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Full Length Research Paper

Methylene blue (cationic dye) adsorption into *Salvadora persica* stems ash

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Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood and silk. On inhalation, it can cause difficulty in breathing, while on direct contact, it may cause permanent injury of the eyes of human and animals, burning sensations, nausea, worming, profuse sweating, mental confusion and methemoglobinemia. In the present study, *Salvadora persica* stem ash was used as an adsorbent for the successful removal of methylene blue (MB) dye from aqueous solutions. The effect of various operating parameters such as initial concentration of dye (20 to 200 mg/L), contact time (5 to 270 min), adsorbent dosage (0.2 to 10 g/L) and pH (2 to 13) was investigated. The results of this study shows that the *S. persica* stem ash was able to remove up to 97% of MB dye from solutions with various initial dye concentrations at initial pH of 13. Also, the equilibrium data were also fitted to the Langmuir and Freundlich equilibrium isotherm models. It was found that the data fitted better to Freundlich ($R^2=0.9314$) than Langmuir ($R^2=0.8836$) model. Finally, it can be concluded that the *S. persica* stem ash can be used for textile industry wastewater treatment.

Key words: Methylene blue (MB), adsorption, *S. persica*, natural adsorbent.

INTRODUCTION

Environmental pollution has recently become a severe problem worldwide (Paul et al., 2011). Dyes are one of the most hazardous chemical compound classes found in industrial effluents and need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora (Royer et al., 2009; Lima et al., 2008). They are also aesthetically objectionable for drinking and other purposes (Royer et al., 2010) and can cause allergy, dermatitis, skin irritation (Brookstein, 2009) and also provoke cancer (Lima et al., 2007) and mutation in humans (Carneiro et al., 2010).

Methylene blue (MB) (a basic and cationic dye) is the most commonly used substance for dyeing cotton, wood and silk. On inhalation it can cause difficulty in breathing, while on the direct contact it may cause permanent injury

of the eyes of human, burning sensations, nausea, profuse sweating, mental confusion and methemoglobinemia (Ponnusami et al., 2008; Rafatullah et al., 2010).

Improper treatment and disposal of dye-contaminated wastewaters from textile, dyeing, printing, ink, and related industries have provoked serious environmental concerns all over the world (Allegre et al., 2006; Liu et al., 2006). Removal of dye in wastewater has been made by physical, physico-chemical, biological and/or chemical processes (Vijayaraghavan and Yun, 2008; Namasivayam and Kavitha, 2002). The conventional treatment process of textile effluents involves numerous stages due to the characteristics of the production process (Vandevivere et al., 1998). Conventional treatment involves a process of coagulation/flocculation. This is a versatile process, which can be used alone or combined with biological treatments, as a way of removing suspended solids and organic material, as well as promoting the extensive removal of dyes from textile

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industry effluents (Tunay, 1996; Anjaneyulu et al., 2005). However, this approach presents the disadvantage of generating a large volume of sludge. This sludge is rich in dyes, as well as other substances used in the textile process. This is a problem, as the waste must be discarded properly to avoid environmental contamination (Vandevivere et al., 1998). Also, biological treatment (Allegre et al., 2006), ozone treatment (Kusvuran et al., 2011), photocatalytic processes (Liu et al., 2006), membrane processes (Yu et al., 2010), nanoparticles (Mahvi et al., 2009) and enzymatic treatment (Gholami-Borujeni et al., 2011) were used for removal of dye from textile effluents. However, some of these methods are limited due to their high operational costs and problems.

The most efficient procedure for removal of synthetic dyes from industrial effluents is the adsorption procedure, because the dye species are transferred from the water effluent to a solid phase, diminishing the effluent volume to a minimum. Subsequently, the adsorbent can be regenerated or kept in a dry place without direct contact with the environment (Lima et al., 2008). Also, adsorption has proven to be a reliable treatment methodology due to its low capital investment cost, simplicity of design, ease of operation and insensitivity to toxic substances, but its application is limited by the high price of some adsorbents and the large amounts of wastewater normally involved. Activated carbon (Demirbas et al., 2008), biopolymers such as chitosan beads (Chiou and Li, 2002), quaternary chitosan (Rosa et al., 2008), and agricultural by-products (Wang et al., 2008; Cicek et al., 2007) are a few of the adsorptive materials that have been tested for the treatment of wastewaters.

In order to reduce preparation cost, the use of low cost starting materials (industrial or agricultural residues) for activated carbon preparation has emerged as a potential alternative (Bhatnagar and Sillanpaa, 2010). Besides the cost reduction, the conversion of agriculture waste in low cost adsorbents also added value to this residues and solve the problem of biomass disposal. Agricultural waste-based carbon has the advantage of exhibiting low ash content, reasonable hardness and high surface area and/or adequate porous structures (Liu et al., 2006; Bhatnagar and Sillanpaa, 2010). The choice of activated carbon precursor largely depends on its availability, cost, and purity, but the manufacturing process and intended applications of the product are also important considerations. Therefore, evaluation of biomass is getting increased attention over the world as it is renewable, widely available, cheap, and environmental friendly (Prahas et al., 2008).

Salvadora persica has wide geographic distribution ranging from Rajasthan (India), Nepal, and Malaysia in the east through Pakistan, Iran, Iraq, Saudi Arabia, and Egypt to Mauritania in the west, and from North Africa through Sudan, Ethiopia, and Central Africa to southwestern Africa (Wu et al., 2001). Young twigs and root-bark of *S. persica* have been used in folk

medicine for a very long time for the treatment of a wide range of conditions such as cough, asthma, scurvy, piles, rheumatism, leprosy, gonorrhoea, headaches and hepatic and other diseases. In this study, adsorption of MB from aqueous solutions on activated carbon prepared from *S. persica* stem was studied. The effects of different parameters including initial pH, adsorbent dosage, MB concentration, and contact time were studied. Additionally, the sorption isotherm was explored to describe the experimental data.

MATERIALS AND METHODS

Chemicals and reagents

MB is a cationic dye with molecular weight of 319.86 g/mol and maximum absorption (λ_{max}) of 665 nm. The MB ($C_{16}H_{18}ClN_3S$) used in this work was of analytical grade (Merck, Germany). The chemical formula of MB is shown in Figure 1 (Wang et al., 2005). For the treatment experiments, the dye solutions with concentrations in the range of 20 to 200 mg/L were prepared by successive dilution of the stock solution (1000 mg/L) with distilled water. All other chemicals used in this study were of analytical grade.

Adsorbent preparation

The stems of *S. persica* were obtained from Persia commercial sources in Iran. This natural adsorbent were firstly washed with distilled water to remove impurity such as sand and leaves and soluble and colored components, dried at 110°C for 12 h, burned at 700°C for 2 h, crushed in a domestic grinder and sieved to obtain particle size in the range of 60-200 mesh (Bazrafshan et al., 2012). The powdered adsorbent was stored in an airtight container until use. No other chemical or physical treatments were used prior to adsorption experiments.

Dye removal experiments

Dye removal experiments with the *S. persica* stem ash were carried out as batch tests in 250 mL flasks under magnetic stirring. Each test consisted of preparing a 100 mL of dye solution with a desired initial concentration and pH by diluting the stock dye solution with distilled water, and transferring it into the beaker on the magnetic stirrer. The pH of the solution was adjusted using 0.1N HCl or NaOH solutions. A known mass of *S. persica* stem ash (adsorbent dosage) was then added to the solution, and the obtained suspension was immediately stirred for a predefined time. After the desired contact time, the samples were withdrawn from the mixture by using a micropipette and centrifuged for 5 min at 4000 rpm. After centrifugation, supernatants were analyzed for the determination of the final concentration of MB by using an UV-VIS spectrophotometer (T80 PG Instruments Ltd) set at a wave-length of 665 nm; maximum absorbance. Then, the amount of MB adsorbed, q_e (mg/g), was obtained as follows:

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

Where, C_0 and C_e are the initial and equilibrium liquid phase concentration of MB (mg/L), respectively; V is the volume of the

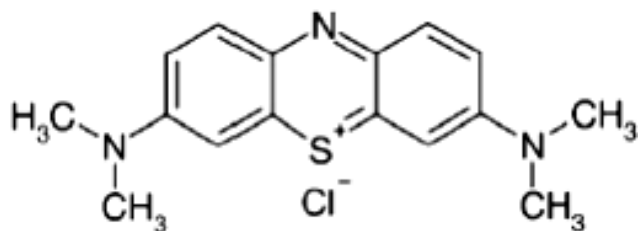


Figure 1. Structure of methylene blue (MB) (Wang et al., 2005).

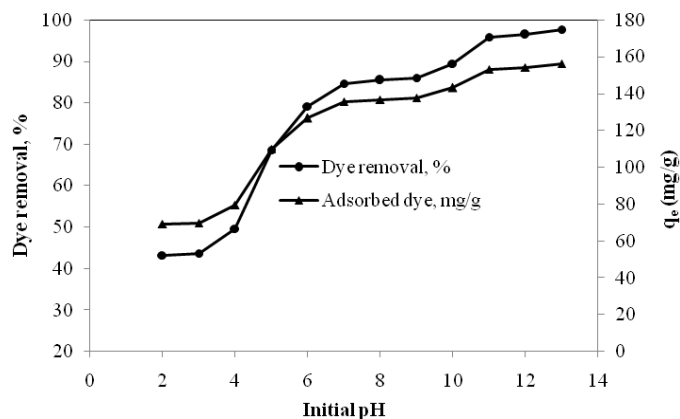


Figure 2. Effect of initial pH on MB adsorption by *S. persica* stem ash (initial dye concentration, 80 mg/L; adsorbent dosage, 5 g/L, time, 60 min; temperature, 20°C).

solution (L) and M is the amount of adsorbent used (g). To express the percent of dye removal, the following equation was used:

$$\% = \frac{(C_0 - C_f)}{C_0} \cdot 100 \quad (2)$$

Where, C_0 and C_f represent the initial and final (after adsorption) dye concentrations, respectively. All tests were performed in duplicate to insure the reproducibility of the results; the mean of the two measurements is reported. All experiments were performed at room temperature. The investigated ranges of the experimental variables were as follows: dye concentration (20 to 200 mg/L), pH of solution (2 to 13), *S. persica* stem ash dosage (0.2, 0.5, 1, 3, 5, 7, 9, 10 g/L) and mixing time (5 to 270 min).

RESULTS AND DISCUSSION

Effect of initial pH

It is known that the solution pH can affect the surface charge of the adsorbent, the degree of ionization of the different pollutants, the dissociation of functional groups on the active sites of the adsorbent as well as the structure of the dye molecule (Ai et al., 2011). The solution pH would affect both aqueous chemistry and

surface binding-sites of the adsorbent. So, the solution pH is an important parameter during the dye adsorption process.

In this study, the effect of pH on the MB adsorption capacities of the *S. persica* stem ash were conducted at varying pH (pH 2 to 13) with 80 mg/L fixed initial dye concentrations and adsorbent dosage of 5.0 g/L for 60 min. As seen in Figure 2, when the pH increased, adsorbed MB also increased. On the other hand, the adsorption of MB dye into *S. persica* stem ash was intimately dependent on pH solution. It could be seen that the uptake of MB increased with increasing pH from 2 to 13 until equilibrium was obtained. The maximum adsorption was found to be 156.22 mg/g (97.64%) for MB at pH 13. Similar results have also been reported by other researchers (Anbia and Hariri, 2010; Yu et al., 2010; Ertas et al., 2010).

It had been reported that the biosorbent interact with the cationic dyes mainly through electrostatic, hydrogen bonding and van der Waals interactions (Das et al., 2006). At low solution pH, the high concentration of H^+ ions promoted the protonation of the functional groups, and thus the sorbents became more positively charged, which inhibits the sorption of the cationic dyes on it. On the other hand, excess H^+ ions would compete with cationic dye molecules for the sorption sites. So the adsorption capacity of the biosorbents decreased greatly at low solution pH. When the solution pH increased, the number of positively charged available sites decreased, meanwhile the number of the negatively charged sites increased. The surface of sorbents became more negatively charged, which improved the interaction between the sorbents and the cationic dye molecules. Therefore, the adsorption capacity of the sorbents increased at higher pH value (Yu et al., 2010).

Effect of adsorbent dosage

...n sites remain unsaturated during the sorption whereas the number of sites available for sorption site increases by increasing the adsorbent dose. The maximum adsorption efficiency of MB into *S. persica* stem ash was found to be 97.24% (11.11 mg/g) at adsorbent concentration of 7 g/L (Figure 3). There was a non significant increase in the percentage removal of MB when the adsorbent concentration increases beyond the 3 g/L, hence adsorbent dosage 3 g/L was selected as optimum dose of adsorbent. This suggests that after a certain dose of biosorbent, the maximum adsorption is attained and hence the amount of pollutants remains constant even with further addition of dose of adsorbent (Chakravarty et al., 2010). Also, when the adsorbent dosage increased, percentage removal of MB also increased but amount of adsorbed MB of per gram adsorbent decreased due to the fact that fixed dye concentration (80 mg/L) led to unsaturated active site on adsorbent surface and increase in the adsorbent

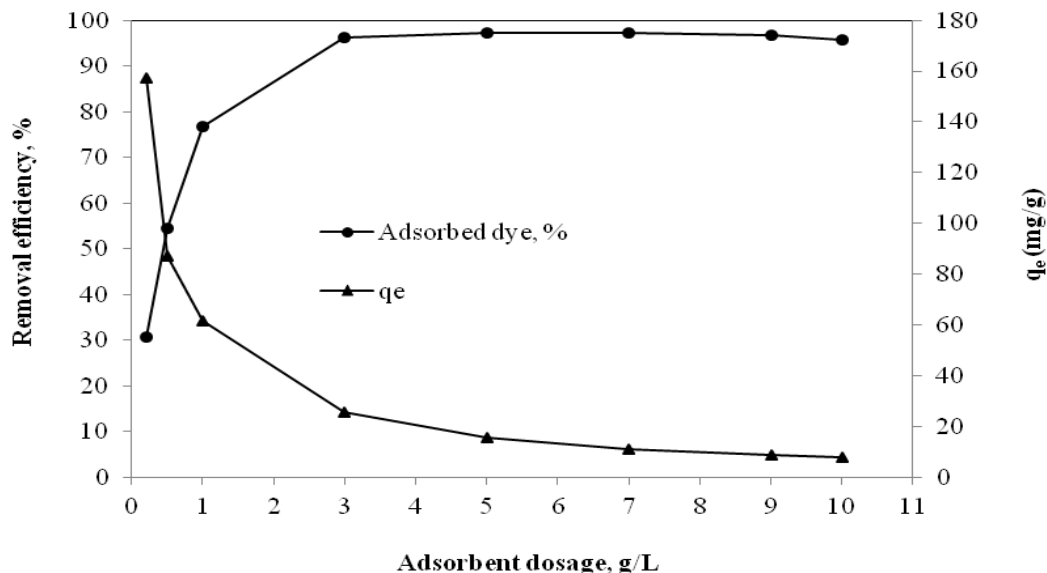


Figure 3. Effect of adsorbent dosage on MB adsorption by *S. persica* stem ash (initial dye concentration: 80 mg/L, pH 11, time: 60 min, temperature: 20°C).

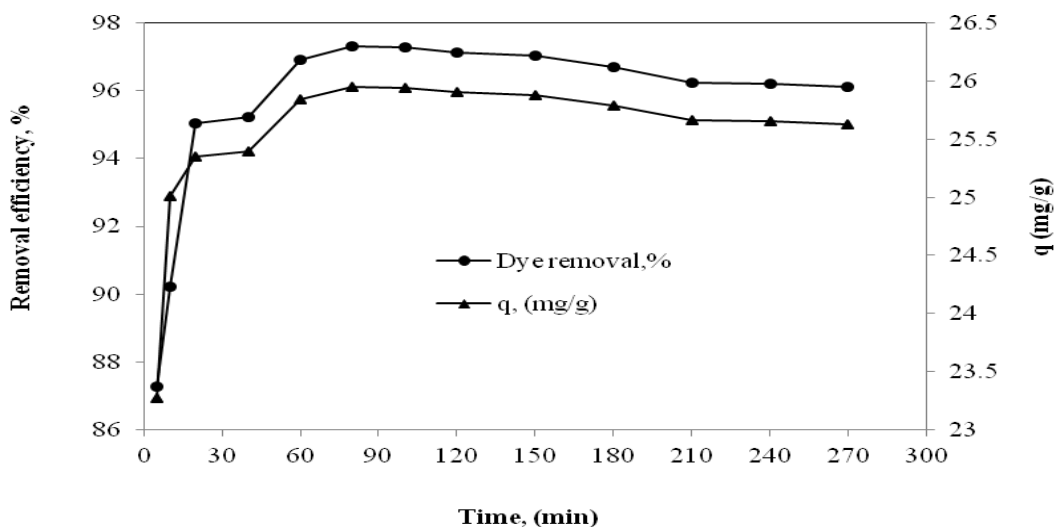


Figure 4. Effect of contact time for the adsorption of MB by *S. persica* stem ash (initial dye concentration: 80 mg/L, pH 11, time: 60 min, temperature: 20°C).

concentrations caused particle aggregation (Calvete et al., 2009).

Effect of contact time

The contact time is one of the most important parameters for practical application. The effects of contact time on adsorption were studied at 20°C, initial dye concentration of 80 mg/L and 3 g/L adsorbent dosage for 5 to 270 min. Figure 4 shows the effect of contact time on the

adsorption capacity and percent removal of MB dye by *S. persica* stem ash at a constant initial concentration. The adsorption capacity and percent removal of MB dye by *S. persica* stem ash considerably increased during the initial adsorption stage and then continued to increase at a relatively slow speed with contact time until a state of equilibrium was attained after 80 min. The maximum adsorption efficiency of MB by *S. persica* stem ash was found to be 97.31% (25.95 mg/g) at contact time of 80 min. Hence, in the present work, 80 min was chosen as the equilibrium time. Generally, the removal rate of

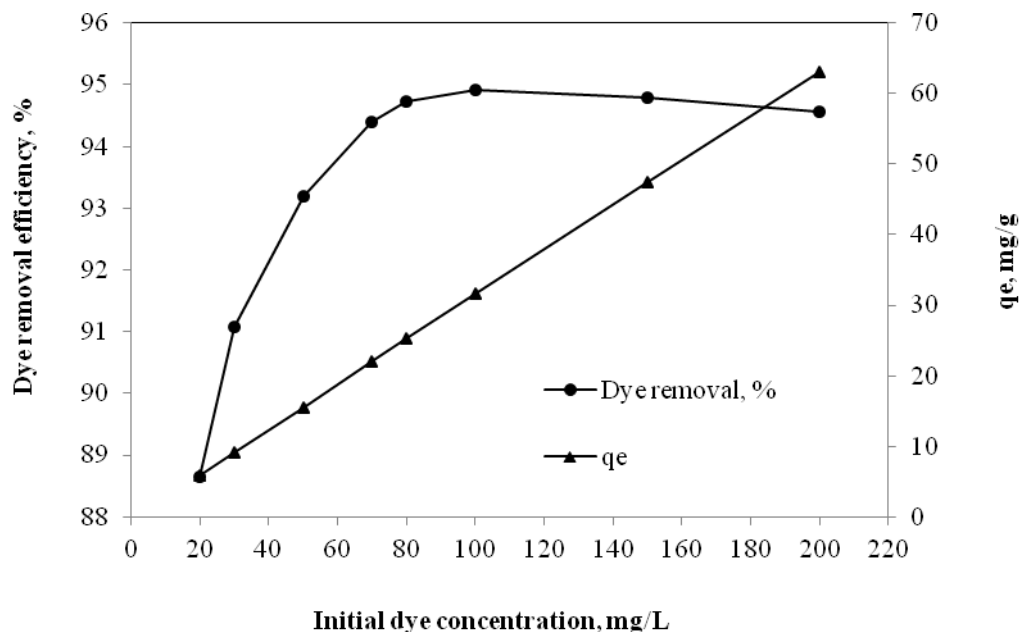


Figure 5. Effect of initial MB dye concentration for the adsorption of MB into *S. persica* stem ash (pH 11.0; adsorbent dosage, 3 g/L; time, 80 min).

sorbate was rapid initially, but it gradually decreased with time until it reached equilibrium. This phenomenon is attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. A similar finding was reported by Cengiz and Cavas (2008).

Effect of initial MB dye concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases (Anbia and Hariri, 2010). The effects of initial dye concentration on adsorption were studied at 20°C and 3 g/L adsorbent concentrations for 80 min. As seen in Figure 5, when the initial dye concentration increased, the amounts of adsorbed dye also increase, so the removal of dye depends on the concentration of the dye. For example, when the initial MB concentration increases from 20 to 200 mg/l, the equilibrium sorption capacities of *S. persica* stem ash increase from 5.91 (88.64%) to 63.04 mg/g (94.56%). Similar trends have also been observed for MB sorption into bamboo-based activated carbon (Hameed et al., 2007), cotton waste (Ertas et al., 2010) and fly ash (Basava and Ram Mohan, 2006). This increase in the proportion of removed dye may be probably due to equilibrium shift during sorption process. A similar result has also been recorded for adsorption of Congo red from

aqueous solution onto calcium-rich fly ash (Acemioglu, 2004).

The initial dye concentrations provide an important driving force to overcome the mass transfer resistance of the dye between the aqueous phases and the solid phases, so increasing initial concentrations would enhance the adsorption capacity of dye. These results is in accordance with the obtained findings by other researchers (Anbia and Hariri, 2010; Cengiz and Cavas, 2008).

Adsorption isotherms

Isotherms study can describe how an adsorbate interacts with adsorbent. The isotherm provides a relationship between the concentration of dye in solution and the amount of dye adsorbed on the solid phase when both phases are in equilibrium. Figures 6 and 7 show the equilibrium isotherms for the adsorption of MB dye by *S. persica* stem ash, and the equilibrium adsorption data were analyzed by using the Langmuir and Freundlich isotherm models.

The Langmuir isotherm model is valid for monolayer adsorption onto surface containing finite number of identical sorption sites which is presented by the following equation:

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e} \quad (3)$$

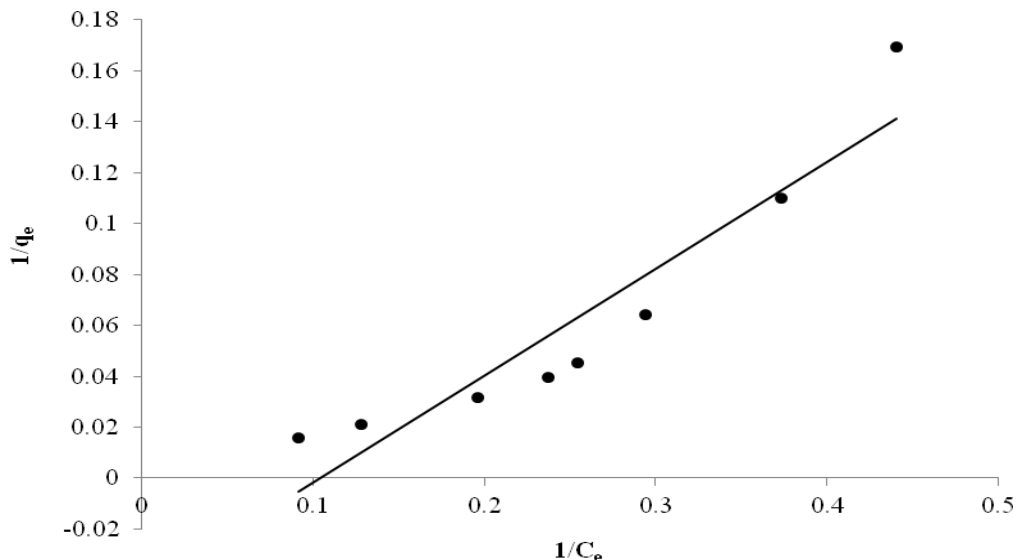


Figure 6. Langmuir isotherm for sorption of MB into *S. persica* stem ash (R²=0.8836).

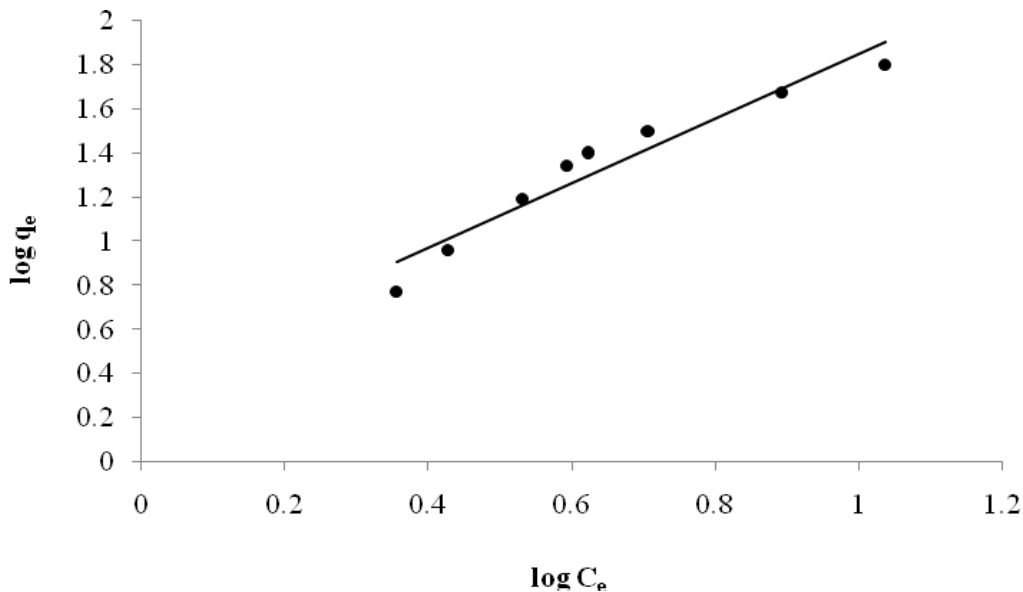


Figure 7. Freundlich isotherm for sorption of MB onto *S. persica* stem ash (R²=0.9314).

Where, q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), C_e is the equilibrium concentration of the solution (mg/L) and q_m is the maximum amount of MB dye required to form a monolayer (mg/g). The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants (K_L) and maximum monolayer adsorption capacity of *S. persica* stem ash (q_m). The values of q_m and K_L can be

determined from the linear plot of $1/q_e$ versus $1/C_e$:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \tag{4}$$

The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly described by the following equation:

Table 1. Isotherm parameters for adsorption of MB onto *S. persica* stem ash at 20°C.

Langmuir isotherm			Freundlich isotherm		
q_m (mg/g)	K_L (L/mg)	R^2	k_f	n	R^2
22.78	0.104	0.8836	2.42	0.68	0.9314

$$q_e = K_f C_e \frac{1}{n} \quad (5)$$

Where, K_f and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich equilibrium constants were evaluated from the intercept and the slope, respectively of the linear plot of $\log q_e$ versus $\log C_e$ based on experimental data. The Freundlich equation can be linearized in logarithmic form for the determination of the Freundlich constants as shown:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

The isotherms based on the experimental data and the parameters obtained from nonlinear regression by both models are shown in Figures 6 and 7. Also, all of the parameters are listed in Table 1. The correlation coefficient of the Freundlich model was higher than that of the Langmuir model, indicating that the Freundlich model is suitable for describing the adsorption equilibrium of MB dye by *S. persica* stem ash. As mentioned earlier on, K_f is the equilibrium constant indicative of adsorption capacity and higher K_f means that the adsorption capacity was bigger. Also, as noted above, the parameter K_L is a function of the strength of adsorption. The larger K_L means that the adsorption bond was stronger.

Conclusions

Methylene blue dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, profuse sweating, mental confusion and methemoglobinemia. Therefore, the treatment of effluent containing such dye is of interest due to its esthetic impacts on receiving waters.

From the present study, it can be seen that the *S. persica* stem can be used effectively for the removal of the MB dye from aqueous solutions. The percentage eliminated was found to depend on the amount of adsorbent, the initial concentration of dye and contact time. The *S. persica* stem was able to remove up to 97% of MB dye from solutions whose initial concentration

varied between 20 to 200 mg/L. The adsorption of MB dye on *S. persica* stem was described by the Langmuir and Freundlich isotherm. The removal of the dye from aqueous solutions was induced by adsorption on surface sites of the solid for low MB dye concentration while both adsorption and internal exchange took place for high concentrations.

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