Research Article

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Adsorption of methyl violet from aqueous solution using brown algae
Padina sanctae-cruis

Metil violetin sulu çözeltiden, kahve rengi alg, Padina sanctae-cruis kullanılarak emilimi

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Abstract

Objective: The presence of dyes in the water is toxic and harmful to human body so, it must be removed from the water. In the present study, the removal of methyl violet (MV) from aqueous solutions using brown algae “Padina sanctae-cruis” was investigated.

Materials and methods: The rate of adsorption was investigated under various parameters such as contact time (5–200), pH (2–11), dye concentration (10–60 mg/L), amount of adsorbent (0.25–5 g/L) and temperature (25–45°C).

Results: The maximum adsorption was achieved in 10 mg/L, pH = 8 and adsorbent dose 2 g/L and 80 min contact time for removal of MV from aqueous solutions. Kinetic studies showed that the pseudo second-order model describes adsorbent kinetic behavior better. Besides, experimental data have been modeled using Langmuir and Freundlich isotherms and the results showed that both models are proper to describe adsorption isotherm behavior. In addition, the equilibrium study shows that the adsorption was physical and favorable. Moreover, a thermodynamic study revealed that the adsorption process is exothermic and spontaneously in nature. Furthermore, Maximum adsorption capacity using adsorbent was 10.02 mg/g.

Conclusions: It could be concluded that the P. sanctae-cruis biomass is a good adsorbent for removing MV dyes from aqueous solutions.

Keywords: Adsorption; Brown algae; Methyl violet; Aqueous solution; Isotherm; Langmuir.

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Anahtar kelimeler: Adsorpsiyon; Kahverengi algler; Metil violet; Sulu Çözelti; İzoterm; Langmuir.
Introduction

Pollution control and economical limitations have been one of the major concerns of global leaders over the last few decades. Dye untreated wastewater discharged from textile and dyestuff industries are important sources of contamination and have toxic or harmful effects on ecosystems and environment. Among all the organic material, removing color is the hardest and most complicated [1]. Colors are the first known pollutions which must be omitted from aqueous solutions, before discharging them to the wastewater [2]. Dyes have artificial sources and have complex structures which are the most common water pollutions. Production of these compounds estimated about 1000 tons per year and assumed that 1–10% of colors discharged directly to the environment. These dyes are indissoluble from a biological point of view and in tough environmental situations, their stability and resistant is too much. Thus treatment of these dyes is so hard [3]. Some of the applications of these products are raw material for producing many kinds of inks, food industry, cosmetics, paper and textiles [4]. Because of economic reasons in synthesis, availability and also being easy to use, stability and their strength in front of the direct light, high temperate, washing materials and microbes' attacks, a variety of colors in comparison to natural colors, these dyes are more common in textile and dying industry [5]. As it discovered the very slight amount of dyes into the water is toxic and harmful to human body. That is why those must be removed from processes and wastewater treatment and elimination of toxic materials from wastewater have some application problems. Physical and chemical processes for solving or eliminating pollutions are: electrochemical, photocatalytic degradation, cation exchange membrane, chemical deposition, Fenton biological treatment, coagulation, flocculation, ultrafiltration and adsorption has been taken into consideration [6]. The adsorption process is one of the most effective methods for eliminating pollutions from wastewater and it is becoming more and more famous and useful among scientists all over the world these days [6, 7]. Adsorption defined as a process that could separate organic or non-organic kinds, such as metals, dyes and odors with use of alive or dead biomass and their derivatives. This method has been studied for removing heavy metals and dyes from wastewater. Activated carbon is a very famous adsorbent but it is very costly. Therefore we need to find cheap adsorbents to replace activated carbon. There are some cheap adsorbents that used in studies before such as: eucalyptus tree bark [8], eggshell [9], rice bran [10], modified Aspergillus flavus biomass [11], shrimp peel [12], red flower [13], algae-molybdate [14], and brown algae Padina sanctae-crucis [15].

The main aim of this study was the removal of methyl violet (MV) from aqueous solutions using P. sanctae-crucis (PSC) brown algae which is native, available and cheap in the environment. To do this, the effect of different parameters such as pH, MV concentration, temperature, contacts time and, adsorbent dosage were investigated. Also, kinetic, isotherms and thermodynamic studies of adsorbent were studied.

Materials and methods

MV dye solution

In this study, methyl violet dye (C. I. 42555) made by Merck Company was applied in order to prepare the dyed solution. Methyl violet dye utilized in this research mainly composed of C25H30N3Cl with a molecular weight equal to 393.96 g/mol. Maximum wavelength of this dye is 584 nm. MV dye has amine side chains. MV changes into various dyes at different pH values: yellow to green at pH range of 0.13–0.5 and green to blue at pH value of 2–3 [16]. In order to prepare a stock solution of MV dye, 1 g powder dye was added to 1 L of double distilled water. In order to prepare the solution with required concentration, stock solution diluted with double distilled water.

Surface characterization of bio-adsorbent

Padina sanctae-crucis (PSC) algae was gathered from the shores of the Persian Gulf in Bushehr province. Then, it was washed with tap water for several times to remove sands and particles. Brown algae were placed in sunlight for a week to dry up completely. Afterwards, they were powdered by Mark Moulinex mill and strained by sieve No. 25 (ASTM E 11). This product was stored in sealed bottles manufactured by polyethylene terephthalate (PET) for later use.

For further investigation, the surface of PSC before and after adsorption of MV dye, scanning electron microscope (SEM) (Hitachi S4160 type) was utilized.

The surface of the bio-adsorbent was covered by a thin layer of gold in vacuum to take photos of the bio-adsorbent surface before and after the adsorption of MV dye and then the surface of adsorbent was inspected by SEM.
Adsorption of MV dye

Adsorption of MV dye in aqueous solutions was carried out discontinuously in Erlenmeyer with 200 mL volume containing 100 mL dye solution. During all the experiments, pHs of the solutions were set by 1 mol/L sodium hydroxide and hydrochloric acid. Measurement of pHs performed by digital pH-meter (Metrohm 744). In this study, effects of different parameters were investigated on adsorption process including initial pH (2–11), the concentration of MV dye (10, 30 and 60 mg/L), temperature (298.15–318.15 K) and adsorbent dosage (0.25–5 g/L).

Adsorption tests were done to determine optimum pH at definite test conditions (298.15 K temperature, 80 min contact time, 2 g/L adsorbent dosage, 150 rpm mixing rate, 10 mg/L initial concentration of MV dye) and mentioned pH range. After optimizing pH, other parameters were also optimized similarly. In order to separate solid phase from the solution after adsorption tests, about 10 mL of the solution was centrifuged for 15 min at 2500 rpm and filtered by Whatman 42 filter. The initial and secondary concentration of the MV dye in aqueous solution was determined by spectrophotometer equipped with UV/VIS (Shimadzu-1700, Japan) at 584 nm maximum wavelength. Subsequently, kinetic behavior of adsorption process was estimated by pseudo first-order and pseudo second-order kinetic models and isotherm behavior was modeled by Langmuir and Freundlich models. In this study, thermodynamic parameters like Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also studied and investigated. In all samples, adsorption efficiency (%) and dye adsorption capacity at equilibrium (qe, mg/g) was determined by the following equations [17]:

\[
q_e = \frac{C_0 - C_e}{M} \times V
\]

\(C_o\) and \(C_e\) are the concentrations of MV dye at initial condition and equilibrium state (mg/L), respectively. \(M\) is the dosage of dried bio-adsorbent (g) and \(V\) is the volume of the solution in adsorption process (L).

All the experiments were performed in duplicate and all data reported in this paper are the average of the two replications.

Results and discussion

Surface characterization of bio-adsorbent

In order to investigate the surface of bio-adsorbent prepared from PSC, scanning electron microscope (SEM) Hitachi S4160 type was applied. In Figure 1A and B, the surface of bio-adsorbent is shown before and after adsorption process of MV dye, respectively. In Figure 1A the surface of bio-adsorbent is observed before adsorption process which has a rough surface, but after adsorption process, some changes on the surface is observed (Figure 1B) that is dedicated to MV dye adsorption by adsorbent prepared from PSC.

Also, the FTIR spectroscopy was used to determine the presence of functional groups in PSC, as shown in Figure 2. The strong and widespread peak observed in the region 3426–3741 cm⁻¹, refers to the hydroxyl (–OH) and amine (–NH₂) groups within the biomass of algae [18]. The peak at 2920 cm⁻¹ refers to the presence of the –C–H functional group and the peaks at 1697 and 1618 cm⁻¹ is referred to the –C=O groups. Additionally, the peaks at 1046 and 1161 cm⁻¹ is related to the C–O and the peaks at 592 and 794 cm⁻¹ are related to the –C=N–C and S=O functional groups [19].

![Figure 1: SEM images of bio-adsorbent prepared from PSC (A) before adsorption, (B) after adsorbing MV dye.](image-url)
Effect of pH

Solution pH is one of the important parameters in controlling adsorption behavior of materials on the surface of adsorbent [20]. In Figure 3, the effect of pH on adsorption efficiency of MV dye by PSC is shown. According to Figure 3, pH increase at the range of 2–8 is followed by an increase in the efficiency of MV dye adsorption by PSC. As pH increases from 8 to 10, adsorption efficiency remains constant with no abrupt changes. Therefore, pH = 8 is selected as optimized pH and adsorption efficiency of MV was 95.52% at pH = 8. Experimental results showed that the amount of dye adsorption at acidic pH was negligible and this is mainly due to extra positive ions (H⁺) in the solution competing with other positive ions for adsorption on the active sites [21]. Increasing the pH of the solution from 2 to 10, raised the efficiency of the MV adsorption; because at alkaline pH the number of anions (OH⁻) at the surface of the adsorbent and inside the solution increases and as a result electrostatic attraction increases between negative surface of active sites and dye cations (=N(CH₃)₃⁺) leading to easier adsorption of dye molecules by the adsorbent [22]. Therefore, pH = 8 was determined as optimum pH and previous studies confirmed the same results [23].

Effects of initial concentration and contact time

In Figure 4, the effects of initial concentration of MV (10, 30 and 60 mg/L) and contact time (5–200 min) on the capacity of PSC bio-adsorbent are shown at 298.15 K. According to the results mentioned, adsorption capacity increased from 4.776 mg/g to 26.463 mg/g as initial concentration of MV dye increased from 10 mg/L to 60 mg/L, respectively. The trend of increase in adsorption capacity was rapid at early times and the rate of adsorption process decreased as time passed; because active sites on the surface of the adsorbent are higher at early times [24] and these sites are occupied by MV dye. It should also be mentioned that at early times of contact time, more than 80% of the 10 mg/L initial concentration of the dye was adsorbed by the adsorbent. As in Figure 4, increasing the initial concentration of the dye, process equilibrium time increased and this equilibrium time was determined to be 20, 40 and 80 min for 10, 30 and 60 mg/L concentration, respectively.

Effect of temperature

Temperature is one of the important parameters in the adsorption process. It has a certain and definite effect on adsorption process because the capacity of equilibrium adsorption of MV on the adsorbent varies with temperature changes [25]. Figure 5 shows the effect of temperature changes on adsorption efficiency of MV. Adsorption
efficiency of MV at equilibrium time (80 min) reduced from 95.52% to 90.22% as temperature increased in the range of 298.15–318.15 K. This shows that adsorption process of MV dye from the aqueous solution using PSC is exothermic which is usual in physical adsorption processes. Therefore, decrease in the efficiency of the adsorption due to temperature increases can be dedicated to changes in active sites of the adsorbent and also the tendency of the adsorbed material to get away from the active sites into the aqueous solution. In previous studies, similar results were reported that efficiency and adsorption capacity of the dye decreased as temperature decreased [26].

**Effect of adsorbent dosage**

Adsorbent dosage is a very significant parameter in adsorption process, as it determines the capacity of the adsorbent for initial concentrations of adsorbed material [9]. Effects of adsorbent dosage and adsorption capacity of cationic MV dye are shown in Figure 6. Based on the results obtained, it was observed that increasing adsorbent dosage leads to increase in adsorption efficiency from 33.19% up to 98.85%. This can be due to increase and availability of adsorption active sites and enough surfaces of adsorbent by increasing its dosage [17]. Besides, a rise in utilization of adsorbent dosage is accompanied by a decrease in adsorption capacity from 13.27 mg/L to 1.977 mg/L which is dedicated to unsaturation of a large number of active sites during adsorption process [8].

**Adsorption isotherm**

Adsorption isotherm defines the relationship between the amounts of adsorbed material, dry adsorbent mass and residual adsorbed material in aqueous solution at a constant temperature and equilibrium state. There are various isotherm models for describing adsorption process in aqueous solution. Two of the most frequently used isotherm models for adsorption processes are Langmuir and Freundlich models.

According to Langmuir isotherm model, adsorption of liquid contaminants takes place at the monotonous and homogeneous surface of the adsorbent. This model can describe adsorption within mono-layers, successfully [6, 15, 27–31]. The linear equation of Langmuir isotherm model is like below:

\[
\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}
\]  
(3)

In Equation (3), \( q_e \) (mg/g) is the amount of adsorbed dye at equilibrium state, \( C_e \) (mg/L) is the concentration of residual dye at equilibrium state within the aqueous solution, \( q_m \) (mg/g) is the maximum adsorption capacity and \( K_L \) (L/mg) is the constant of Langmuir isotherm model. Another important parameter that defines isotherm Langmuir model is dimensionless parameter \( R_L \) that shows the intensity of equilibrium or adsorption. The value of \( R_L \) implies the state and quality of adsorption isotherm model. If \( R_L > 1 \), \( R_L = 0 \), \( R_L = 1 \) and \( 0 < R_L < 1 \) the process is undesirable, irreversible, linear and desirable, respectively [6, 15, 27–31]. The value of dimensionless \( R_L \) parameter is calculated using Equation (4):

\[
R_L = \frac{1}{1 + K_L C_0}
\]  
(4)

In Equation (4), \( K_L \) (L/mg) is the constant of isotherm Langmuir model and \( C_0 \) (mg/L) is the initial concentration of the dye in the aqueous phase.

Another isotherm model that is widely used in previous researches for isotherm behavior is Freundlich
isotherm model. This model assumes that adsorption takes place on non-monotonous active sites within heterogeneous surfaces of the adsorbent [6, 15, 27–31]. The linear equation form of Freundlich isotherm model is like below:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]  

(5)

In this equation, \(q_e\) is equilibrium adsorption capacity (mg/g), \(C_e\) is equilibrium concentration of MV dye in the solution (mg/L), \(n\) is the adsorption force and \(K_f\) is the index of adsorption capacity. In order to determine the parameters of Freundlich and Langmuir isotherm models, the linear plot of \(\log q_e\) versus \(\log C_e\) and \(C_e/q_e\) versus \(C_e\) are applied, respectively. These linear relations are illustrated in Figures 7 and 8 and the calculated values of these models are reported in Table 1. Maximum MV dye adsorption using PSC was 10.02 mg/g and Langmuir constant value (\(K_L\)) was calculated as 2.203 L/mg. The maximum adsorption capacity of MV dye for this adsorbent and other bio-adsorbents are showed in Table 2. As shown in this Table, \(q_{max}\) obtained is comparable to the other bio-adsorbents in the removal of MV [32–34]. The dimensionless parameter of \(R_L\) for MV adsorption was 0.0434 (0 < \(R_L\) < 1) confirming that adsorption of MV dye with PSC is desirable and physical. Adsorption force (\(n\)) was calculated as 2.613 based on Freundlich isotherm model defining that adsorption process is physical and desirable. The correlation coefficient of Langmuir and Freundlich models was 0.9892 and 0.9432, respectively showing that both models can describe isotherm behavior of MV adsorption with PSC, but Langmuir model can describe the process a little bit more than Freundlich model.

### Kinetic study

Adsorption kinetic defines the best model to describe experimental data. There are a number of models for determination of adsorbent behavior. These models investigate the mechanisms of adsorption processes and explain the methods for experimental data. In this study, data was analyzed by adsorption equilibrium approaches consisting of pseudo first-order and pseudo second-order models. Analysis performed at different concentrations of 10, 30 and 60 ppm with 150 rpm mixing rate.

Pseudo first-order or Lagergren model is one of the most frequent models used to describe kinetic behavior of adsorption process. This model is described as follows [6, 15]:

![Figure 7: Linear relation between ln (qe – qt) versus t for adsorption of MV dye adsorption with PSC bio-adsorbent.](image1)

![Figure 8: Linear relation between t/qt versus t for MV dye adsorption by PSC bio-adsorbent.](image2)
\[
\frac{dq}{dt} = K_t (q_e - q_t)
\]  

(6)

Integrating Equation (6) at initial and boundary conditions of \( t = 0 \) to \( t = t \) and \( q = 0 \) to \( q = q_t \) yields to the following equation [6, 15, 35]:

\[
\ln (q_e - q_t) = \ln q_e - K_t t
\]

(7)

where \( q_e \) and \( q_t \) are adsorbed MV dye (mg/g) at equilibrium time, \( t \) and \( K_t \) (min\(^{-1}\)) is adsorption rate constant of pseudo first-order model. In order to calculate the constant values and parameters of this model, \( \ln (q_e - q_t) \) is plotted versus \( t \) (Figure 9) which is a straight line with \( K_t \) and \( \ln q_e \) as slope and intercept of this line, respectively. These values are shown in Table 3. In addition, correlation coefficient at different initial concentrations of 10, 30 and 60 mg/L of MV were 0.9634, 0.9502 and 0.9775, respectively. These values confirm that pseudo first-order model can describe the kinetic process with appropriate accuracy.

Pseudo second-order model equation is like below:

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

(8)

Initial adsorption rate, \( h \) (mg/g · min), is defined as below:

\[
h = K_2 q_e^2
\]

(9)

In Equation (8), \( K_2 \) (g/mg · min) is the constant of pseudo second-order adsorption rate and \( q_e \) and \( q_t \) (mg/g) are adsorption capacity at equilibrium and adsorption capacity at time \( t \), respectively [36]. The parameters of pseudo second-order model for MV dye adsorption are calculated by plotting \( t/q_t \) versus \( t \) (Figure 10). The values of these parameters for pseudo second order model are reported in Table 3. It should be mentioned that correlation coefficient (\( R^2 \)) for this model at different initial concentrations of 10, 30 and 60 mg/L of MV dye were 0.9998, 0.9997 and 0.9998, respectively. This confirms that pseudo second-order model can describe the kinetics of MV dye adsorption by PSC better in comparison with pseudo first-order model.

### Thermodynamic investigations

Thermodynamic parameters show the nature of adsorption process. In this research, thermodynamic parameters like Gibbs free energy (\( \Delta G^o \)), enthalpy (\( \Delta H^o \)) and entropy (\( \Delta S^o \)) were also identified. Gibbs free energy is calculated by the following equation [6, 15, 37]:

\[
\Delta G^o = -RT \ln K_d
\]

(10)

R is universal gas constant (8.314 J/mol·K), \( T \) is the absolute temperature in Kelvin and \( K_d \) (\( q_e/C_e \)) is distribution coefficient. The parameters of enthalpy (\( \Delta H^o \)) and entropy (\( \Delta S^o \)) are determined via Equation (11):

\[
\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]

(11)
According to Equation (11), enthalpy and entropy are the slope and intercept of the linear diagram of ln \( K_D \) versus 1/T (Figure 11). Thermodynamic parameters of adsorption process of MV dye using PSC at a temperature range of 298.15–318.15 K are listed in Table 4. Gibbs free energy of the adsorption process at 298.15 K, 308.15 K and 318.15 K were −5.866, −4.8628 and −4.0434 kJ/mol, respectively. These values demonstrate that adsorption process is spontaneous. Besides, Gibbs free energy value decreased as temperature increased showing a reduction in the degree of the spontaneity of adsorption process. Enthalpy of the process was also reported to be negative confirming that the reaction is exothermic. The value of \( \Delta S^\circ \) at a temperature range of 298.15–318.15 K was reported to be −91.088 J/mol · K. This value reveals a reduction in a random collision between MV dye molecules and solid surface of the adsorbent during the process. Furthermore, this value of entropy implies a decrease in the concentration of adsorbed material on the interface of the solid and liquid phase and accordingly concentration of adsorbed material into the solid phase increases.

### Table 4: The values of thermodynamic parameters (enthalpy, entropy and Gibbs free energy) for adsorption process of MV using PSC.

| T (K) | \( \Delta G^\circ \) (kJ/mol) | \( \Delta H^\circ \) (J/mol) | \( \Delta S^\circ \) (J/mol · K) |
|-------|--------------------------|--------------------------|------------------------------|
| 298.15 | −5.866                   | −33.019                  | −91.088                      |
| 308.15 | −4.8628                  |                          |                              |
| 318.15 | −4.0434                  |                          |                              |

Figure 11: Linear relationship between ln \( K_D \) and 1/T for determination of thermodynamic parameters during adsorption process of MV dye by PSC.

Conclusion

In the present study, PSC used as an adsorbent to remove methyl violet dye from aqueous solutions. Different parameters like initial pH, temperature, contact time, initial concentration of dye in the solution and adsorbent dosage were investigated and results showed that the maximum adsorption of methyl violet was achieved in the MV concentration of 10 mg/L, pH = 8, adsorbent dose 2 g/L and time of 80 min and adsorption efficiency was reported to be 98.85% during these conditions. Kinetic behavior of the adsorption process was also studied using pseudo first-order and pseudo second-order kinetic models. Measured data showed that pseudo second-order kinetic model can describe kinetic behavior better than pseudo first order model in MV dye adsorption. Isotherm behavior investigations conducted using Langmuir and Freundlich models and correlation coefficient (\( R^2 \)) of each model showed that both models exhibit appropriate isotherm behavior. According to the values of \( R^2 \) and \( n \) calculated from Langmuir and Freundlich models, respectively, the adsorption process was found to be desirable and physical. Additionally, Maximum MV dye adsorption using PSC was 10.02 mg/g and this result was comparable to the results of other researchers. Thermodynamic parameters such as Gibbs free energy, entropy and enthalpy were also studied. Negative values of Gibbs free energy, entropy and enthalpy showed that MV dye adsorption process using PSC is spontaneous, physical and exothermic. Negative entropy value proved that adsorption process is mainly dedicated to electrostatic attraction between adsorbent surface and adsorbed material within the aqueous solution. Considering the efficiency of adsorption and frequency and accessibility of this kind of weed, it is highly recommended for filtration and contamination adsorption in aqueous solutions.

Authors’ contributions: Mr. Reza Mahini and Mr. Rauf Foroutan, M.Sc. student, performed the experiments and Dr. Hossein Esmaeili supervised this study.

Conflict of interest statement: The authors have no conflict of interest for this manuscript.

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