

Biosorption of Methylene Blue from Aqueous Solutions by Hazelnut Shells: Equilibrium, Parameters and Isotherms

Mehmet Doğan · Harun Abak · Mahir Alkan

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Abstract This paper presents a study on the batch adsorption of a basic dye, methylene blue (MB), from aqueous solution onto ground hazelnut shell in order to explore its potential use as a low-cost adsorbent for wastewater dye removal. A contact time of 24 h was required to reach equilibrium. Batch adsorption studies were carried out by varying initial dye concentration, initial pH value (3–9), ionic strength (0.0–0.1 mol L⁻¹), particle size (0–200 μm) and temperature (25–55°C). The extent of the MB removal increased with increasing in the solution pH, ionic strength and temperature but decreased with increase in the particle size. The equilibrium data were analysed using the Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm were determined. By considering the experimental results and adsorption models applied in this study, it can be concluded that equilibrium data were represented well by Langmuir isotherm equation. The maximum adsorption capacities for MB were 2.14×10^{-4} , 2.17×10^{-4} , 2.20×10^{-4} and 2.31×10^{-4} mol g⁻¹ at temperature of 25, 35, 45 and 55°C, respectively. Adsorption heat revealed that the adsorption of MB is endothermic in nature. The results indicated that the MB strongly interacts with the hazelnut shell powder.

Keywords Biosorption · Methylene blue · Hazelnut shell · Langmuir isotherm

Nomenclature

q_m	Monolayer capacity of the adsorbent, mol g ⁻¹
K	Adsorption constant, L mol ⁻¹
C_e	Equilibrium dye concentration in solution, mol L ⁻¹
q_e	Equilibrium dye concentration on adsorbent, mol g ⁻¹
K_F	Freundlich constant, mol g ⁻¹
n	Freundlich isotherm exponent
T	Temperature, K
I	Ionic strength, mol L ⁻¹
W	Mass of adsorbent, g
V	Volume of aqueous solution to be treated, L
C_0	Initial dye concentration in aqueous solution, mol L ⁻¹
R^2	Regression coefficient
PS	Particle size

1 Introduction

Dyes are used in many industries such as food, paper, carpets, rubbers, plastics, cosmetics, and textiles in order to color their products. As a result, these industries generate a considerable amount of colored wastewater. The discharge of colored wastewater from these industries into natural streams has caused

M. Doğan (✉) · H. Abak · M. Alkan
Faculty of Science and Literature,
Department of Chemistry, Balıkesir University,
10145 Balıkesir, Turkey
e-mail: mdogan@balikesir.edu.tr

many significant problems such as increasing the toxicity and chemical oxygen demand (COD) of the effluent, and also reducing light penetration, which has a derogatory effect on photosynthetic phenomena (Bulut and Aydın 2006). Many dyes have toxic effect as well as carcinogenic, mutagenic and teratogenic effects (McKay et al. 1985) on aquatic life and also on humans (Gregory et al. 1991). Some of the dyes present in these effluents resist biological oxidation and, therefore, they require tertiary treatment (An et al. 1996; Liakou et al. 1997; Sarasa et al. 1998; Bhattacharyya and Sharma 2005). It is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater (Banat et al. 1996). The presence of very small amounts of dyes in water is highly visible and undesirable (Robinson et al. 2001; Banat et al. 1996). Over 100,000 commercially available dyes exist and more than 7×10^5 tonnes per year are produced annually (Pearce et al. 2003; McMullan et al. 2001). Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that 2% of dyes that are produced are discharged directly in aqueous effluent (Pearce et al. 2003; Robinson et al. 2001). Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents (Sun and Yang 2003; Ravi Kumar et al. 1998; Crini 2006).

During the past three decades, several physical techniques like, flocculation, froth flotation, etc., and chemical and decolorization methods such as electrochemical, biochemical or photochemical have been reported (Ghoreishi and Haghghi 2003; Crini 2006; Mittal 2006). Amongst the numerous techniques, adsorption techniques are widely used to remove certain types of pollutants in wastewater treatment processes. Recovery of costly toxic substances from the wastewater is an added advantage of the adsorption procedure. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of contaminants (Weng and Pan 2006; Mittal 2006). Most commercial systems

currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability (Crini 2006). However, the technology for manufacturing good quality activated carbon is still very cost-prohibitive and the regeneration or disposal of the spent carbon is often problematic. There is also considerable loss of carbon in the waste sludge unless the adsorption is carried out through fixed process. This has prompted the use of various materials as adsorbents in order to develop cheaper alternatives by utilizing agricultural and other wastes. Such low-cost adsorbents have been investigated at the laboratory scale for the treatment of coloured effluents with different degrees of success (Bhattacharyya and Sharma 2005). Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from industry and agriculture, have been proposed by several workers. These materials could be used as sorbents for the removal of dyes from solution. Some of the reported sorbents include clay materials such as bentonite, kaolinite, perlite, zeolites; agricultural wastes such as bagasse pith, maize cob, rice husk, coconut shell; industrial waste products such as waste carbon slurries, metal hydroxide sludge; biosorbents such as chitosan, peat, biomass; and others such as starch, cyclodextrin, cotton (Crini 2006). Many efforts, however, have been made to investigate the use of various low cost organic adsorbents (Sanghi and Bhattacharya 2002; Allen and Koumanova 2005). They should be cheap, easily available and disposable without regeneration. These materials are derived from natural resources, plant wastes or industrial by-products as peat, wood, barley and rice husk, etc. Most of them are cellulose-based and can be used without any previous thermal or chemical treatment (Ferrero 2007).

Methylene blue (MB) is not strongly hazardous, but it can cause some harmful effects. Adsorption of MB from the aqueous phase is a useful tool for product control of adsorbents (Hamdaoui 2006). The recent studies on MB adsorption onto activated carbon (Shaobin et al. 2005), rice husk (Vadivelan and Vasanth Kumar 2005), peanut hull (Renmin et al. 2005), KOH-activated and steam-activated carbons (Wu et al. 2005), pumice powder (Feryal 2005), glass fibers (Sampa and Binay 2005), oxihumolite (Pavel

et al. 2005), pyrophyllite (Aslıhan et al. 2005; Gücek et al. 2005), Indian rosewood sawdust (Garg et al. 2004), neem leaf powder (Bhattacharyya and Sharma 2005), perlite (Doğan et al. 2004), jute processing wastes (Banerjee and Dastidar 2005), eggshells (Tsai et al. 2006) and fly ash (Wang et al. 2005) have been reported. The by-products from the agricultural and industrial industries could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials. Hazelnut shells present in large amounts in some countries such as Turkey and Italy, as food industry waste. Its major use today is as combustible owing the considerable calorific value (Ferrero 2007). The aim of this work is to study the removal of MB from aqueous solution by adsorption onto hazelnut shell. Factors affecting adsorption, such as pH, ionic strength, particle size and temperature, were evaluated. Adsorption isotherms were determined and modelled by Langmuir and Freundlich models. Based on the results of isotherm analysis, thermodynamic parameters for such systems were determined. Results of this study will be useful for future scale up using this material as a low-cost adsorbent for the removal of cationic dyes.

2 Material and Methods

2.1 Materials

Hazelnut shells were supplied from the Black Sea Region of Turkey. They were firstly dried, crushed and sieved to obtain a particle size between 0–75, 75–150 and 150–200 μm . Methylene blue was chosen as the target compound because it has a net positive charge which would be favorably adsorbed by electrostatic force onto negatively charged surface. MB (CI=52015; chemical formula: $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$; molecular weight=319.86 g mol^{-1} ; maximum wavelength=663 nm) supplied by Merck was used as adsorbate and was not purified prior to use. The structure of the dye containing a secondary amine group is presented in Fig. 1. The aromatic moiety of MB contains nitrogen and sulfur atoms. In the aromatic unit, dimethylamino groups attach to it. The aromatic moiety is planar and the molecule is positively charged. The dimensions of MB molecule are 16.9 $^{\circ}\text{A}$ for the length, 7.4 $^{\circ}\text{A}$ for the breadth, and 3.8 $^{\circ}\text{A}$ for

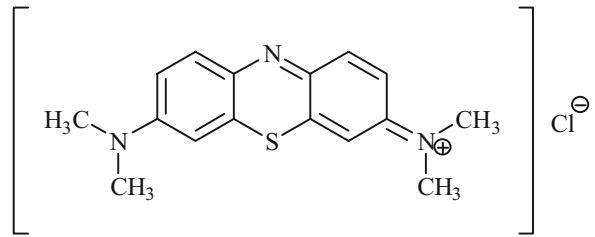


Fig. 1 The structure of MB

the thickness (Weng and Pan 2006). Other chemicals were obtained from Merck and Fluka.

2.2 Batch Mode Adsorption Study

MB was dried at 110 $^{\circ}\text{C}$ for 2 h before use. All of the MB solution was prepared with ultrapure water. For the adsorption experiments, 50 mL of dye solution of known initial concentration in 100 mL screw-cap conical polyethylene flasks was shaken in a rotary shaker with 0.25 g of hazelnut shell at desired pH and temperature at 200 rpm for 24 h. pH was adjusted using 0.1 N HCl and 0.1 N NaOH with Orion 920A pH meter with a combined pH electrode. The pH-meter was standardized with NBS buffers before every measurement. The effects of pH, ionic strength, particle size and temperature were studied. At the end of the adsorption period, the solution was centrifuged for 10 min at 5,000 rpm. After centrifugation, the dye concentration in the supernatant solution was analyzed using a Perkin Elmer Lambda 25 model UV Visible spectrophotometer by monitoring the absorbance changes at a wavelength of maximum absorbance (663 nm). Preliminary experiments showed that the effect of the separation time on the amount of adsorbed dye was negligible. Each experiment was carried out in duplicate and the average results are presented. Calibration curves are obtained with standard MB solutions. The amounts of MB adsorbed were calculated by subtracting final solution concentrations from the initial concentration of aqueous solution. Blank solutions were used for each series of experiments.

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

where q_e is the MB amount adsorbed per gram of adsorbent, C_0 and C_e is the initial and equilibrium concentration of MB in solution (mol L^{-1}), V is volume of MB solution (L), and W is the mass of adsorbent (g; Özdemir et al. 2006; Doğan et al. 2000).

3 Results and Discussion

At equilibrium the adsorption process is considered to be at dynamic state in which the rate of the adsorption process equals that of the desorption process. Adsorption equilibrium is governed by several factors such as the nature of adsorbate and adsorbent as well as the solution composition, pH and temperature.

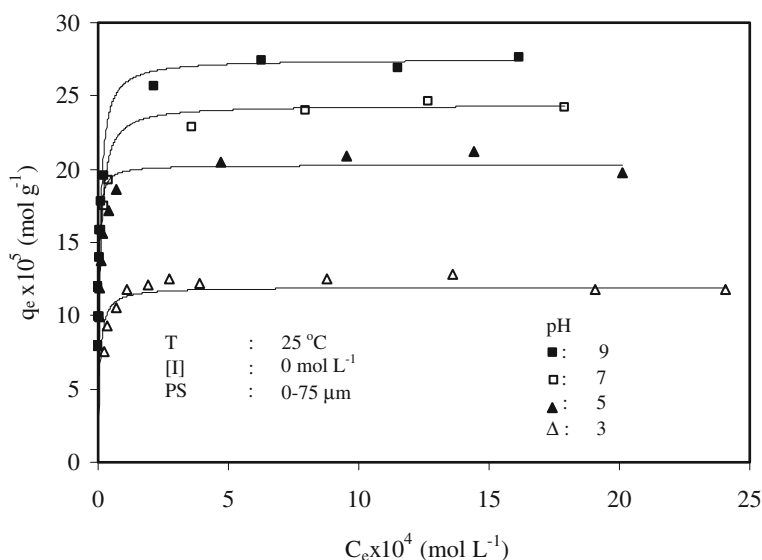
3.1 Adsorption Equilibrium

3.1.1 Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process, particularly on adsorption capacity (Bulut and Aydın 2006; Doğan and Alkan 2003a, b). The interaction between sorbate and sorbent is affected by the pH of an aqueous medium in two ways: firstly, since dyes are complex aromatic organic compounds having different functional groups and unsaturated bonds, they have different ionization potentials at different pH, resulting in the pH dependent net charge on dye molecules. Secondly, the surface of the biosorbent consists of biopolymers with many functional groups, so the net charge on biosorbent, which could be measured in the form of zeta potential, is also pH dependent. Therefore, the interaction between dye molecule and biosorbent is basically a combined result of charges on dye molecules and the surface of the biosorbent (Maurya

et al. 2006). The influence of the pH on the adsorption behaviour of dyes onto various adsorbent was considered by many authors (Demirbaş et al. 2002; Doğan et al. 2007; Namasivayam et al. 2001; Annadurai et al. 2002; Batzias and Sidiyas 2004; Özacar and Şengil 2005; Alkan et al. 2004a, b, 2005). The introduction of strong acid or bases could alter the surface properties of the sorbents as well as the ionic character and aggregation state of the dyes. The amount of MB adsorbed over hazelnut shell was monitored in the pH range 3–9 at 25°C. The effect of pH on the adsorption of MB by hazelnut shell is shown in Fig. 2. It is evident that uptake increased consistently with pH. Several investigations have reported that MB adsorption usually increases as the pH is increased (Gupta et al. 2004; Singh et al. 2003; Janos 2003). The increase in sorption depended on the properties of the adsorbent surface and the dye structure. This behavior of dye sorption can be explained on the basis of surface charge of the biosorbents. It has been reported that such biosorbents have net negative charge in the aqueous phase (Kapoor et al. 1999). With increase in pH, the net electronegativity of the biosorbent increases due to deprotonation of different functional groups (Schiewer and Volesky 1995; Kapoor et al. 1999; Harris and Ramelow 1990). Therefore, there is an increase in attractive electrostatic force between the negatively charged biosorbent particle and positively charged MB dye ion. Summers and Roberts (1988)

Fig. 2 Effect of pH to MB adsorption on hazelnut shell



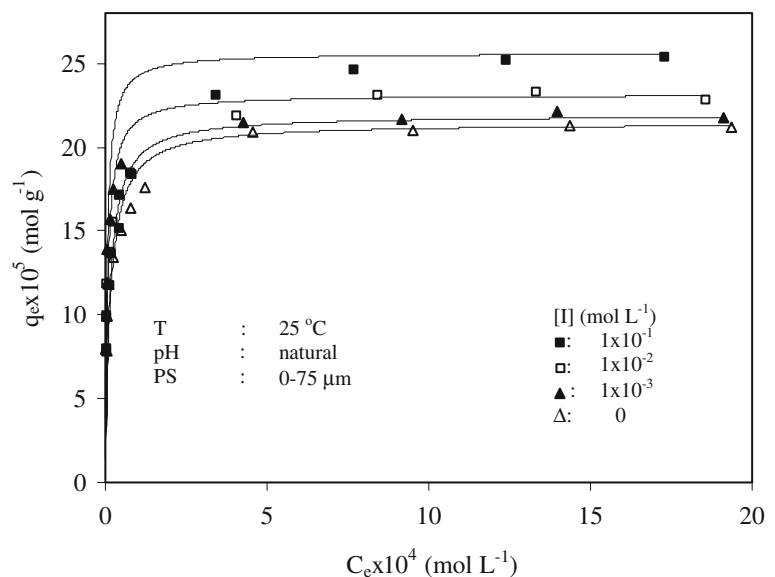
have reported for the granulated activated carbon (GAC) adsorbent that the chemical nature of the surface is influenced by solution pH, which therefore plays an important role in the adsorption of solutes from aqueous solutions. These natural cellulose products contain a number of phenolic-OH groups as well as COO^- groups. The low adsorption of dye in highly acidic solution also shows possibility of development of positive charge on the adsorbent, which inhibits the adsorption of dye over it. However, on moving towards the basic range the uptake of dye increases due to change in its polarity, which might have developed electric double layer around the adsorbent (Mittal 2006). At higher pH, the surface of hazelnut shell particles may become negatively charged, which enhances the positively charged MB cations through electrostatic forces of attraction (Bulut and Aydın 2006).

3.1.2 Effect of Ionic Strength

Wastewaters from textile-manufacturing or dye-producing industries contain various types of suspended and dissolved compounds apart from the dyes which can be considered as impurities in the dye removal process. These impurities could be acids, alkalis, salts or metal ions (Maurya et al. 2006). The ionic strength of the solution is one of the factors that control both electrostatic and non-electrostatic interactions between the adsorbate and the adsorbent surface (Ferrero 2007).

The enthalpy of biosorption would be affected not only by the pH value on the electron donating capability, but also by the salt concentration on the hydrophobic and electrostatic interaction between dye and surface functional adsorptive sites (Bhattacharyya and Sharma 2005). The influence of ionic strength on the adsorption ability of the hazelnut shell for MB was investigated using NaCl solutions of concentrations ranging from 0.0 to 0.1 mol L^{-1} . The presence of NaCl in the solution may have two opposite effects. On the one hand, since the salt screens the electrostatic interaction of opposite charges of the adsorbent surface and the dye molecules, the adsorbed amount should decrease with increase of NaCl concentration. On the other hand, the salt causes an increase in the degree of dissociation of the dye molecules by facilitating the protonation (Doğan et al. 2007). As shown in Fig. 3, which demonstrates the effect of ionic strength on the equilibrium adsorption amount, increasing the ionic strength of the medium exhibited a positive effect on the adsorbed amounts of MB. Figure 3 suggests that increased ionic strength favors the approximation association process of the hazelnut shell, giving rise to new sites where dye molecules can be trapped. The adsorbed amount increases as the dissociated dye ions free for binding electrostatically onto the solid surface of oppositely charged increase (Doğan et al. 2007). The latter effect seems to be dominant on the adsorption capacity of the surface. These results are consistent with the results of Narine

Fig. 3 Effect of ionic strength to MB adsorption on hazelnut shell



and Guy (1981), German-Heins and Flury (2000), Guo et al. (2003) and Doğan et al. (2007). From this point of view, this result indicates that the hazelnut shell can be used for removal of MB dye from salty waters.

3.1.3 Effect of Particle Size

Adsorption of MB dye for three different particle sizes of hazelnut shell (0–75, 75–150 and 150–200 μm) was studied keeping the other parameters as constant. The results of variation of these particle sizes on dye adsorption are shown in Fig. 4. It can be observed that as the particle size decreases, the adsorption of the dye increases. This is due to larger surface area that is associated with smaller particles. For larger particles, the diffusion resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently, the amount of dye adsorbed is small. It is also observed that as the particle size decreases, the dye uptake, that is the amount of dye adsorbed on the particles increases (Annadurai 2002).

3.1.4 Effect of Temperature

A study of the temperature dependence of adsorption reactions gives valuable knowledge about the enthalpy and entropy changes during adsorption (Alkan and Doğan 2003). The adsorption process was carried out at four different temperatures from 25 to 55°C with an

interval of 10°C. Figure 5 indicates that the extent of adsorption improved steadily with an increase in adsorption temperature. As shown in Fig. 5, the biosorption capacity of the hazelnut shell was increased for MB dye with increasing temperature from 25 to 55°C due to increased surface activity and increased kinetic energy of dye molecule. Since the biosorption increased when temperature increased, therefore, the system was endothermic. Similar observations were reported in the literature. For example, Aksu and Tezer (2001) reported that the adsorption capacity of the green alga *Chlorella vulgaris* for Ramazol Black B was increased with increases in temperature. MB adsorption on hazelnut shell powder was definitely endothermic in nature requiring some amount of activation. Similar endothermic adsorption of MB was observed earlier on Guyava leaves (Singh and Srivastava 1999), kaolinite (Ghosh and Bhattacharyya 2002), and sepiolite (Doğan et al. 2007).

From the experimental data obtained at various temperatures, the enthalpy change for MB adsorption can be estimated from the van't Hoff isochore (Tokiwawa 1983; Nasseem and Tahir 2001):

$$\left[\frac{\partial \ln K}{\partial (1/T)} \right]_{\theta} = - \frac{\Delta H_{\text{ads}}^0}{R_g} \quad (2)$$

The subscript θ means that the equilibrium constant at each temperature is measured at constant

Fig. 4 Effect of particle size to MB adsorption on hazelnut shell

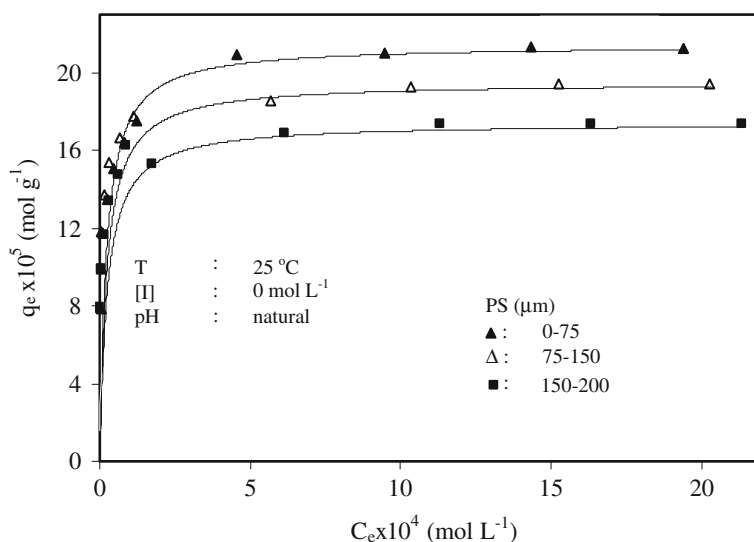
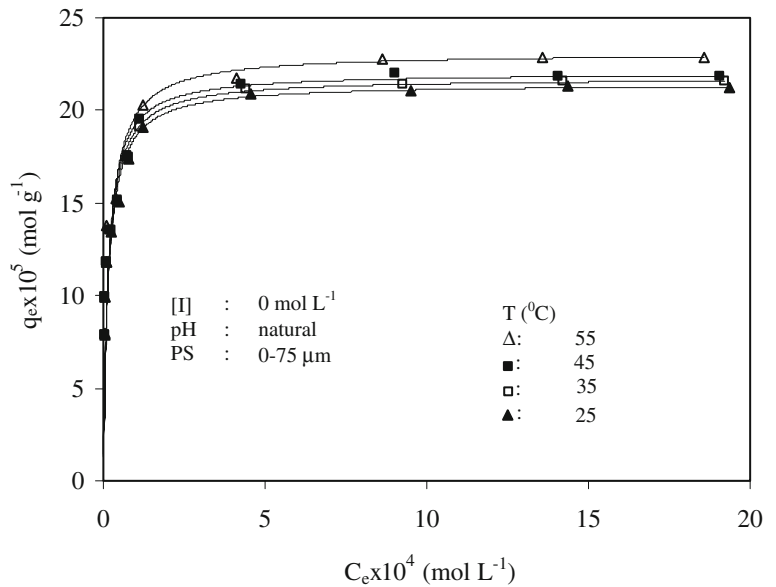


Fig. 5 Effect of temperature to MB adsorption on hazelnut shell



coverage. Under these conditions, from the Langmuir equation at $\theta=0.5$; $K=1/C_e$ and so

$$\left[\frac{\partial \ln C_e}{\partial (1/T)} \right]_{\theta=0.5} = \frac{\Delta H_{ads}^0}{R_g} \tag{3}$$

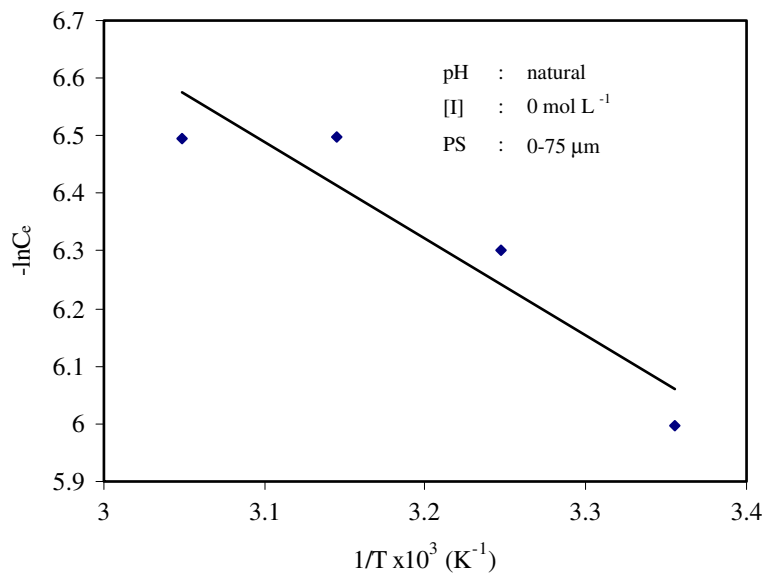
where R_g is the gas constant and T is temperature (K). This value of ΔH_{ads}^0 is called the isosteric heat of adsorption referring to the fact that it applies to a certain value of the coverage. The Langmuir model implies that ΔH_{ads}^0 should be constant, but it is more likely to be a function of coverage ($\theta=q_e/q_m$). The

value of ΔH_{ads}^0 was calculated as $13.59 \text{ kJ mol}^{-1}$ from the data given in Fig. 6 according to Eq. (3). The result shows that the interaction between surface and adsorbate molecule is physical interaction and is endothermic process in nature.

3.2 Biosorption Isotherms

Adsorptions isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface and also, are critical in optimizing

Fig. 6 Plots of $-\ln C_e$ versus $1/T$ for adsorption of MB dye on hazelnut shell



the use of hazelnut shell as an adsorbent. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption (Lorenc-Grabowska and Gryglewicz 2007). Biosorption data are most commonly represented by an equilibrium isotherm, which is a plot of the quantity of sorbate retained on biosorbent q_e (solid phase concentration of the sorbate) as a function of the concentration of the sorbate in the liquid phase C_e (liquid phase concentration of the sorbate at equilibrium). At equilibrium, a dynamic equilibrium is established in the concentration of sorbate between two phases. The equilibrium isotherm is of fundamental importance for the design and optimization of the adsorption system for the removal of dye from aqueous solution. Therefore, it is necessary to establish the most appropriate correlation for the equilibrium curves. There are several isotherm equations, which can be used to describe the equilibrium nature of adsorption. Most of the isotherm models used to describe adsorption in solution are based on the semiempirical equations. In the present study, two of the most commonly used models, namely Langmuir and Freundlich isotherms, were used to describe the biosorption equilibrium.

The Langmuir isotherm model is an analytical equation basically developed for gas phase adsorption onto the homogeneous surface of glass and metals (Maurya et al. 2006). The assumptions of the Langmuir isotherm are that (1) adsorption energy is constant over all sites; (2) adsorbed atoms or molecules are adsorbed at definite, localized sites; (3) each site can accommodate only one molecule or atom; (4) there is no interaction between adsorbates. At adsorption equilibrium, a saturation point is reached at which no further adsorption can occur. Thus, the Langmuir isotherm reaches a plateau at the saturation point. The Langmuir isotherm can be represented by (You et al. 2006)

$$q_e = \frac{q_m K C_e}{1 + K C_e} \quad (4)$$

The linear form of the Langmuir Eq. (4) is

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \quad (5)$$

The Freundlich isotherm is an empirical expression that encompasses the heterogeneity of the surface and an exponential distribution of the sites and their energies. This isotherm has been further extended by considering the influence of adsorption sites and the competition between different adsorbates for adsorption on the available sites. Freundlich isotherm has been observed for a wide range of heterogeneous surfaces including activated carbon, silica, clays, and polymers. The Freundlich equation can be written as (You et al. 2006):

$$q_e = K_F C_e^{1/n} \quad (6)$$

Its linear form is given below:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

Here, q_e is the quantity of solute adsorbed per unit weight of adsorbent (mol g^{-1}), C_e is the equilibrium concentration of solute remaining in the solution (mol L^{-1}), q_m and K are the Langmuir model constants. These constants are called the adsorption capacity (maximum surface coverage) and bonding energy constant, respectively. $1/n$ is the heterogeneity factor of the adsorbent and K_F is constant. The surface heterogeneity is due to the existence of crystal edges, type of cations, surface charges, surface modification groups, and degree of crystallinity of the surface. The $1/n$ value indicates the relative distribution of energy sites and depends on the nature and strength of the adsorption process. The Freundlich isotherm does not predict the saturation of the adsorbent surface by the adsorbate. The K_F value can be taken as a relative indicator of the adsorption capacity of the adsorbents for a narrow subregion having equally distributed energy sites toward adsorbates (You et al. 2006).

For the determination of model constants, the Langmuir and Freundlich models could be analyzed using linear forms as described in Eqs. (5) and (7). Straight lines were fitted to the points by the method of least squares, where the slope of the regression line is $1/q_m$ and the intercept is $1/Kq_m$ for Langmuir model, and that is $1/n$ and that is $\ln K_F$ for Freundlich model, respectively. The linear regression lines obtained had highly significant correlation coefficients (R^2), indicating a good fit to the Langmuir equation. Table 1 shows the model constants along

Table 1 Isotherm parameters calculated for adsorption of MB on hazelnut shell

Parameters				Langmuir isotherm				Freundlich isotherm
T (°C)	pH	$[I]$ (mol L ⁻¹)	PS (μm)	q_m (mol g ⁻¹) × 10 ⁵	K (L mol ⁻¹) × 10 ⁻⁵	R^2	R_L	R^2
25	Natural	0	0–75	21.44	0.65	0.9999	0.75–0.007	0.8904
35	Natural	0	0–75	21.75	0.66	0.9999	0.80–0.008	0.8911
45	Natural	0	0–75	22.04	0.69	0.9999	0.80–0.008	0.8918
55	Natural	0	0–75	23.10	0.72	0.9997	0.90–0.009	0.9278
25	Natural	0.001	0–75	21.92	1.95	0.9999	0.80–0.002	0.8043
25	Natural	0.010	0–75	23.14	0.95	0.9997	0.90–0.005	0.9069
25	Natural	0.100	0–75	25.62	0.44	0.9998	0.90–0.010	0.9279
25	3	0	0–75	11.95	1.63	0.9985	0.30–0.002	0.5885
25	5	0	0–75	20.28	1.48	0.9983	0.99–0.001	0.8084
25	7	0	0–75	24.38	1.39	0.9998	0.80–0.004	0.8313
25	9	0	0–75	27.51	1.52	0.9998	0.80–0.004	0.8500
25	Natural	0	75–150	19.50	1.17	0.9999	0.90–0.003	0.8749
25	Natural	0	150–200	17.42	1.93	0.9999	0.50–0.004	0.8501

with correlation coefficients for biosorption of MB onto hazelnut shell. For the Langmuir model, correlation coefficient, R^2 (Table 1) varied from 0.9983 to 0.9999, while for Freundlich, it varied from 0.5885 to 0.9279. The comparison of correlation coefficients (R^2) of the linearized form of both equations indicates that the Langmuir model yields a better fit for the experimental equilibrium adsorption data than the Freundlich model. This suggests the monolayer coverage of the surface of hazelnut shell by MB molecules. This may be associated with the homoge-

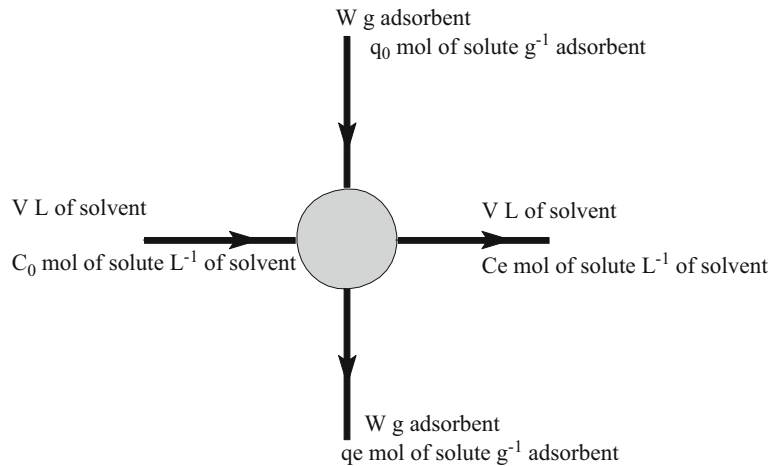
neous surface of the hazelnut shell (Lorenc-Grabowska and Gryglewicz 2007). A comparison between the adsorption capacities of hazelnut shell and other adsorbents under similar conditions is presented in Table 2. When comparing our results for hazelnut shell with the results of others, it can be concluded that the hazelnut shell has adsorbed MB dye as effectively as the other adsorbents listed. A lower hazelnut production cost compared to other adsorbents such as activated carbon is another advantage of hazelnut shell for use as an adsorbent.

Table 2 Previously reported adsorption capacities on various adsorbents of MB

Adsorbents	q_m (mol g ⁻¹) × 10 ⁵	References
Dead macro fungi	54.7–62.2 ^a	Maurya et al. 2006
Bio-sludge ash	0.35–0.73	Weng and Pan 2006
Coir pith carbon	1.57 ^a	Kavitha and Namasivayam 2007
Neem leaf powder	2.34 ^a	Bhattacharyya and Sharma 2005
Cedar sawdust	38.1 ^a	Hamdaoui 2006
Crushed brick	25.8 ^a	Hamdaoui 2006
Wheat shells	4.43 ^a	Bulut and Aydın 2006
Indian rosewood sawdust	3.16–13.7 ^a	Garg et al. 2004
Rice rusk	10.9 ^a	Vadivelan and Kumar 2005
Jute processing waste	6.01 ^a	Banerjee and Dastidar 2005
Pyrophyllite	18.8 ^a	Gücek et al. 2005
Eggshell and eggshell membrane	0.21–0.06 ^a	Tsai et al. 2006
Fly ash	3.59 ^a	Wang et al. 2005
Activated carbon	116.3 ^a	Legrouri et al. 2005
Unexpanded perlite	18.04–71.18	Doğan et al. 2000
Expanded perlite	4.65–8.21	Doğan et al. 2000
Sepiolite	1.81–2.69	Özdemir et al. 2006
Hazelnut shell	11.95–27.51	In this study

^a Converted from mg g⁻¹ to mol g⁻¹

Fig. 7 A single-stage batch adsorber

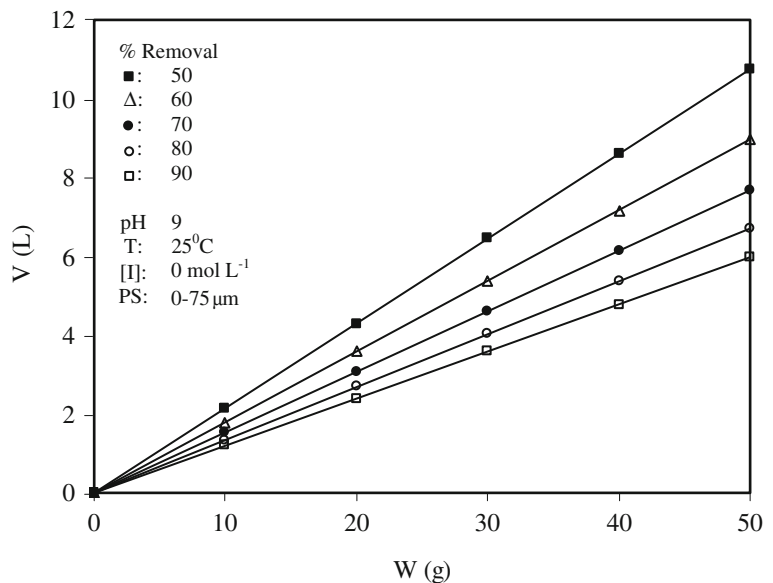


The shape of the isotherm may also be considered with a view to predicting if an adsorption system is “favorable” or “unfavorable.” The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter, R_L (Hall et al. 1966), which is defined by

$$R_L = \frac{1}{1 + KC_e} \quad (8)$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values reported in Table 1, show that the adsorption behavior of MB dye was favorable ($0 < R_L < 1$).

Fig. 8 Volume of effluent (V) treated against adsorbent mass (W) for different percentages of MB removal



3.3 Single Stage Batch Biosorption

The schematic diagram for a single-stage adsorption process is shown in Fig. 7. The solution to be treated contains V L solvent, and the dye concentration is reduced from C_0 to C_e (mol L^{-1}) in the adsorption process. The adsorbent is added to the extent of W g adsorbate-free hazelnut shell, and the solute dye concentration increases from q_0 to q_e (mol g^{-1}). If fresh adsorbent is used, $q_0 = 0$. The mass balance equates the dye removed from the liquid to that picked up by the solid (McKay et al. 1980).

$$V(C_0 - C_e) = W(q_e - q_0) = Wq_1 \quad (9)$$

The Langmuir data may now be applied to Eq. (9) and substituting for q_e from Eq. (5) and rearranging gives

$$\frac{W}{V} = \frac{C_0 - C_e}{q_e} \equiv \frac{C_0 - C_e}{\left(\frac{q_m K C_e}{1 + K C_e}\right)} \quad (10)$$

Equation (10) permits analytical calculation of the adsorbent solution ratio for a given change in solution concentration, C_0 to C_e . A series of plots are shown in Fig. 8. Figure 8 shows a series of plots derived from Eq. (10) for the adsorption of MB on hazelnut shell. An initial dye concentration of 3×10^{-3} mol L⁻¹ at 25°C and pH 9 is assumed, and the figures show the amount of effluent which can be treated to reduce the dye content by 50, 60, 70, 80 and 90% using various masses of adsorbent.

4 Conclusions

The results of present investigation show that hazelnut shell, low cost material, has suitable adsorption capacity with regard to the removal of MB from its aqueous solution. The cost and adsorption characteristics favor hazelnut shell to be used as an effective adsorbent for the removal of MB from wastewater. The adsorption of MB on hazelnut shell was endothermic indicating that a temperature above the ambient temperature would be favourable for carrying out the removal of the dye. The results indicate that MB adsorption onto hazelnut shell is physical in nature. The experimental equilibrium data obtained were applied to the Langmuir and Freundlich isotherm equations to test the fitness of these equations. By considering the experimental results and adsorption models applied in this study, it can be concluded that adsorption of MB obeys Langmuir isotherm confirming the monolayer adsorption capacity of MB onto hazelnut shell, the linearization mode of the Langmuir equation influences the estimation of parameters. The dimensionless separation factor (R_L) showed that hazelnut shell can be used for removal of MB from aqueous solutions.

References

Aksu, Z., & Tezer, S. (2001). Equilibrium and kinetic modelling of biosorption of remazol black B by *Rhizopus*

- arrhizus* in a batch system: Effect of temperature. *Process Biochemistry*, 36, 431–439.
- Alkan, M., Çelikçapa, S., Demirbaş, Ö., & Doğan, M. (2005). Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite. *Dyes and Pigments*, 65, 251–259.
- Alkan, M., Demirbaş, Ö., Çelikçapa, S., & Doğan, M. (2004a). Sorption of acid red 57 from aqueous solution onto sepiolite. *Journal of Hazardous Materials*, B116, 135–145.
- Alkan, M., Demirbaş, Ö., & Doğan, M. (2004b). Removal of acid yellow 49 from aqueous solution by adsorption. *Fresenius Environmental Bulletin*, 13(11a), 1112–1121.
- Alkan, M., & Doğan, M. (2003). Adsorption kinetics of Victoria blue onto perlite. *Fresenius Environmental Bulletin*, 12(5), 418–425.
- Allen, S. J., & Koumanova, B. (2005). Decolourisation of water/wastewater using adsorption (Review). *J Univ Chem Technol Metall*, 40, 175–192.
- An, H., Yi, Q., Xiasheng, G., & Tang, W. Z. (1996). Biological treatment of dye wastewaters using an anaerobic system. *Chemosphere*, 33, 2533–2542.
- Annadurai, G. (2002). Adsorption of basic dye on strongly chelating polymer: batch kinetics studies. *Iranian Polymer Journal*, 11(4), 237–244.
- Annadurai, G., Juang, R. S., & Lee, D. J. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *Journal of Hazardous Materials*, B92, 263–274.
- Aslıhan, G., Savas, S., Sedat, B., & Ali, M. M. (2005). Adsorption and kinetic studies of cationic and anionic dyes on pyrophyllite from aqueous solutions. *Journal of Colloid and Interface Science*, 286, 53–60.
- Banat, I. M., Nigam, P., Singh, D., & Marchant, R. (1996). Microbial decolorization of textile-dye-containing effluents: A review. *Bioresource Technology*, 58, 217–227.
- Banerjee, S., & Dastidar, M. G. (2005). Use of jute processing wastes for treatment of wastewater contaminated with dye and other organics. *Bioresource Technology*, 96(17), 1919–1928.
- Batzias, F. A., & Sidiras, D. K. (2004). Dye adsorption by calcium-chloride treated beech sawdust in batch and fixed-bed systems. *Journal of Hazardous Materials*, B114, 167–174.
- Bhattacharyya, K. G., & Sharma, A. (2005). Kinetics and thermodynamics of methylene blue adsorption on *Neem* (*Azadirachta indica*) leaf powder. *Dyes and Pigments*, 65, 51–59.
- Bulut, Y., & Aydın, H. (2006). A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 194, 259–267.
- Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology*, 97, 1061–1085.
- Demirbaş, O., Alkan, M., & Dogan, M. (2002). The removal of Victoria blue from aqueous solution by adsorption on a low-cost material. *Adsorption*, 8, 341–349.
- Doğan, M., & Alkan, M. (2003a). Adsorption kinetics of methyl violet onto perlite. *Chemosphere*, 50, 517–528.
- Doğan, M., & Alkan, M. (2003b). Removal of methyl violet from aqueous solutions by perlite. *Journal of Colloid and Interface Science*, 267, 32–41.
- Doğan, M., Alkan, M., & Onganer, Y. (2000). Adsorption of methylene blue on perlite from aqueous solutions. *Water, Air and Soil Pollution*, 120, 229–248.

- Doğan, M., Alkan, M., Türkyılmaz, A., & Özdemir, Y. (2004). Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *Journal of Hazardous Materials, B109*, 141–148.
- Doğan, M., Özdemir, Y., & Alkan, M. (2007). Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. *Dyes and Pigments, 75*(3), 701–713.
- Ferrero, F. (2007). Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust. *Journal of Hazardous Materials, 142*, 144–152.
- Feryal, A. (2005). Adsorption of basic dyes from aqueous solution onto pumice powder. *Journal of Colloid and Interface Science, 286*, 455–458.
- Garg, V. K., Amita, M., Kumar, R., & Gupta, R. (2004). Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: A timber industry waste. *Dyes and Pigments, 63*, 243–250.
- German-Heins, J., & Flury, M. (2000). Sorption of brilliant blue FCF in soils as affected by pH and ionic strength. *Geoderma, 97*, 87–101.
- Ghoreishi, S. M., & Haghghi, R. (2003). Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent. *Chemical Engineering Journal, 95*, 163–169.
- Ghosh, D., & Bhattacharyya, K. G. (2002). Adsorption of methylene blue on kaolinite. *Applied Clay Science, 20*, 295–300.
- Gregory, A. R., Eliot, S., & Kluge, P. (1991). Ames testing of direct black 3B parallel carcinogenicity. *Journal of Applied Toxicology, 1*, 308–313.
- Guo, Y., Yang, S., Fu, W., Qi, J., Li, R., Wang, Z., et al. (2003). Adsorption of malachite green on micro- and mesoporous rice husk-based active carbon. *Dyes and Pigments, 56*, 219–229.
- Gupta, V. K., Suhas, A. I., & Saini, V. K. (2004). Removal of rhodamine B, fast green, and methylene blue from wastewater using red mud, an aluminum industry waste. *Industrial and Engineering Chemistry Research, 43*, 1740–1747.
- Gücek, A., Şener, S., Bilgen, S., & Mazmanlı, M. A. (2005). Adsorption and kinetic studies of cationic and anionic dyes on pyrophyllite from aqueous solutions. *Journal of Colloid and Interface Science, 286*, 53–60.
- Hall, K. R., Eagleton, L. C., Acrivos, A., & Vermeulen, T. (1966). Pore and solid diffusion kinetics in fixed bed adsorption under constant conditions. *Industrial & Engineering Chemistry Fundamentals, 5*, 212–219.
- Hamdaoui, O. (2006). Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. *Journal of Hazardous Materials, B135*, 264–273.
- Harris, O. P., & Ramelow, G. J. (1990). Binding of metal ions by particulate biomass derived from *Chlorella vulgaris* and *Scenedesmus quadricauda*. *Environmental Science and Technology, 24*(2), 220–224.
- Janos, P. (2003). Sorption of basic dyes onto iron humate. *Environmental Science and Technology, 37*, 5792–5798.
- Kapoor, A., Viraraghavan, T., & Cullimore, D. R. (1999). Removal of heavy metals using the fungus *Aspergillus niger*. *Bioresource Technology, 70*(1), 95–104.
- Kavitha, D., & Namasivayam, C. (2007). Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. *Bioresource Technology, 98*(1), 14–21.
- Legrouri, K., Khouyab, E., Ezzinea, M., Hannachea, H., Denoyelc, R., Pallierd, R., et al. (2005). Production of activated carbon from a new precursor molasses by activation with sulphuric acid. *Journal of Hazardous Materials, B118*, 259–263.
- Liakou, S., Pavlou, S., & Lyberatos, G. (1997). Ozonation of azo dyes. *Water Science and Technology, 35*, 279–286.
- Lorenc-Grabowska, E., & Gryglewicz, G. (2007). Adsorption characteristics of Congo Red on coal-based mesoporous activated carbon. *Dyes and Pigments, 74*, 34–40.
- Maurya, N. S., Mittal, A. K., Cornel, P., & Rother, E. (2006). Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH. *Bioresource Technology, 97*, 512–521.
- McKay, G., Otterburn, M. S., & Aga, D. A. (1985). Fullers earth and fired clay as adsorbent for dye stuffs, equilibrium and rate constants. *Water, Air, and Soil Pollution, 24*, 307–322.
- McKay, G., Otterburn, M. S., & Sweeney, A. G. (1980). *Water Research, 14*, 21–27.
- McMullan, G., Meehan, C., Conneely, A., Kirby, N., Robinson, T., Nigam, P., et al. (2001). Microbial decolourisation and degradation of textile dyes. *Applied Microbiology and Biotechnology, 56*, 81–87.
- Mittal, A. (2006). Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers. *Journal of Hazardous Materials, B133*, 196–202.
- Namasivayam, C., Kumar, M. D., & Begum, R. A. (2001). 'Waste' coir pith—a potential biomass for the treatment of dyeing wastewaters. *Biomater. Bioenerg., 21*, 477–483.
- Narine, D. R., & Guy, R. D. (1981). Interactions of some large organic cations with bentonite in dilute aqueous systems. *Clays Clay Miner, 29*, 205–212.
- Nassem, R., & Tahir, S. (2001). Removal of Pb(II) from aqueous/acidic solutions by using bentonite as an adsorbent. *Water Research, 35*, 3982–3986.
- Ozacar, M., & Sengil, I. A. (2005). Adsorption of metal complex dyes from aqueous solutions by pine sawdust. *Bioresource Technology, 96*, 791–795.
- Özdemir, Y., Doğan, M., & Alkan, M. (2006). Adsorption of cationic dyes from aqueous solutions by sepiolite. *Microporous and Mesoporous Materials, 96*(1–3), 419–427.
- Pavel, J., Pavel, S., Milena, R., & Sylvie, G. (2005). Sorption of basic and acid dyes from aqueous solutions onto oxihumolite. *Chemosphere, 59*, 881–886.
- Pearce, C. I., Lloyd, J. R., & Guthrie, J. T. (2003). The removal of colour from textile wastewater using whole bacterial cells: A review. *Dyes and Pigments, 58*, 179–196.
- Ravi Kumar, M. N. V., Sridhari, T. R., Bhavani, K. D., & Dutta, P. K. (1998). Trends in color removal from textile mill effluents. *Colorage, 40*, 25–34.
- Renmin, G., Yingzhi, S., Jian, C., Huijun, L., & Chao, Y. (2005). Effect of chemical modification on dye adsorption capacity of peanut hull. *Dyes and Pigments, 67*, 175–181.
- Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001). Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresource Technology, 77*, 247–255.

- Sampa, C., & Binay, K. D. (2005). On the adsorption and diffusion of methylene blue in glass fibers. *Journal of Colloid and Interface Science*, 286, 807–811.
- Sanghi, R., & Bhattacharya, B. (2002). Review on decolorisation of aqueous dye solutions by low cost adsorbents. *Coloration Technology*, 118, 256–269.
- Sarasa, J., Roche, M. P., Ormad, M. P., Gimeno, E., Puig, A., & Ovelleiro, J. L. (1998). Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation. *Water Research*, 32, 2721–2727.
- Schiewer, S., & Volesky, B. (1995). Modelling of proton–metal ion exchange in biosorption. *Environmental Science and Technology*, 29(12), 3049–3058.
- Shaobin, W., Zhua, Z. H., Anthony, C., Haghseresht, F., & Luc, G. Q. (2005). The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *Journal of Colloid and Interface Science*, 284, 440–446.
- Singh, K. P., Mohan, D., Sinha, S., Tondon, G. S., & Gosh, D. (2003). Color removal from wastewater using low-cost activated carbon derived from agricultural waste material. *Industrial and Engineering Chemistry Research*, 42, 1965–1976.
- Singh, D. K., & Srivastava, B. (1999). Removal of basic dyes from aqueous solutions by chemically treated Psidium Guyava leaves. *Indian Journal of Environmental Health*, 41, 333–345.
- Summers, R. S., & Roberts, P. V. (1988). GAC adsorption of humic substances II. Size exclusion and electrostatic interactions. *Journal of Colloid and Interface Science*, 122, 382–397.
- Sun, Q., & Yang, L. (2003). The adsorption of basic dyes from aqueous solution on modified peat-resin particle. *Water Research*, 37, 1535–1544.
- Tokiwa, F. (1983). *Surfactants* pp. 17–25. Tokyo, Japan: Kao Co.
- Tsai, W. T., Yang, J. M., Lai, C. W., Cheng, Y. H., Lin, C. C., & Yeh, C. W. (2006). Characterization and adsorption properties of eggshells and eggshell membrane. *Bioresource Technology*, 97(3), 488–493.
- Vadivelan, V., & Vasanth Kumar, K. (2005). Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *Journal of Colloid and Interface Science*, 286, 90–100.
- Wang, S., Boyjoo, Y., & Choueib, A. (2005). A comparative study of dye removal using fly ash treated by different methods. *Chemosphere*, 60(10), 1401–1407.
- Weng, C.-H., & Pan, Y.-F. (2006). Adsorption characteristics of methylene blue from aqueous solution by sludge ash. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 274, 154–162.
- Wu, F. C., Tseng, R.-L., & Hu, C.-C. (2005). Comparisons of pore properties and adsorption performance of KOH-activated and steam-activated carbons. *Microporous and Mesoporous Materials*, 80, 95–106.
- You, L., Wu, Z., Kim, T., & Lee, K. (2006). Kinetics and thermodynamics of bromophenol blue adsorption by a mesoporous hybrid gel derived from tetraethoxysilane and bis(trimethoxysilyl)hexane. *Journal of Colloid and Interface Science*, 300, 526–535.