American Journal of Environmental Sciences

Original Research Paper

Investigation of Methylene Blue Dye Adsorption from Polluted Water Using *Oleander* Plant (*Al Defla*) Tissues as Sorbent

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Article history
Received: 05-03-2016
Revised: 30-05-2016
Accepted: 04-06-2016

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Abstract: The main purpose of this research was to investigate the ability of *Oleander* plant (*Al Defla*) tissues to adsorb Methylene Blue (MB) dye from polluted water. The experiments were carried out through batch-adsorption technique to investigate the influence of the following experimental parameters on adsorption process namely, adsorbent quantity, MB initial concentration, adsorbent particles size, ionic strength, pH and temperature. The observation indicated an ability of the plant tissues to adsorb MB from water. Adsorption of Methylene Blue was increased on increasing the temperature, pH, adsorbent amount and the initial dye concentration factors. While it decreases with increase of salt concentration and increase of the adsorbent particles size. Plant fruit clusters are more likely to adsorb MB dye from water than leaves. Langmuir and Freundlich isotherms were used to model the adsorption data, which was fitted with these models. The isotherms parameters indicated that the adsorption was monolayer physical process.

Keywords: Methylene Blue Dye, Adsorption, Polluted Water, *Oleander* Plant, Langmuir and Freundlich Isotherms

Introduction

Water pollution is considered one of the early and important research field that interest researchers. It is not surprising that the volume of research in the field of water pollution is much bigger than other research areas of contamination.

Pollution of water due to discharging colored effluents from textile, printing, dying and other industries presents a major environmental problem due to their adverse health effects on living organisms. Therefore, many conventional techniques were developed for treatment of polluted water to remove dying pollutants such as: Chemical coagulation, membrane separation, electrolysis, ion exchange, activated carbon adsorption, Liquid-Liquid extraction and biological treatments (Khraisheh *et al*., 2004; Muthuraman *et al*. 2009; Sharma *et al*., 2011; Geçgel *et al*., 2013; Reddy *et al*., 2013; Zhang *et al*., 2015). Most of these techniques are not feasible on large scale and have economic disadvantage. By far, the adsorption technique is the most widely and versatile used. The efficiency of the adsorption process generally depends on removal capacity, removal efficiency, rate of adsorption and the cost of adsorbent used (Sharma *et al*., 2010; Gupta *et al*., 2011). Many researchers are searching for new, cheap and easily available resources for removal of dye effluents from water. Agricultural waste materials are receiving much attention nowadays due to high availability and low cost. Many biosorbent materials have been used to remove dye effluents from water such as: Pea shells, buriti shells, ground nut shell, sawdust, potato plant wastes, coconut shells, almond shell, wheat husk, cotton stalk …etc. (Deng *et al*., 2011; Gupta *et al*., 2011; Geçgel *et al*., 2013; Pezoti *et al*., 2014; Markovic *et al*., 2015).

Deep blue solution is formed when Methylene Blue dye (MB) dissolved in water. MB is used in hair temporary coloring, coloring paper, dyeing wools and cotton. It is considered as toxic dye and has adverse health effects on human and animals (Rafatullah *et al*., 2010; Deng *et al*., 2011; Wong *et al*., 2013).

Methylene Blue (MB) is a basic ionic thiazine dye heterocyclic compound with molecular formula $C_{16}H_{18}N_3SCl$. However, the presence of MB dye in wastewater is undesirable and its removal is very important. Adsorption technique using activated charcoal for removal of dyes is well known and found to be superior and efficient by many researchers. However, there is disadvantage for this process that its cost and the regeneration of activated carbon is costly (Lee and Ong, 2014). For this reason, there is growing search for an alternative low-cost sorbent to the activated carbon.

*Oleande*r plant known locally as *Al Defla* in Jordan and known in ancient texts as "*the desert rose*" is an evergreen plant that belongs to the family *Apocynaceae* (Langford and Boor, 1996; Graeme, 2011). It grows thick, green in mountainous climates, naturalized to almost all continents in the world and highly used in roadsides, parks and landscapes in tropical and subtropical climates. *Oleander* plant is considered one of the very poisonous garden plants and its raw extract is highly toxic (Wasfi *et al*., 2008). Despite of this, oleander can be used in the pharmaceutical industry for the production of various remedies (Adam *et al*., 2001). The plant leaves are 5-21 cm long dark green, thick and in pairs or whorls of three. The fruits are narrow capsules of 5-23 cm long, which on ripen split to release the seeds.

The use of *oleander* plant fruit clusters and leaves as sorbents for the removal of methylene blue from aqueous solution were not found in the literature so far. Therefore, the main purpose of this research was to study the possibility of utilizing *oleander* plant tissues (leaves and fruit clusters) as economically convenient and easily obtainable sorbent material for removing methylene blue from wastewater. The study has investigated the influence of initial MB concentration, adsorbent material quantity, adsorbent material size, ionic concentration, pH of the medium and temperature as influencing factors on the adsorption process.

Materials and Methods

Preparation of Adsorbent Plant Samples

The following steps were followed for the preparation of adsorbent plant samples:

- Mature healthy plant samples that did not show any presence of parasites were collected during the month of November
- Leaves and fruit clusters were separated and washed separately with normal clean tap water first and then with distilled water and finally were rinsed with deionized water to remove any sediment particles that may be attached to the plant tissue surfaces
- Fruit clusters and leaves were first air dried for five days and then were kept overnight in an oven at 50°C until constant weight is reached
- Fruits and leaves were grounded separately into powder and sieved through proper mesh to obtain experimental particle size range of 0.125-1.00 mm. The samples were stored in clean 250 mL plastic jars to be used later in the experiments

Chemicals

Methylene Blue (MB) as model cationic dye, potassium chloride (KCl), hydrochloric acid (HCl), sodium hydroxide (NaOH), acetic acid (CH_3COOH) and sodium acetate (NaOAc) were purchased from Sigma-Aldrich company and were used without purification.

Preparation of Solutions

Preparation of MB Dye Solutions

One-liter stock solution was prepared by dissolving 1.0 g of MB solid powder in double distilled water. The required experimental solutions were prepared by diluting the stock solution using distilled water. The concentration of MB dye solution was determined at λ_{max} = 668 nm (Nasuha and Hameed, 2011; Geçgel *et al*., 2013).

Preparation of Ionic Salt Solutions

Different solutions of KCl were prepared with concentrations of 1.0, 0.7, 0.4 and 0.2 M.

Preparation of Buffer Solutions

Three buffer solutions with pH = 1.0, 4.5 and 6.2 were prepared using appropriate salts and acids.

Instrumentation

Shimadzo double beam UV-visible spectrophotometer (model UV 1601), pH-Meter Metrohm with uncertainty value of ±0.01, digital electronic balance of ±0.0001 uncertainty and HP Tabletop Orbital Shaker (Thermo Scientific) were used in this study.

Calibration Curves

Calibration curve for different concentrations (1, 3, 5, 7 and 10 ppm) of MB dye solutions were recorded at constant temperature (25°C) with distilled water as a blank solution.

Adsorption Studies Procedures

The experimental part for adsorption studies of the plant tissues have been divided into two parts:

- Studying the ability of *oleander* dried fruit clusters to adsorb MB from polluted water
- Studying the ability of *oleander* dried leaves to adsorb MB from polluted water

Experiments of batch adsorption model were performed to investigate the influence of the following six experimental factors on MB dye adsorption process: (i) Adsorbent material amount, (ii) initial MB dye concentration, (iii) adsorbent particles size, (iv) salt concentration, (v) pH of the medium and (vi) temperature. The investigation was carried out by keeping all factors constant and varying the parameter under investigation only. The adsorption experiments were conducted in constant 250 mL volume of dye solution placed in 250 mL stoppered conical flasks. To study the influence of each factor we used 0.30 g fruit clusters or leaves powder of (0.125-0.250 mm) particle size, MB dye concentration of 5 ppm, pH of the solution was natural without adjustment and temperature was kept constant at 25°C (i.e., room temperature to be representative of environmentally relevant condition) were selected as experimental factors. The resulting solution mixture was agitated at constant rate every five minutes using tabletop orbital shaker. The absorbance changes of MB dye was recorded at the specified time intervals at the characteristic wavelength (λ_{max} = 668 nm) of maximum absorbance using UV-Visible spectrophotometer. All the experiments were repeated three times and the mean values were used for further calculations. The amount of MB dye adsorbed on the adsorbent surface was computed using mass-balance procedure.

Adsorption Equilibrium Experiments

Calibration curves were obtained using standard MB solutions and the amount adsorbed was calculated using mass-balance procedure. Concentrations were calculated using Beer-Lambert law plot.

Adsorption experiments for equilibrium studies were carried out using batch adsorption technique by using 0.3 g of the powder adsorbent material with particle size of (0.125-0.25 mm). They were placed in four different stoppered 250 mL conical flasks and MB dye solution (250 mL) of different initial concentrations (3, 5, 7 and 9 ppm). The experimental conditions pH was adjusted at 7.0 the natural pH value without adjustment and temperature was kept constant at (25°C) room temperature to be representative of environmentally relevant condition. The flasks were shaken at equal intervals and constant rate. The investigation was carried out for a time of 210 min to ensure the establishment of equilibrium. Samples of MB dye solution were withdrawn at regular intervals for the remaining dye analysis.

The adsorption capacity and residual concentration remains in the aqueous solution data were used in Langmuir and Freundlich isotherm models investigations.

Results and Discussion

Study of the Adsorption Ability of Oleander Plant (Al Defla) Fruit Clusters to Adsorb MB Dye from Polluted Water Solution

This study was carried out at six experimental sets to investigate the influence of the following factors on fruit clusters of *oleander* plant to adsorb MB dye from polluted water: Adsorbent amount, initial MB dye concentration, adsorbent particles size, salt ionic strength, the medium pH and temperature.

Effect of Adsorbent Material (Fruit Clusters) Amount

The adsorption of MB dye was investigated by changing adsorbent material (i.e., fruit clusters) quantity (in particular 0.10, 0.30, 0.50, 0.70, 0.80, 0.90 and 1.00 g) and keeping the following values constant: MB dye initial concentration (5 ppm), pH = 7.0, adsorbent particles diameter (0.125-0.250 mm) and temperature (25°C). The observations for the change in absorbance quantity using UV-visible spectrophotometer were recorded at intervals of 0, 30, 60, 90, 150 and 210 min and then after 24 h and finally after 48 h. The results (Fig. 1) show that when the sorbent amount increases from 0.10 to 0.80 g the percentage of MB dye removal by *Oleander* fruit clusters increases from 40.20 to 69.52%. While, when sorbent amount increases from 0.80 to 1.0 g the removal percentage decreases from 69.52 to 68.43%. The increase in MB dye removal at the beginning may be attributed to the increase in the surface area and the presence of more adsorption sites (Sharma *et al*., 2010; Liu *et al*., 2011). While, the decrease in removal percentage at the end when increasing sorbent amount may be explained as the dye molecules with the same concentration are more shared per unit sorbent because of the increase in total sorbet surface, causing less unit sorption (Ertas *et al*., 2010).

Effect of Initial MB dye Concentration on Adsorption Process

To investigate the influence of the initial concentration of MB dye on the removal of the MB dye by *oleander* plant fruit clusters, the experiments were carried out at a temperature of 25°C, pH = 7.0 and adsorbent weight of 0.3 g. Moreover, MB dye solution (250 mL) with concentrations of 3, 5, 7 and 9 ppm were used in each flask. Then, the change in absorbance for each solution using UV-visible spectrophotometer was followed. Figure 2 represent the results obtained and show that on using MB dye concentration of 3, 5, 7 and 9 ppm the removal percentage was 51.98, 58.87, 60.17 and 74.31% respectively. These observations indicate that on increasing the initial concentration there is an increase in the removal percentage. This can be attributed to the initial MB dye concentration with high number of MB dye molecules provide the driving force to overcome the resistance to the mass transfer of MB dye between the aqueous and solid phases (Sharma *et al*., 2010).

The increase in initial concentration also enhances the interaction between adsorbent and MB dye which leads to enhance the adsorption uptake of the MB dye. These observations were similar to other studies used other plant materials for removal of methylene blue from aqueous solution (Sharma *et al*., 2010; Ertas *et al*., 2010).

The maximum MB dye removals by fruit clusters occurred nearly at 120 min under experimental conditions. After 120 min, the amount of MB dye adsorbed was very slight. Therefore, at this time, a saturation state was reached and it was assigned as an equilibrium time.

Effect of Fruit Cluster's Particles Size on Adsorption of MB Dye

In this experiment different particle size (0.125-0.25 mm), (0.50-1.00 mm) and (> 1.00 mm) of *Oleander* fruit clusters were used and keeping all other factors (sorbent amount (0.3 g), MB dye initial concentration (5 ppm) and temperature 25°C) constant. The change in MB dye absorbance was observed during a period of 200 min at different intervals for each flask. The results show that on using smaller particle size of the fruit clusters, the adsorption quantity increases (Fig. 3). This can be explained as on using smaller particles size the exposed area of adsorbent material increases and hence increasing the efficiency and capacity of MB dye adsorption.

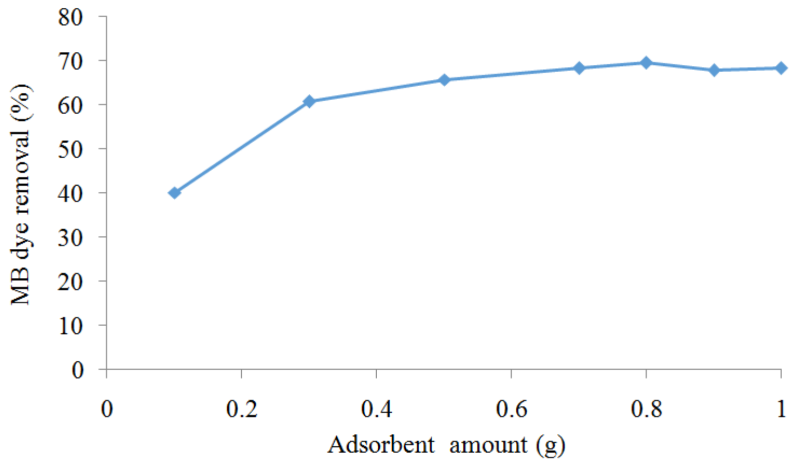

Fig. 1. Effect of adsorbent (fruit clusters) amount on removal of MB dye (pH = 7.0, C_i = 5 ppm, adsorbent particles diameter (0.125-0.250 mm), temp. = 25°C, time = 210 min.)

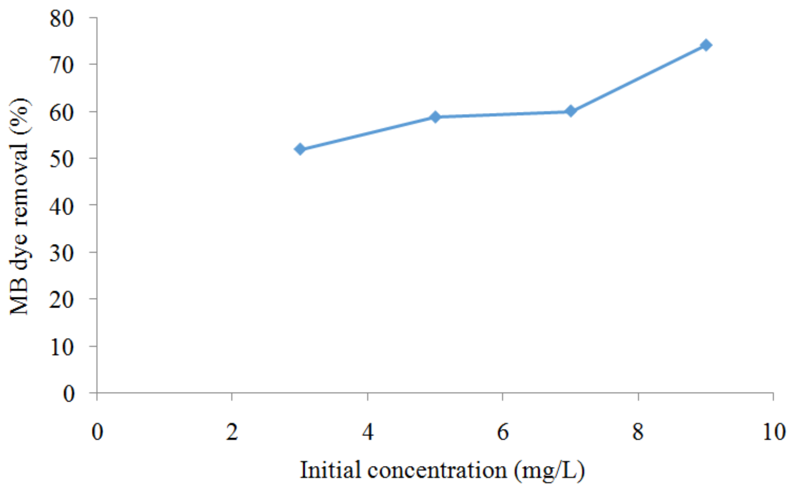

Fig. 2. Effect of initial MB dye concentration on removal of MB dye (pH = 7.0, adsorbent dose = 0.3 g, temp. = 25°C, time = 120 min.)

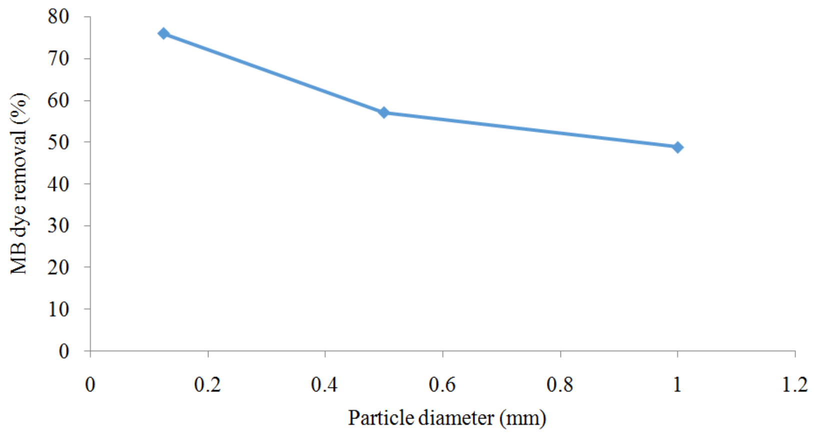

Fig. 3. Effect of adsorbent (fruit clusters) particle size on removal of MB dye (pH = 7.0, C_i = 5 mg L^{-1}, temp. = 25°C, adsorbent dose = 0.3 g, time = 210 min.)

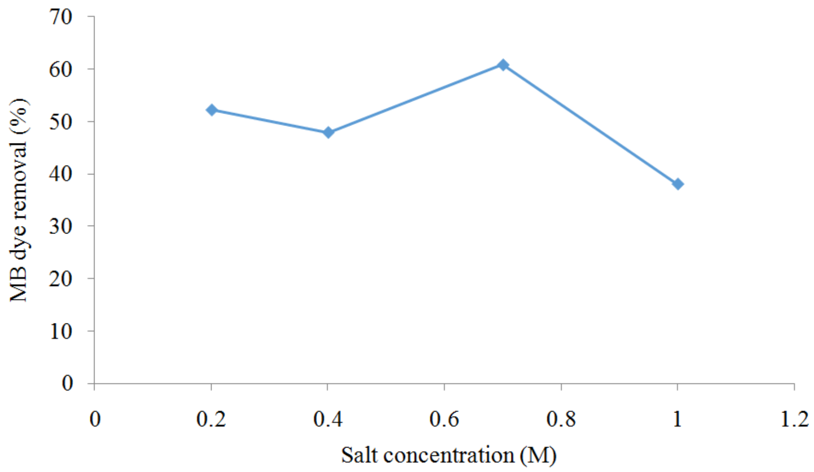

Fig. 4. Effect of salt concentration (M) on removal of MB dye (pH = 7.0, C_i = 5 mg L^{-1}, temp. = 25°C, adsorbent dose = 0.3g, time = 210 min.)

Influence of Ionic Strength on Adsorption of MB Dye

The wastewater commonly contain salts that makes it necessary to study the influence of ionic strength on MB dye adsorption. Effect of salt concentration has been studied using various concentrations of potassium chloride (i.e., 0.2, 0.4, 0.7 and 1.0 *M*) in MB dye solution and keeping other factors constant. The change in MB dye adsorption was observed at different intervals for a period of 210 min for each solution (Fig. 4). The results indicated that the presence of ionic salts in the solution of MB dye reduces the ability of *Oleander* fruit clusters to adsorb the dye from polluted water solution. It is observed that the adsorption was higher in case of using distilled water without any ions. This can be explained due to the presence of K^+ ions from the salt which competes with the MB dye positive ions for the sites available for adsorption (Gupta *et al*., 2011). As the ionic strength increases the repulsion forces between the positively charged K^+ and the MB dye cations and hence decreasing the adsorption efficiency of MB dye by the *Oleander* fruit clusters.

On comparing the four solutions containing different concentrations of KCl, It was observed that the adsorption was higher in case of the solution with 0.7 M KCl concentration throughout the study period. In case of the other three solutions containing 0.2, 0.4 and 1.0 M KCl, it was observed that on increasing the salt concentration the adsorption ability of *Oleander* fruit clusters decreases (Fig. 4). This is may be due to the presence of common ionic effect phenomena because of the chloride ion from the KCl and that of the chloride ion of partial negative charge on MB dye. The common ion effect reduces the solubility of MB dye and suppresses the degree of dissociation.

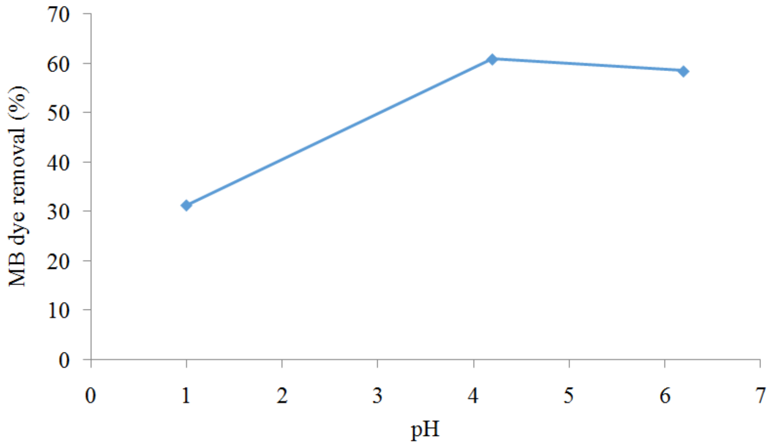

Fig. 5. Effect of the medium pH on removal of MB dye (C_i = 5 mg L^{-1}, temp. = 25°C, adsorbent dose = 0.3 g, time = 210 min.)

Effect of pH on Adsorption of MB Dye

The pH value is very important parameter that must be taken into consideration during adsorption investigations. pH value influences the ionization and solubility of MB dye and hence the adsorption of the MB dye onto the used adsorbent material. Also, the pH changes the charge of the sorbent material surface which become positive at low pH value (i.e., acidic medium) and negative at high pH value (i.e., basic medium) (Ertas *et al*., 2010). To investigate the influence of pH factor on the MB dye removal ability of the *Oleander* fruit clusters, we used three acidic buffer solutions with a pH of 1.0, 4.5 and 6.2. The absorbance was recorded at different intervals during a period of 210 min for each solution. The results of the study are shown in Fig. 5. The observations showed that the presence of acids in the dye solution reduces the ability of *Oleander* fruit clusters to adsorb MB dye. This can be attributed to the existence H^+ ions in excess in the solution and hence the surface of adsorbent becomes positive. The high concentration of H^+ ions on the adsorbent surface compete with MB dye cations having positive charge (through electrostatic repulsion forces) for the free vacant adsorption sites and due to this the MB dye uptake will decrease (Gupta *et al*., 2011). It is also found that the maximum adsorption of MB dye was found at neutral medium (pH = 7.0).

Influence of Temperature on Adsorption of MB Dye

To study the influence of solution temperature on the adsorption ability of *Oleander* fruit clusters, we have conducted different set of experiments at different temperatures i.e., 10°C, 20°C, 30°C and 40°C using water bath to control the temperature. The MB dye adsorption was recorded at different intervals during a period of 180 min for each experiment at each temperature. The initial concentration of MB dye (5 ppm), adsorbent weight 0.3 g and pH of 7.0 were kept constant. The results shown in Fig. 6 indicated that the increase in temperature increases the ability of fruit clusters to adsorb MB dye from water solution. This proves that the adsorption process takes place here is an endothermic (Ertas *et al*., 2010). The tendency to increase the MB dye adsorption on increasing temperature may be due to the increase of the mobility and the kinetic energy of the large MB dye ions which increases collision with the surface of the adsorbent material and leads to more sorption of MB dye on the surface of the fruit clusters. Furthermore, there may be a swelling effect arises within the fruit clusters internal structure due to increase in temperature enables the large dye ions to penetrate further. Similar observations were recorded with other studies for removal of MB dye using other plant materials (Sarioglu and Atay, 2006; Ertas *et al*., 2010)

Study of the Adsorption Ability of Oleander Plant (Al Defla) Leaves to Adsorb MB Dye from Water Solution

This study was carried out similarly as in section (3.1.) by repeating the six steps mentioned before. The experimental part is shown in section 2.6. The results showed an increase in the adsorption ability of *Oleander* leaves in case of increasing the weight of the adsorbent material, pH and temperature, while it decreases on increasing the concentration of the salt and increasing the leaves particles diameter (size of the adsorbent).

On comparing between *Oleander* fruit clusters and leaves as adsorbents, the results shown in Fig. 7-9 indicate that there is a difference in the ability of plant tissues to adsorb MB dye. It is found that fruit clusters are more able to adsorb MB dye from water solution compared to that of the leaves.

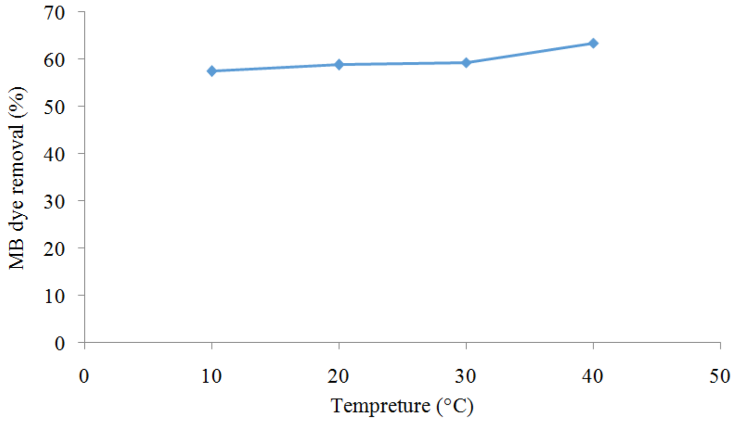

Fig. 6. Effect of the temperature on removal of MB dye (pH = neutral, C_i = 5 mg L^{-1}, adsorbent dose = 0.3g, time = 120 min.)

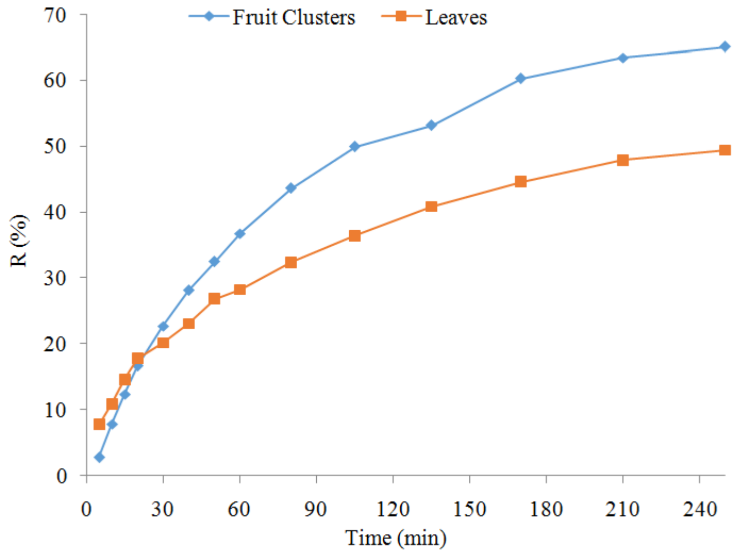

Fig. 7. Comparing removal efficiency of MB between Fruit clusters and Leaves at pH = 4.5; C_i = 5 ppm; temp. = 25°C; adsorbent dose = 0.3 g

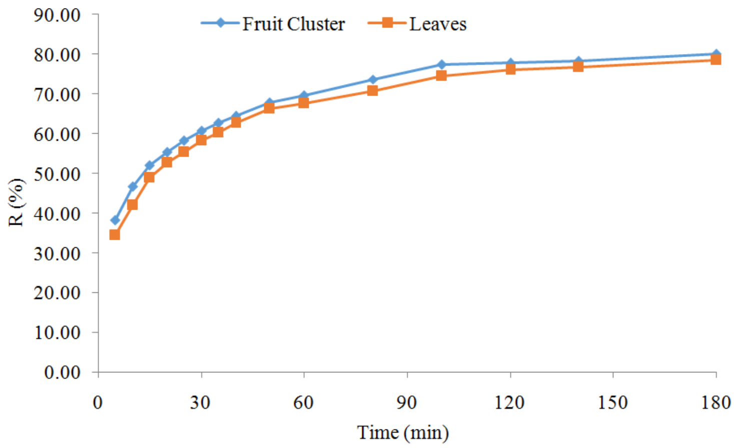

Fig. 8. Comparing removal efficiency of MB between Fruit clusters and Leaves using adsorbent particle diameter = 0.125-0.500 mm, pH = 7.0; C_i = 5 ppm; temp. = 25°C; adsorbent dose = 0.3 g

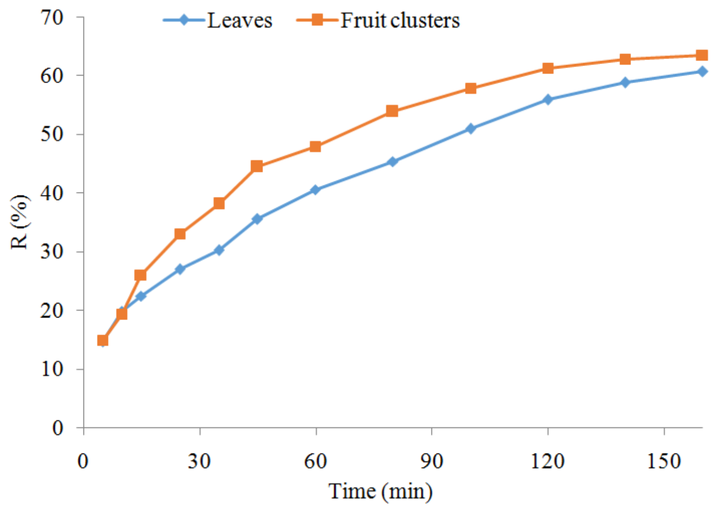

Fig. 9. Comparing removal efficiency of MB between Fruit clusters and Leaves using salt concentration = 0.7 M; pH = 7.0; C_i = 5 ppm; temp. = 25°C; adsorbent dose = 0.3 g

Adsorption Isotherm Investigation for MB Dye

Calibration curves are obtained with standard MB solutions and the amount adsorbed was found by mass-balance procedure. Concentration was calculated from the absorbance measurements using Beer-Lambert law plot. Drawing the calibration graph between the initial concentration of MB dye and the absorbance showed a straight line which confirmed that the absorbance and concentration are proportional and Beer's law is valid for this situation.

Adsorption experiments for equilibrium studies were carried out using batch adsorption technique. In which 0.3 g of the adsorbent material powder with particle size of (0.125-0.25 mm) was placed in four different stoppered 250 mL conical flasks and MB dye solution (250 mL) of different initial concentrations (3, 5, 7 and 9 ppm) were added to each flask. The experimental conditions pH was adjusted at 7.0, the natural pH value where the maximum percentage of removal was shown at this pH value and temperature was kept constant at (25°C) room temperature to be representative of environmentally relevant condition. The flasks were shaken at equal intervals and constant rate. The investigation was carried out for a time of 210 min to ensure establishment of equilibrium. The residual MB dye analysis were carried out by withdrawing solution samples at regular time intervals.

The sorbate MB dye uptake (adsorption capacity i.e., the amounts of dye removed by sorbents) is computed from mass balance and the removal efficiency were calculated using the following Equation 1 and 2 respectively (Deng *et al*., 2011):

$$q_e = \frac{(Ci - Ct)V}{W} \tag{1}$$

$$R(\%) = \frac{(Ci - Ct)}{Ci} \times 100 \tag{2}$$

Where:

q_e = Adsorption capacity (i.e., the amount of MB dye adsorbed) (mg/g) at the time of equilibrium
C_i = Initial dye concentration (mg/L)
C_t = Residual dye concentration (mg/L) at time *t*
V = Volume of aqueous solution (L)
W = Mass of the adsorbent material used (g)
R = Removal efficiency

For equilibrium investigations to correlate the residual MB concentration that remains in the solution and adsorption capacity, data were analyzed using Langmuir and Freundlich isotherm models (Mohammadi *et al*., 2011). Langmuir isotherm considers monolayer adsorption at a surface comprised of fixed amount of identical sites for adsorption and each site can accommodate only one MB dye molecule. Also, it is used to determine whether it would be economical to add *oleander* tissues to the water to remove MB dye and whether it is effective for removal of MB dye contaminant. The Langmuir isotherm linearized form is represented in Equation 3 (Fathi *et al*., 2014):

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m C_e} \tag{3}$$

Where:

C_e = MB dye concentration at equilibrium (mg/L)
q_e = Amount of MB dye adsorbed on adsorbent (mg/g)

Q_m = Maximum amount adsorbed per unit of adsorbent (monolayer adsorption capacity (mg/g))
K_L = Langmuir constant (L/mg) related to the free energy of adsorption

The constants K_L and Q_m which are related to the free energy of adsorption and maximum adsorption capacity (their values are shown in Table 1), were calculated from the slope ($1/Q_m$) and the intercept ($1/K_LQ_m$) of the linear plot of $1/C_e$ versus $1/q_e$ (Fig. 10-11).

Table 1. Langmuir and Freundlich isotherms constant parameters and correlation coefficients calculated for the adsorption of MB dye onto *Al Defla* Fruit clusters and leaves.

Langmuir (Fruit cluster)		Freundlich (Fruit cluster)		Note
Q_m	555.555	n	1.0225	Monolayer Physical process
K_L	0.002	K_f	1.6770	
R^2	0.9969	R^2	0.9974	
R_L (conc 9)	0.4955			
Langmuir (Leaves)	Freundlich (Leaves)			
Q_m	21.46	n	1.1320	Monolayer Physical process
K_L	0.083	K_f	1.6330	
R^2	0.9969	R^2	0.9962	
R_L (conc 9)	0.364			

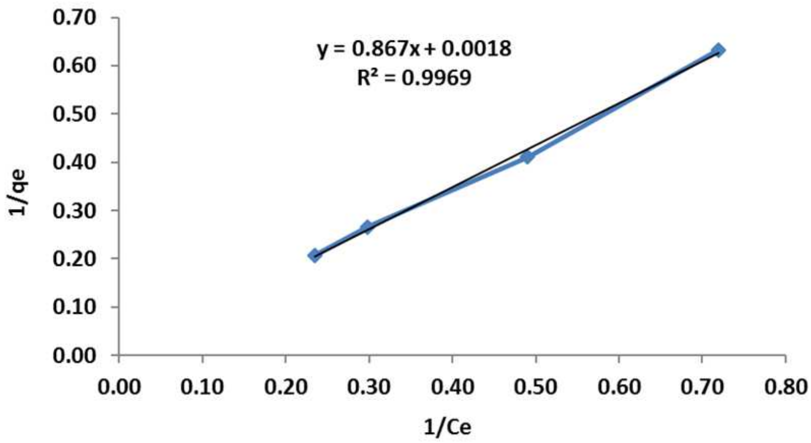

Fig. 10. Langmuir isotherm plot for the adsorption on Al Defla fruit cluster (sorbent dose = 0.3 g, pH = neutral, initial MB dye concentration of 3,5,7,9 mg L^{-1})

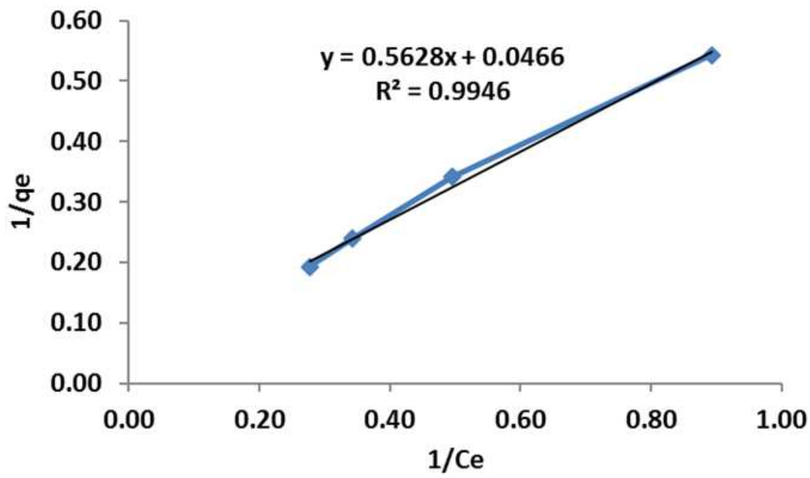

Fig. 11. Langmuir isotherm plot for the adsorption on Al Defla leaves (sorbent dose = 0.3 g, pH = neutral, initial MB dye concentration of 3,5,7,9 mg L^{-1})

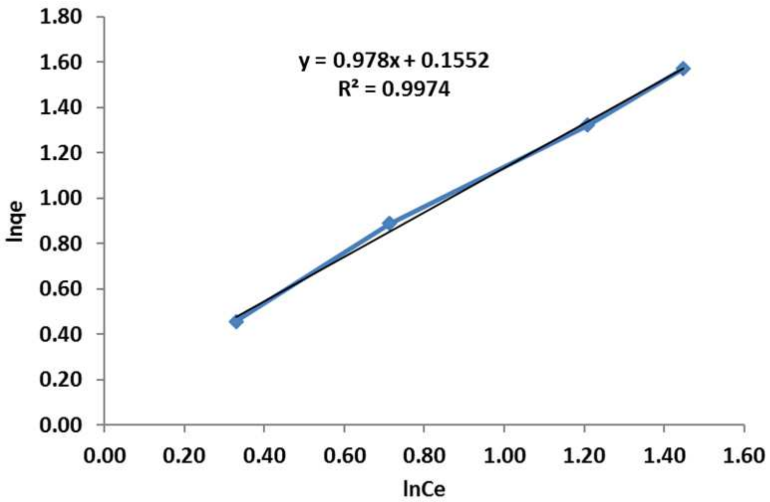

Fig. 12. Freundlich isotherm plot for the adsorption on Al Defla fruit cluster (sorbent dose = 0.3 g, pH = neutral, initial MB dye concentration of 3,5,7,9 mg L^{-1})

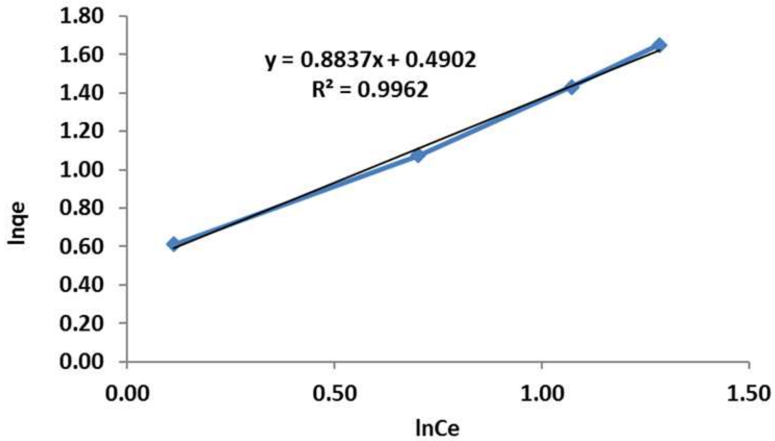

Fig. 13. Freundlich isotherm plot for the adsorption on Al Defla leaves (sorbent dose = 0.3 g, pH = neutral, initial MB dye concentration of 3,5,7,9 mg L^{-1})

The dimensionless equilibrium parameter (R_L) used to express the essential characteristics of Langmuir adsorption isotherm is expressed by the following relationship (4) (Somasekhara and Nirmala, 2013):

$$R_L = \frac{1}{1 + K_L C_i} \tag{4}$$

where, K_L is Langmuir constant (L/mg) and C_i (mg/L) is the initial concentration of MB dye. The value of R_L indicate the type of Langmuir isotherm to be irreversible if ($R_L = 0$), linear if ($R_L = 1$), unfavorable if ($R_L > 1$) and favorable if ($0 < R_L < 1$) (Somasekhara and Nirmala, 2013).

The Freundlich isotherm model assumes that the adsorption process takes place on different surfaces. This model isotherm can be stated mathematically as in Equation 5 (Markovic *et al*., 2015):

$$q_e = K_f C_e^{1/n} \tag{5}$$

The linearized form of the above Freundlich equation can be expressed as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{6}$$

where, C_e is concentration of MB dye at equilibrium (mg/L); q_e is the adsorbed amount of MB dye on adsorbent (mg/g); K_f and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity respectively. These constants K_f

and n were determined from the plot of $ln\ C_e$ versus $ln\ q_e$ based on the Freundlich linear form equation (ln K_f is the intercept and 1/n is the slope) (Fig. 12-13). If the value of n > 1, then adsorption is physical process; if $n < 1$, then adsorption is chemical process; and if $n = 1$, then adsorption is linear.

The linear plots obtained between $1/C_e$ versus $1/q_e$ and (ln C_e) versus (ln q_e) (Fig. 10-13) show that the adsorption process obeys Langmuir and Freundlich isotherm models and indicate the applicability of these isotherms on the adsorption process. The Langmuir and Freundlich constants and correlation coefficients are shown in Table 1. The values of the equilibrium parameter were between 0 and 1 ($0 < R_L < 1$) for both fruit clusters and leaves indicate that adsorption onto *oleander* plant fruit clusters and leaves are favorable and assumes monolayer adsorption process. While, the values of adsorption intensity (n) in Freundlich isotherm for both fruit clusters and leaves were higher than 1 ($n > 1$) indicating that adsorption is a physical process for both adsorbents. The values of n were 1.0225 for plant fruit clusters and 1.132 for plant leaves (i.e., within the range of 1-10) indicating good adsorption (Desta, 2013).

Results revealed that both Langmuir and Freundlich isotherm models fitted with the sorption data of both fruit clusters and leaves and both models found to have nearly similar regression coefficient value ($R^2 > 0.99$). Since *Oleander* plant tissues is locally freely available, abundant low-cost adsorbent and has considerable capacity to remove MB dye from polluted water, it may treated as economically valuable for removal of MB dye from wastewater.

It was also demonstrated that the adsorption of MB dye increased with the increase of contact time. The removal of MB dye using fruit clusters or leaves of the oleander plant as adsorbent were found to be fast in the beginning and then become slow and stagnate with increasing time of contact. The required time for the equilibrium to be reached between the adsorbent and MB dye solution was less than 210 min. This can be explained probably that adsorption is taken place through adsorption on the surface of the adsorbent until the surface pores (i.e., the functional sites) become fully occupied (Deng *et al*., 2011).

In addition, the equilibrium time depends on the MB dye initial concentration. Since the agitation speed and intervals were constant, the diffusion of MB dye molecules from the solution to the adsorbent surface was affected by the MB dye initial concentration. The higher the initial MB dye concentration the higher was the diffusion rate because of the increasing in the driving force of the concentration (Deng *et al*., 2011).

Conclusion

Removal of MB dye from polluted water by adsorption using *oleander* plant fruit clusters and leaves as adsorbents have been investigated under different experimental parameters and the results can be summarized as follow:

- The Oleander plant (*Al Defla*) tissues (leaves and fruit clusters) has good ability to adsorb MB dye from water
- The fruit clusters of *Al-Defla* plant has higher adsorption ability than leaves
- The percentage of MB dye removal was increased with increasing temperature, pH of the medium, adsorbent amount and initial dye concentration parameters
- The percentage of MB dye remove always decreased with the increase of salt concentration in the dye solution and increase of the adsorbent material particles size
- The adsorption isotherm results indicates that adsorption process onto both *Oleander* fruit clusters and leaves is monolayer physical process. Moreover, the sorption data fitted into both Freundlich and Langmuir isotherm models

Acknowledgement

The authors would like to acknowledge and thank Al Al-Bayt University for the support.

Author Contributions

Rajab Abu-El-Halawa: Designing, experimental, data analysis, interpretation and writing.

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Hamzah H. Abu-Sittah: Collecting materials and experimental work.

Ethics

This article is original and contains unpublished material. All of the authors have read and approved the manuscript and there are no ethical issues involved.

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