggests that MB uptake process was exothermic in nature. The negative correlation between temperature and

dye biosorption capacity may be due to the weakening of bonds between the dye molecules and the active site of the biosorbent (Chowdhury and Saha 2010a). Also with increasing temperature, the solubility of MB increases. Consequently, the interaction forces between the solute and the solvent are stronger than those between the solute and the biosorbent. As a result, the solute is more difficult to adsorb (Chowdhury and Saha 2010a). Similar findings have been reported for biosorption of MB by Brazil nut shells (de Oliveira Brito et al. 2010) and *Ulothrix* sp. (Dogar et al. 2010).

Biosorption isotherms

The analysis of a biosorption process depends on the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the biosorbent's surface at a given condition, called an isotherm. An isotherm is a thermodynamic basis of a biosorption separation processes and determines the extent to which a material can be adsorbed onto a particular surface (Chowdhury et al. 2011c). A variety of isotherms have been developed to describe equilibrium relationships. However, no single model is universally applicable; all involve assumptions which may or may not be valid in particular cases. In the present study, the two parameter isotherms of Freundlich, Langmuir and Dubinin–Radushkevich (D–R) were employed to study the biosorption process of MB onto HFs (Table 1).

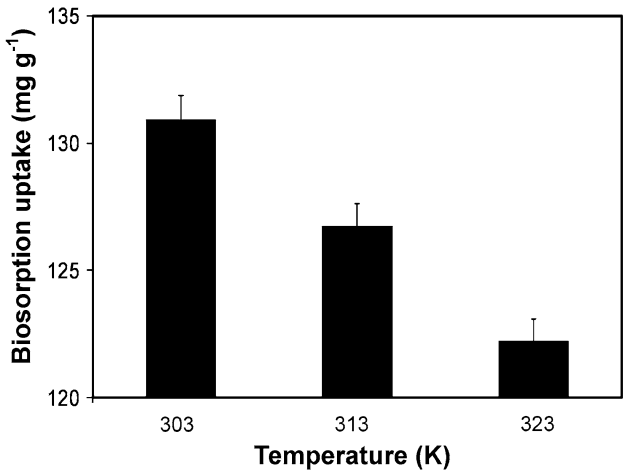

Fig. 6 Effect of temperature on biosorption of MB by HFs (experimental conditions: initial MB concentration = 50 mg L^{-1}, pH 7.0, biosorbent dose = 1 g/0.1 L^{-1}, agitation speed = 150 rpm, contact time = 3 h, *error bars* represent the standard deviation at $n = 3$)

The Langmuir, Freundlich and D–R isotherm model parameters determined using non-linear regression analysis are summarized in Table 2. To quantitatively compare the accuracy of the models, the correlation coefficients (R^2) were also calculated and are also listed in Table 2. According to the R^2 values in Table 2, the Langmuir isotherm model shows best fit to the equilibrium MB biosorption data than the other isotherm models at all studied temperatures (Fig. 7). The suitability of the Langmuir isotherm model suggests monolayer coverage of dye molecules on the biosorbent surface. The maximum MB biosorption capacity of HFs is 134.76 mg g^{-1} at 303 K. The value of the Freundlich constant n is significantly higher than unity at all the temperatures studied indicating that the MB biosorption behavior of HFs can be considered as favorable (Chowdhury et al. 2011b).

The D–R isotherm model constant β gives an idea about the mean free energy E (kJ mol^{-1}) of sorption per mole of the adsorbate which in turn can give information about the type of sorption mechanism. E can be calculated using the relationship (Chakraborty et al. 2011):

$$E = \frac{1}{\sqrt{2\beta}} \tag{3}$$

If the magnitude of E is between 8 and 16 kJ.mol^{-1}, the biosorption process is supposed to proceed via chemisorption, while for values of $E < 8$ kJ mol^{-1}, the sorption process is of physical nature (Chakraborty et al. 2011). The estimated values of E for the present study were found to be >8 kJ mol^{-1} at all temperatures studied (Table 2) implying that the biosorption mechanism of MB on HFs involves chemical ion-exchange.

Biosorption kinetics

Biosorption kinetics is expressed as the solute removal rate, which in turn controls the residence time of the sorbate in

Table 2 Isotherm constants for biosorption of MB by HFs

T (K)	Langmuir			Freundlich			Dubinin-Radushkevich			
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	n	R^2	q_m (mg g^{-1})	β ($mmol^2$ J^{-2})	E (kJ mol^{-1})	R^2
303	134.76	3.67	0.994	82.85	7.49	0.967	97.33	2.04×10^{-9}	15.67	0.912
313	130.34	3.19	0.991	75.27	6.77	0.954	92.45	2.48×10^{-9}	14.21	0.906
323	127.09	2.71	0.987	69.96	6.28	0.952	88.81	2.73×10^{-9}	13.52	0.892

the solid-solution interface. In addition, information on the kinetics of solute uptake rate is also required to select the optimum condition for full-scale batch sorption processes. Several sorption kinetic models have been established to describe the reaction order of sorption systems based on solution concentration. These include pseudo-first-order model, pseudo-second-order model, Weber and Morris sorption kinetic model, first-order reversible reaction model, external mass transfer model, first-order equation of Bhattacharya and Venkobachar, Elovich's model and Ritchies's equation (Chowdhury and Saha 2010b). However, the pseudo-first-order and pseudo-second-order kinetic models are the most well-liked model to study the sorption kinetics of dyes and have been widely used in the kinetic study of dye sorption using various kinds of sorbent materials (Chowdhury and Saha 2010b). By acknowledging their wide application and usefulness in sorption studies, the pseudo-first-order and pseudo-second-order kinetic models (Table 1) were used to study the kinetics of MB biosorption onto HFs in the present study.

The pseudo-first-order and pseudo-second-order rate constants (k_1, k_2, q_e) determined using non-linear regression analysis along with the corresponding R^2 values are listed in Table 3. As can be seen from Table 3, the low R^2 (<0.90) values for the pseudo-first-order model indicate that this model was not suitable for describing the biosorption kinetics of MB. However, the relatively high R^2 (>0.99) values for the pseudo-second-order model suggest that the ongoing biosorption process obeys pseudo-second-order kinetics at all studied temperatures. Also, as can be seen in Table 3, the calculated q_e values ($q_{e,cal}$) show good agreement with the experimental q_e values ($q_{e,exp}$), confirming that the biosorption of MB onto HFs follows the pseudo-second-order kinetic model. A comparison of the pseudo-second-order model with the experimental kinetic data is illustrated in Fig. 8. The applicability of the pseudo-second-order kinetic model indicates that the biosorption process of MB onto HFs is chemisorption and the rate-determining step is probably surface sorption. Similar phenomena have been observed for biosorption of MB by pineapple leaf powder (Weng et al. 2009) and rejected tea (Nasuha et al. 2010).

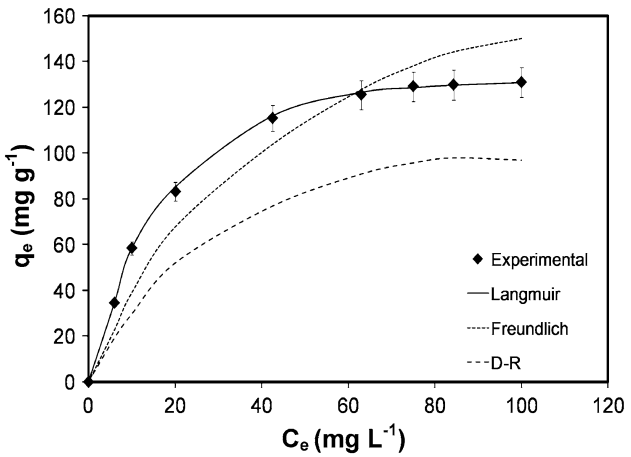

Fig. 7 Comparison between the measured and modeled isotherm profiles for biosorption of MB by HFs (experimental conditions: initial MB concentration = 50 mg L^{-1}, pH 7.0, biosorbent dose = 1 g/0.1 L^{-1}, agitation speed = 150 rpm, contact time = 3 h, temp. = 303 K, *error bars* represent the standard deviation at $n = 3$)

Activation energy

The activation energy (E_a) for biosorption of MB by HFs was determined using the Arrhenius equation (Chowdhury and Saha 2010a):

$$\ln k = \ln A - \frac{E_a}{RT} \tag{3}$$

where k is the rate constant, A the Arrhenius constant, E_a the activation energy (kJ mol^{-1}), R the gas constant (8.314 J mol^{-1}K^{-1}) and T is the temperature (K). The value of E_a for biosorption of MB by HFs, as estimated from the slope of the linear plot of lnk_2 versus 1/T, was 72.79 kJ mol^{-1}. The magnitude of E_a gives information on the nature of the sorption process, i.e., whether it is physical or chemical, with the values of E_a <40 kJ mol^{-1} corresponds to physisorption and higher values represent chemical reaction process (Chowdhury and Saha 2010a). As such it can be said that the biosorption process of MB onto HFs is chemisorption.

The Eyring equation was used to calculate the standard enthalpy ($\Delta H^{\#}$), and entropy of activation ($\Delta S^{\#}$) (Chowdhury et al. 2011a):

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \tag{4}$$

Table 3 Kinetic parameters for biosorption of MB by HFs

T (K)	$q_{e,exp}$ (mg g^{-1})	Pseudo-first order			Pseudo-second order		
		$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
303	130.94	85.37	6.81×10^{-2}	0.892	131.52	4.54×10^{-3}	0.995
313	126.75	82.18	5.47×10^{-2}	0.883	127.38	2.12×10^{-3}	0.999
323	122.23	78.59	4.62×10^{-2}	0.895	123.04	7.56×10^{-4}	0.997

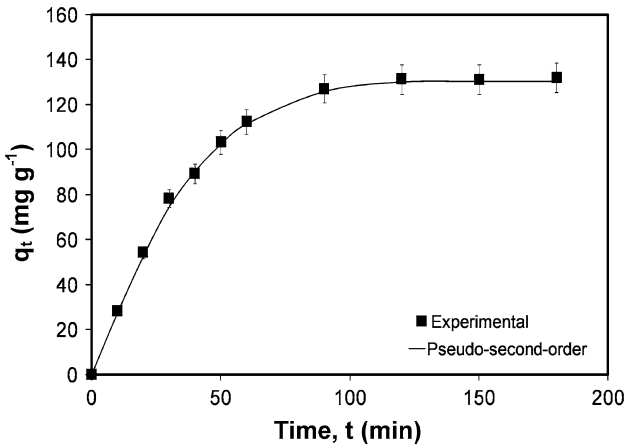

Fig. 8 Pseudo-second-order kinetics for biosorption of MB by HFs (experimental conditions: initial MB concentration = 50 mg L^{-1}, pH 7.0, biosorbent dose = 1 g/0.1 L^{-1}, agitation speed = 150 rpm, contact time = 3 h, temp. = 303 K, *error bars* represent the standard deviation at $n = 3$)

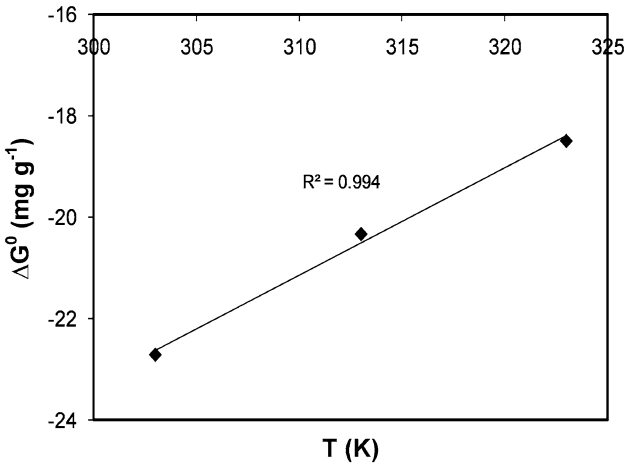

Fig. 9 Plots of Gibb's free energy change versus temperature for biosorption of MB by HFs

where k is the rate constant, k_B the Boltzman constant (1.3807×10^{-23} J K^{-1}), h the Plank constant (6.6261×10^{-34} J s), R the gas constant (8.314 J $mol^{-1}K^{-1}$) and T is the temperature (K). The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were calculated from the slope and intercept of the plot of $\ln(k_2/T)$ versus $1/T$ and were found to be -75.38 kJ mol^{-1} for $\Delta H^{\#}$ and -143.61 J mol^{-1} K^{-1} for $\Delta S^{\#}$. The negative value of $\Delta H^{\#}$ indicates exothermic nature of the biosorption process. The negative value of $\Delta S^{\#}$ suggests that biosorption of MB onto HFs is an associative mechanism (Chowdhury et al. 2011a).

The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were used to compute the free energy of activation ($\Delta G^{\#}$) from the relation:

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (5)$$

The values of $\Delta G^{\#}$ were found to be -31.86, -30.43, and -28.99 kJ mol^{-1} at $T = 303$, 313, and 323 K, respectively. The negative values of $\Delta G^{\#}$ suggest that the energy was released in the biosorption reaction to convert reactants into products.

Biosorption thermodynamics

Thermodynamic consideration of a biosorption process is necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change ($\Delta G°$) is a critical factor for determining the spontaneity of a process and can be computed by the classical Van't Hoff equation (Chowdhury and Saha 2010a):

$$\Delta G° = -RT \ln K_C \quad (6)$$

where R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$), T is the absolute temperature (K) and K_C is the distribution coefficient for biosorption defined as:

$$K_C = \frac{C_a}{C_e} \quad (7)$$

in which C_a is the equilibrium adsorbate concentration on the biosorbent (mg L^{-1}) and C_e is the equilibrium adsorbate concentration in solution (mg L^{-1}).

It is also known that $\Delta G°$ is a function of change in enthalpy ($\Delta H°$, kJ mol^{-1}) as well as change in standard entropy ($\Delta S°$, J $mol^{-1}K^{-1}$) according to the following equation:

$$\Delta G° = \Delta H° - T\Delta S° \quad (8)$$

The values of $\Delta G°$ were estimated to be -22.71, -20.33 and -18.49 kJ mol^{-1} at $T = 303$, 313 and 323 K, respectively. The negative value of $\Delta G°$ at different temperatures indicates spontaneous nature of the biosorption process. Furthermore, decrease in the negative value of $\Delta G°$ with increasing temperature suggests that the biosorption process was more favorable at lower temperatures. $\Delta H°$ and $\Delta S°$ were determined from the intercept and slope of the plot of $\Delta G°$ versus T (Fig. 9). The value of $\Delta H°$ was calculated as -86.55 kJ mol^{-1}, and -1.75 kJ mol^{-1} K^{-1} for $\Delta S°$. The negative value of $\Delta H°$ is indicative of the fact that the biosorption reaction was exothermic. The negative value of $\Delta S°$ suggests that the process is enthalpy driven.

Comparison of HFs with other sorbents

A comparative study of the maximum dye uptake capacity of HFs has been carried out with other reported sorbents. The maximum amount of MB uptake by HFs has been compared to the maximum MB uptake capacity of other reported sorbents and is presented in Table 4. From

Table 4 Comparison of MB sorption capacity of HFs with other reported low-cost sorbent materials

Sorbent	Maximum sorption capacity (mg g^{-1})	Reference
Hen feathers	134.76	This study
Meranti sawdust	120.48	Ahmad et al. (2009)
Pineapple stem	119.05	Hameed et al. (2009)
Dehydrated peanut hull	108.6	Ozer et al. (2007)
Coconut husk	99	Low and Lee (1990)
Coffee husk	90.1	Oliveira et al. (2008)
Garlic peel	82.64	Hameed and Ahmad (2009)
Rubber seed shell	82.64	Oladoja et al. (2008)
Fallen phoenix tree's leaves	80.9	Han et al. (2007)
Ground hazelnut shells	76.9	Ferrero (2007)
Peanut hull	68.03	Gong et al. (2005)
Walnut sawdust	59.17	Ferrero (2007)
Luffa cylindrical fibers	47	Demir et al. (2008)
Yellow passion fruit waste	44.70	Pavan et al. (2008)
Olive pomace	42.3	Banat et al. (2007)
Rice husk	40.59	Vadivelan and Kumar (2005)
Cherry sawdust	39.84	Ferrero (2007)
Banana peel	20.8	Annadurai et al. (2002)
Orange peel	18.6	Annadurai et al. (2002)
Wheat shells	16.56	Bulut and Aydin (2006)
Egg shell	16.43	Sharma et al. (2009)
Coconut coir	15.59	Tsai et al. (2006)
Indian rosewood sawdust	11.8	Garg et al. (2004)
Neem leaf powder	3.67	Bhattacharyya and Sharma (2005)
Fly ash	1.91	Saha and Datta (2009)
Tamarind fruit shell	1.72	Saha (2010)

Table 4 it is evident that the maximum sorption capacity of HFs for MB is comparable and moderately higher than that of many corresponding sorbent materials. Differences in dye uptake capacity are due to the differences in properties of each sorbent material such as structure, functional groups and surface area. The easy availability and cost effectiveness of HFs are some additional advantages, which make it better biosorbent for the removal of MB from aqueous solutions.

Conclusion

In this study, the efficacy of HFs as biosorbent for removal of MB from aqueous solutions was investigated. Batch mode biosorption studies indicate that the biosorption was strongly dependent on solution pH, initial dye concentration, biosorbent dose and reaction temperature. The equilibrium biosorption data obtained at different temperatures fitted well in the Langmuir isotherm model indicating monolayer biosorption on a homogeneous surface. The maximum monolayer biosorption capacity was found to be 134.76 mg g^{-1} at 303 K which is considerably higher than that of many other sorbent materials reported in the literature. The mean free energy (E) calculated from the D–R isotherm model as well as the activation energy (E_a) determined using the Arrhenius equation confirms that the biosorption involved chemical ion-exchange. Kinetic studies show that the MB removal followed pseudo-second-order rate equation, while thermodynamic studies suggest that the biosorption process was spontaneous and exothermic. Finally, it can be concluded that HFs, a common and easily available waste biomaterial can be used as an economical biosorbent for the removal of MB from aqueous solutions.

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