IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.18 No.3 (September 2017) 31 - 48
ISSN: 1997-4884

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# Removal of Dyes from Synthetic Wastewater by Agriculturalwaste

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## Abstract

Adsorption is one of the most important technologies for the treatment of polluted water from dyes. Theaim of this study is to use a low-cost adsorbent for this purpose. A novel and economical adsorbent was used to remove methyl violet dye (MV) from aqueous solutions. This adsorbent was prepared from bean peel, which is an agricultural waste. Batch adsorption experiments were conducted to study the ability of the bean peel adsorbent (BPA) to remove the methyl violet (MV) dye. The effects of different variables, such as weight of the adsorbent, pH of the MV solution, initial concentration of MV, contact time and temperature, on the adsorption behaviour were studied. It was found experimentally that the time required to achieve equilibrium was 120 min for all dye concentrations (10-50 mg/l). The BPA was characterised using Fourier transform infrared (FTIR)before and after adsorption of the MV dye. Langmuir, Freundlich and Temkin isotherm models were used to analyse the experimental isotherm data. The Freundlich isotherm gives a better fit than the other isotherm models. The adsorption kinetic data were tested using pseudo-first-order and pseudo–second-order models. Additionally, the intraparticle diffusion model was used to investigate the mechanism of the adsorption process. It was found that boundary layer diffusion (external mass transfer) is the rate-determining step. The thermodynamic parameters, including ΔH, ΔS and ΔG, were investigated at different temperatures (298, 313 and 323 K) and concentrations (5, 10, 20 and 30 mg/l) to understand the nature of the adsorption process. The thermodynamic study indicates that the adsorption of MV dye onto BPA is physical, exothermic and spontaneous in nature.

**Key words:** Adsorption, Peel beans, isotherm, kinetic model, Methyl violet

## Introduction

Dyes are a common group of industrial wastewater pollutants. Dyes are soluble, coloured organic compounds that are used in many industries to colour clothes, paints, paper, plastic, leather, cosmetics and ceramics.

The wastewater effluents from these industries contain dyes which may be potentially hazardous to aquatic life and human beings if they are discharged into the environment. Since most dyes are toxic and even carcinogenic, it is important to remove these dyes from wastewater before the water is discharged into the environment [1].

Different technologies involving physical, chemical and biological treatment are used for the removal of dyes from water and wastewater, such as coagulation, filtration, reverse osmosis, ion-exchange, adsorption, chemical treatment by reduction, oxidation and neutralisation [2, 3, 4]. All these methods have advantages and disadvantages [5]. Among the various methods, adsorption methods are some of the most effective and economic ways to treat water polluted with dyes [5, 6, 7]. Activated carbon is one of the most widely used adsorbents for wastewater treatment because of its high capacity [8]. However, because of its high cost, there is growing interest in using inexpensive alternative materials instead of carbon.

Agricultural waste has little or no economic value and can be used as an alternative to activated carbon.

Various researchers have studied the use of low-cost materials, such as agricultural peel [9], agricultural waste [10, 11], sugarcane bagasse [12] and rice hulls [13], for the removal of dyes from aqueous solutions. These agriculture wastes can be used directly as adsorbents without any treatment [5, 8] or may be used as adsorbents after certain treatments or conversion to activated carbon [14, 15, 16]. The objective of the present work is to study the possibility of using low-cost agricultural waste (bean peel) as an adsorbent for the removal of MV dye from water.

The effects of different parameters, such as pH of the solution, mass of the adsorbent, concentration of dye, contact time and temperature, on the dye removal were studied.

The adsorption isotherm models, adsorption kinetics and thermodynamic parameters were also evaluated and reported. The adsorbent, BPA, was characterised using FTIR analysis.

## Materials and Experimental

### Adsorbent

Bean peel adsorbent (BPA) was collected from local Iraqi vegetable market waste. It was washed well with distilled water to remove particles adhering to the surface, dried in an oven at 90°C for 24 hrs and powdered.

The powder was then soaked in a 1 M HCl and washed with distilled water several times until the pH value reached 7, after which it was dried in the oven at 90°C for 24 hrs and sieved into two size ranges, (0.14-0.6mm) and (0.6-1mm). These two size ranges were used as adsorbents for the present study.

### Adsorbate Solution

Methyl violet 6B dye (MV) was used as the adsorbate. This dye was purchased from Sigma-Aldrich Company, molecular formula – $C_{24}H_{28}N_3Cl$, molecular weight – 394. The dye was used directly without purification. The chemical structure of the MV dye used in the present work is shown in Fig. (1).

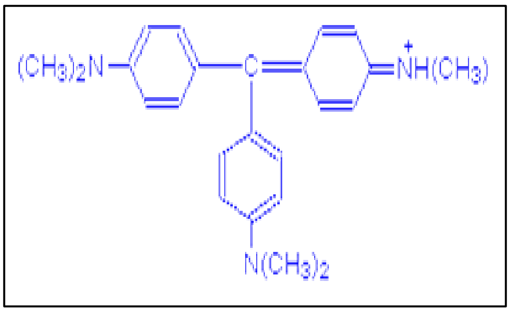

Fig. 1, Chemical structure of MV dye

A dye stock solution of concentration 200 mg/l was prepared by dissolving 0.2 g of the dye in 1000 ml of distilled water. Dye solutions of different concentrations (10, 20, 30 and 50 mg/l) were prepared by appropriate dilutions of the stock solution.

The pH of the dye solutions was adjusted to the required value by adding a few drops of either 0.1 M HCl or 0.1M NaOH. The properties of MV are illustrated in table (1).

Table 1, Properties of MV dye

| Properties | Data |
|---|---|
| Common name | Methyl violet |
| Suggested | Methyl violet |
| C.I. Number | 42535 |
| Ionization | Basic |
| Maximum | 583 |
| Color | Violet |
| Molecular | $C_{24}H_{28}N_3Cl$, |
| Molecular | 394 |

All chemicals and reagents used in the present study were of analytical grade.

Instruments

A UV-1100 spectrophotometer was used to determine the concentration of the MV dye solutions from their absorbance, observed at the wavelength of maximum absorbance ($\lambda_{max}$ = 580 nm). A Perkin Elmer Spectrum 100 FTIR spectrometer was used for characterising the BPA at wave numbers 400-4000 $cm^{-1}$.

Batch Adsorption Experiments

Batch experiments were conducted to study the effect of different parameters, such as pH of the solution (2-12), particle diameter of BPA (0.14-0.6 and 0.6-1mm), weight of BPA (0.025-0.25 g), initial dye concentration (5-50 mg/l), contact time (10-180 min) and temperature (25-60°C), on the adsorption of the MV dye.

Adsorption experiments were carried out at a temperature of $25^0$C and a pH of 7, except for experiments conducted to study the effect of temperature and pH. In a typical adsorption experiment, 50 ml of the dye solution of a given concentration was added to a 100-ml bottle containing a certain weight of BP adsorbent. The solution was agitated using a shaker at 200 rpm for an appropriate period of time. The BPA was then separated from the dye solution. The concentration of the remaining dye in solution was measured by a UV-spectrophotometer at the $\lambda_{max}$ of 580 nm. The amount of dye adsorbed at equilibrium $q_e$ (mg/g) on BPA was calculated using the following equation:

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

where$q_e$ is the amount of MV dye adsorbed per unit weight of BPA after equilibrium (mg/g). $C_o$ and $C_e$are the initial and equilibrium concentrations ofthe MV dye (mg/l), respectively is the volume of dye solution (litter) and $W$ is the weight of the adsorbent (g).The percentage removal of dye can be calculated as follows:

$$\%\,\mathrm{Re}\,moval = \frac{(C_o - C_e)}{C_o} \times 100 \quad \ldots (2)$$

The data obtained from experiments were used to study the equilibrium and kinetics models as well as to study the thermodynamics of the adsorption process.

## Results and Discussion

### FTIR analysis

FTIR analysis is important for identifying the important functional groups present on the BPA surface. The FTIR spectra of BPA were measured before and after adsorption to investigate the changes in the vibrational frequencies of the functional groups of the BPA due to adsorption of the MV dye. This FTIR spectrum is presented in Fig. (2).

As shown in Fig. (2), the FTIR spectrum of the adsorbent was measured within the wavenumber range of 400-4000 cm$^{-1}$. The spectrum of the adsorbent displays a number of adsorption peaks. The FTIR spectrum consists of five adsorption bands: (1) the broad hydrogen band (3200-3500 cm$^{-1}$) due to the presence of –OH groups in BPA; (2) the band (2850-3000 cm$^{-1}$) corresponding to the C-H stretching region; (3) the band (1690-1760 cm$^{-1}$) due to the carbonyl group C=O stretching vibration; (4) the absorption band in the range of 1500-1700 cm-1 corresponds to the bending vibrations of H2O molecules physically adsorbed on to BPA and the C=C vibrations; and (5) the band in the range of 1000-1320 cm-1 corresponds to the C-O bending vibrations of alcohols, carboxylic acids, esters or ethers. A reduction in the peaks can be seen after adsorption, but the peak positions still remain in the same range. This indicates that the adsorption of the MV dye onto BPA is by physical adsorption. Table (2) shows the locations of functional groups on the BPA surface.

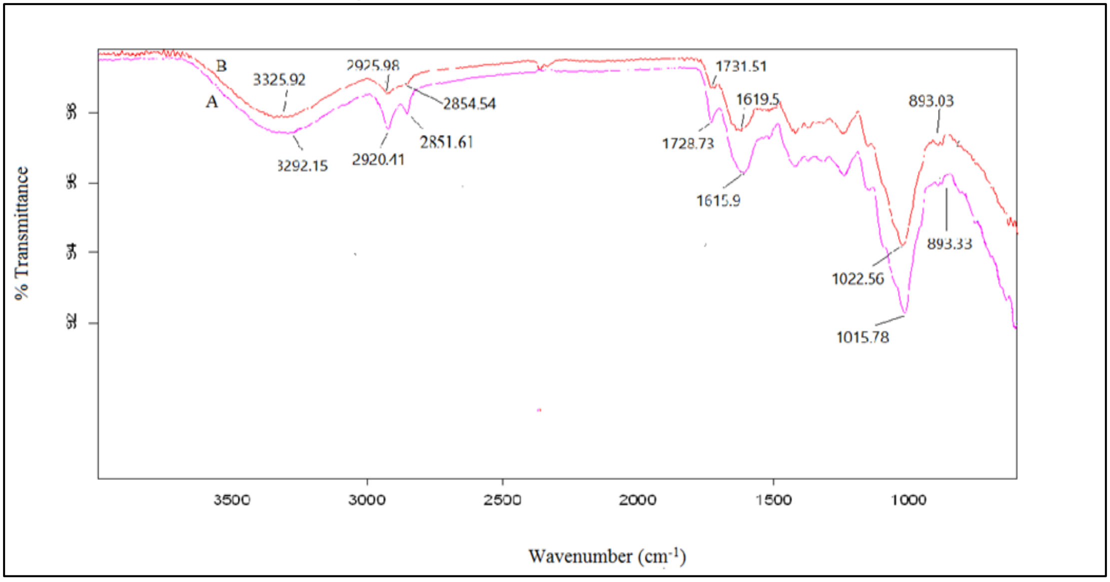

Fig. 2, FTIR spectrum for BPA before adsorption (A) and after adsorption (B) of MV dye

Table 2, Wavenumber (cm$^{-1}$) for the dominant peaks of the functional groups on BPA from FTIR analyses

| Wavenumber Before | Wavenumber After adsorption | Functional Groups | Wavenumber Ranges of functional groups (cm$^{-1}$) | Type of vibration |
|---|---|---|---|---|
| 3292.15 | 3325.92 | 3100-3500 | Alcohols & Phenols | H-bonded O-H stretching |
| 2920.41 | 2925.98 | 2850-3000 | Alkanes | C-H stretching Alkane C-H bonds |
| 2851.61 | 2854.54 | | | |
| 1728.73 | 1732.51 | 1690-1760 | Carboxylic acid | C=O stretching Carbonyl |
| 1615.9 | 1619.5 | 1500-1700 | Aromatics | C=C bend |
| 1015.78 | 1022.78 | 1000-1320 | Esters, Alcohols, carboxylic, ethers | C-O stretching |
| 893.33 | 893.03 | 650-1000 | Alkenes | =C-H bend |

### Effect of pH

Solution pH is one of the important parameters in the adsorption process, and it influences the surface charge of the adsorbent and the degree of ionisation of the dye in solution [17.18, 19, 20]. The experiment was carried out using 30 mg/l MV dye, 0.1 g BPA and pH ranging from 2 to 12. The effect of pH on the adsorption of MV dyes onto BPA is shown in Fig. (3).

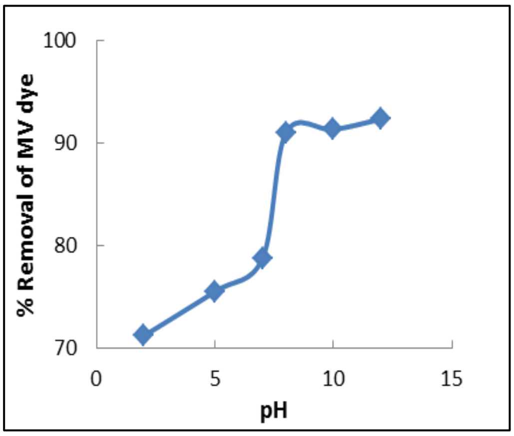

Fig. 3, the effect of pH on the adsorption of MV dye onto PB

As shown in Fig. (3), the adsorption of the MV dye increases as the pH increases and reaches a maximum at approximately pH 8. The same trend has been obtained by many researchers [1, 6. 17, 18, 21]. This result may be due to the cationic nature of the MV dye. At a low pH, a high concentration of hydrogen ions ($H^+$) is present in the solution. Therefore, the positively charged MV dye molecules and hydrogen ions compete for binding sites on the adsorbent surface. This can also be explained by considering that at low pH, the surface of the adsorbent becomes more positively charged. This causes repulsion between the adsorbent and dye molecules, thus reducing the adsorption of dye on the adsorbent.

Other studies have reported the same conclusion [1, 18, 21]. At high pH, the surface of the adsorbent becomes more negatively charged, thus increasing the amount of dye adsorbed on its surface [1, 15, 16, 18, 22]. This indicates that the adsorption process is based on the electrostatic interaction between the positively charged MV dyes and negatively charged sites on the adsorbent surface [23, 24].

Additionally, at pH 8 or more, the dye begins to precipitate, which may be due to the formation of a complex with OH. Therefore, the increase of percentage removal at pH values equal to or higher than 8 is due to precipitation. On the basis of the previous observation, the pH value of approximately 7 was recommended in the present work.

### Effect of adsorbent weight and particle size of adsorbent

The effect of varying weight of BPA on the removal of MV dye from water was studied using adsorbent weights ranging from 0.025 to 0.25 g. The other experimental parameters were kept constant, using MV concentration of 30 mg/l, pH of 7 and a shaking time of 2 hrat 200 rpm. The experiment was carried out using two BPA size ranges (0.14-0.6 mm and 0.6-1 mm). The experimental data for the two size ranges are presented in Fig.(4).

Fig. (4 a) shows the effect of the particle size of the adsorbent on the adsorption process. It is clear from this figure that the percentage removal of the MV dye increased with the decrease of particle size. This is due to the increased surface area of the BPA caused by decreasing particle size.

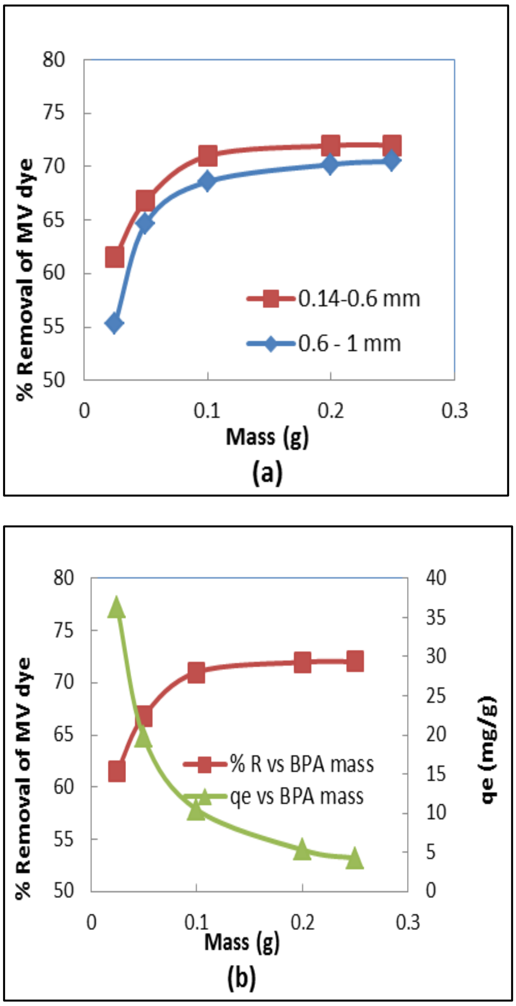

Fig. 4, effect of adsorbent weight on the adsorption of MV dye onto BPA (30 mg/l MV dye conc., 120 sec contact time, 220 r.p.m. agitation speed, 25°C temp.)

Additionally, it can be observed from Fig. (4) that the increase in the weight of the BPA causes an increase in the percentage removal of the MV dye, but a decrease in the adsorption capacity ($q_e$). Fig. (4) shows that the percentage removal increases with adsorbent weight until a value of 0.1 g, after which it reaches equilibrium. This weight gives percentage removals of 71% and 68% for the particle size ranges (0.14 - 0.6 mm) and (0.6 -1 mm), respectively. This may be due to the increase in the BPA surface area and the availability of adsorption sites with increasing weight of the BPA.

This observation is in agreement with other previous studies [25, 21, 26, 27].

Therefore, the best removal was found at the dose of 0.1 g with the particle size range (0.14-0.6 mm).

Effect of Contact Time and Initial Dye Concentration

The contact time to reach equilibrium is an important parameter in wastewater treatment [1]. To study the effect of contact time on the adsorption capacity of the BPA, experiments were carried out using a fixed weight of adsorbent (0.1 g) and various initial concentrations of the MV dye (10, 20, 30 and 50 mg/l) at a pH of 7for different time intervals (15-180 min), as shown in Fig. (5).

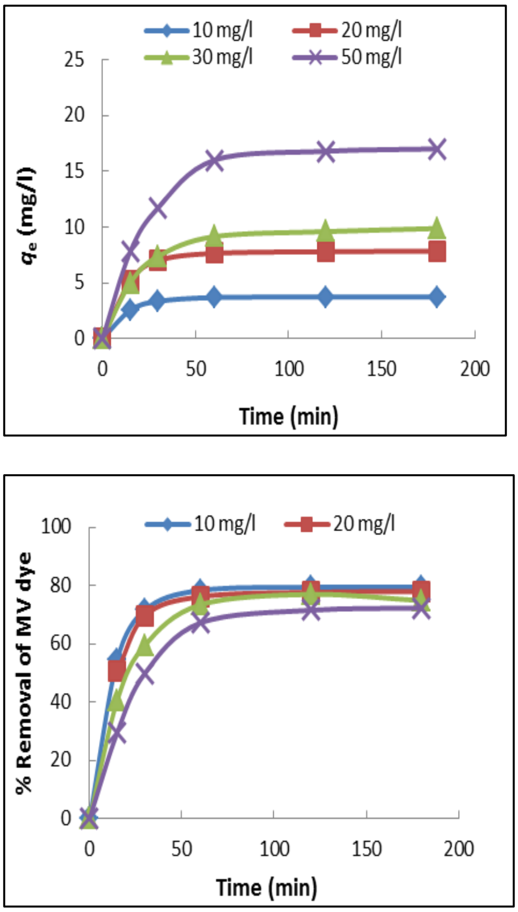

Fig. 5, effect of contact time and initial dye concentration on the adsorption of MV dye onto BPA (0.1 g adsorbent weight, 25 °C Temperature.

The amount of dye adsorbed, qe, at different concentrations increases rapidly in the initial stages up to60 min, after which it gradually decreases with further progress of the adsorption, finally reaching equilibrium between 60 and 120 min.

After 120 min, there is no change in the adsorption capacity.

The rapid adsorption in the initial stage can be attributed to the higher availability of active sites on the adsorbent surface.

With the passage of time, these active sites are gradually occupied by dye molecules, which lead to a decrease in the number of active sites available for the residual dye molecules in solution. Similar behaviour has been reported in previous literature [12, 15, 27, 28, 29].

Therefore, the contact time required for the BPA to reach equilibrium is 120 min for different initial dye concentrations, and this time was set as the agitation time for adsorption studies.

## Adsorption Isotherm Studies

The adsorption isotherm provides a representation of the adsorption process through an equation or curve relating the number of dye molecules adsorbed onto the surface of an adsorbent ($q_e$) to the equilibrium concentration of dye molecules in solution ($C_e$) at a constant temperature. Several isotherm models were employed to describe the adsorption process. The fits of the Langmuir, Freundlich and Temkin adsorption isotherm models were investigated in order to model the experimental data of adsorption of the MV dye on the BPA.

### 1- Langmuir isotherm model

Was developed by Irving Langmuir in 1916 [30]. This model is based on the following assumptions: (1) molecules are adsorbed as a monolayer; (2) the surface of the adsorbent is homogeneous; (3) all adsorption sites are identical and energetically equivalent; (4) each site can accommodate only one molecule; there is no interaction between adsorbed molecules [1, 28, 29]. The linear form of the Langmuir isotherm model is expressed by Langmuir [30].

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \qquad \ldots (3)$$

where, $q_{\max}$ is the maximum capacity (mg/g) and $b$ is the Langmuir equilibrium constant (l/mg). The experimental isotherm data were correlated using the Langmuir model, Eq. (3), as shown in Fig. (6). The linear plot of $C_e/q_e$ against $C_e$ indicates that the adsorption of MV dye onto BPA follows the Langmuir isotherm model.

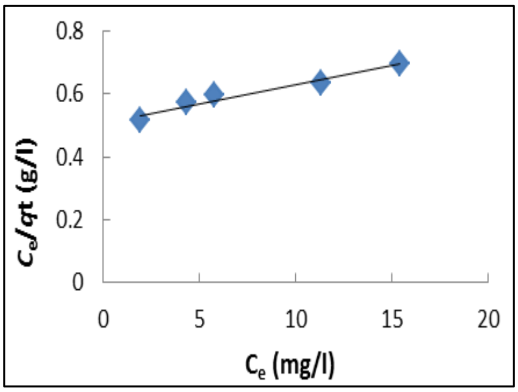

Fig. 6, Linear plot of Langmuir isotherm model for the adsorption of MV dye onto BPA (25 °C Temperature)

The Langmuir constants, $q_{\max}$ and b, were calculated from the slope and intercept of the linear plot. The Langmuir constants with correlation coefficients are tabulated in Table 3.

The type of adsorption isotherm can be determined using the dimensionless parameter ($R_L$), known as the separation factor. Using the value of b deduced from the Langmuir model, $R_L$ can be calculated using the following equation [15, 17, 27, 31].

$$R_L = \frac{1}{1+bC_O} \qquad \ldots (4)$$

where $C_O$ is the initial MV dye concentration. The value of $R_L$ indicates the following types of isotherms: irreversible if $R_L = 0$, favourable if $0 < RL < 1$, linear if $R_L = 1$, unfavourable if $R_L > 1$[1, 15, 27, 32]. $R_L$ values were calculated at different MV dye concentrations, and their values are listed in Table (3). The values are in the range of 0.3794-0.8106, which indicates that the adsorption process is favourable, as shown in Table 3. Additionally, the change of $R_L$ with MV dye concentration is presented in Fig. (7).

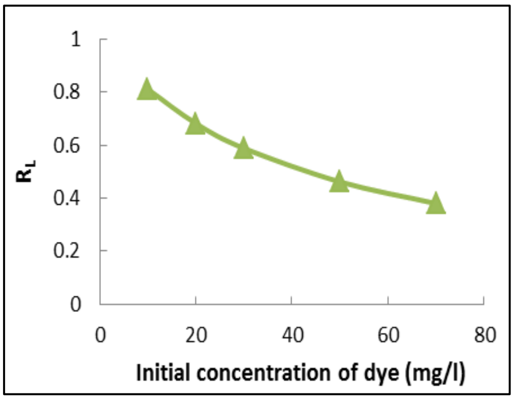

Fig. 7, change of separation factor, $R_L$, with initial MV dye concentration

This figure shows that when the dye concentration is increased, a value of $R_L$ close to zero means that the adsorption of dye is less favourable at high initial dye concentrations. This is consistent with reports from previous research [32].

2- Freundlich isotherm model

Empirical equation that is commonly used to describe multilayer adsorption ona heterogeneous surface. The linear form of the equation is represented by Freundlich [33].

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \qquad \ldots (5)$$

Where $k_f$ is the Freundlich constant related to adsorption capacity $(mg/g)(l/mg)^{1/2}$ and n is the Freundlich constant related to the adsorption intensity. The Freundlich isotherm was applied to the experimental data, and the Freundlich constants, $k_f$ and n, were determined from the linear plot of log $q_e$ against log $C_e$, as shown in Fig. (8).

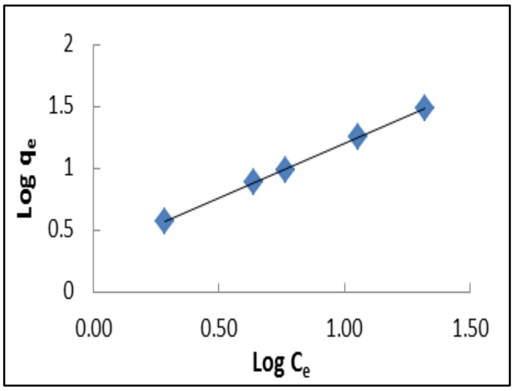

Fig. 8, Linear plot of Freundlich isotherm model for the adsorption of MV dye onto BPA (25 °C Temperature)

The Freundlich constants with the correlation coefficient are tabulated in Table (3). The value of n indicates the adequacy of the adsorption process as follows: unfavourable adsorption if $n < 1$, linear adsorption if $n = 1$, favourable adsorption if $n > 1$ [34]. In the present work, the value of n is greater than unity ($n = 1.135$), indicating that the adsorption process of the MV dye on the BPA is favourable.

Table 3, the Langmuir, Freundlich and Temkin isotherms constants and correlation coefficients for adsorption of MV dye onto BPA at 25°C

| Models | Isotherm Parameter | | | |
|---|---|---|---|---|
| Langmuir Isotherm | $q_{max,}$ (mg/g) | b, (l/mg) | $R_L$, (l/mg) | $R^2$ |
| | 84.034 | 0.0234 | 0.3794-0.8106 | 0.9584 |
| Freundlich Isotherm | kf, (mg/g)$(l/mg)^{1/2}$ | 1/n | n | R2 |
| | 2.090 | 0.8813 | 1.135 | 0.9999 |
| Temkin Isotherm | α(l/g) | β (kJ/mol) | | $R^2$ |
| | 0.716 | 7.836 | | 0.9322 |

3- Temkin isotherm model

This model takes into account the effects of direct interactions between the adsorbent and adsorbate (MV dye) on the adsorption isotherm, and assumes that as the surface is covered with a layer of the adsorbate molecules, the heat of adsorption of all molecules in the layer decreases linearly with coverage due to this interaction [35, 36]. The linear form of the Temkin isotherm is expressed by

$$q_e = \beta \ln \alpha + \beta \ln C_e \qquad \dots (6)$$

$$\beta = \frac{RT}{b_T}$$

where $\alpha$ is the Temkin isotherm constant (l/g), $\beta$is the Temkin constant related to the heat of adsorption (J/mol), R is the gas constant (8.314 J/mol. K),T is the temperature (K) and $b_T$ is the Temkin isotherm constant.

The Temkin isotherm (Eq.6) was used to analyse the experimental data and the Temkin isotherm constants, $\alpha$ and $\beta$ were determined from the linear plot of $q_e$ versus $\ln C_e$, as shown in Fig. (9).

The Temkin constants with correlation coefficients are listed in Table (3).

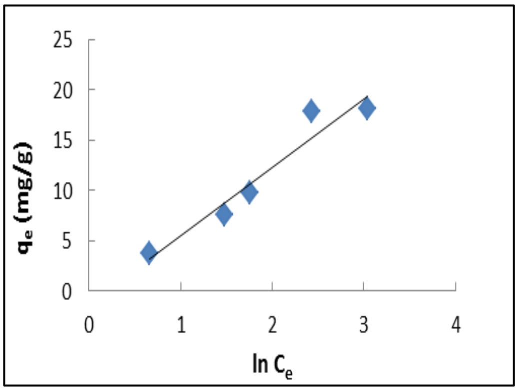

Fig. 9, linear plot of Temkin isotherm model for the adsorption of MV dye onto BPA (25 °C Temperature)

The correlation coefficients for all isotherm models studied are tabulated in Table (3).The correlation coefficient ($R^2$= 0.9999) for the Freundlich model is greater than those of the other models ($R^2$ = 0.9584and $R^2$ = 0.9322), that is, the Langmuir and Temkin isotherm models, respectively.

These results indicate that the Freundlich isotherm model gives the best fit to the experimental data, and therefore, the adsorption of the MV dye on the bean peel is best described by the Freundlich isotherm model. The fitting of experimental data with the Freundlich isotherm has been reported by previous researchers using natural materials for the adsorption of dyes [8, 34].

Depending on the assumptions of the Freundlich isotherm model, the adsorption process may be physical adsorption as well as multilayer adsorption with a heterogeneous distribution of active sites on the BPA surface [34]. The maximum adsorption capacity obtained ($q_{\max}$) is 84.03 mg/g. The value of the constant n is greater than unity, indicating that adsorption process of the present work is favourable.

## Adsorption Kinetics Studies

Kinetic studies are important to determine the rate-controlling step of the adsorption process. This is an important parameter for selecting the optimal operating conditions required during the design of the adsorption process [21, 27]. The kinetic study involves studying the effect of contact time on the adsorption of the MV dye at a given initial dye concentration, as shown in Fig. (5).

In the present work, kinetic studies were carried out at different initial dye concentrations. Two kinetic models were utilised to analyse the experimental data in the present study, including the pseudo-first-order and pseudo-second-order kinetic models at different initial dye concentrations.

### 1- Pseudo-First-Order Kinetic Model

This model was presented by Lagergren [37]. The linear form of this model is given by

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad \ldots (7)$$

Where $q_e$ and $q_t$ are the amounts of the MV dye adsorbed on the BPA (mg/g) at equilibrium and at time t, respectively, and $K_1$ is the rate constant (min$^{-1}$) of the pseudo-first-order model. The plot of log ($q_e$-$q_t$) versus t (Eq. 7) should be linear as shown in Fig. (10).

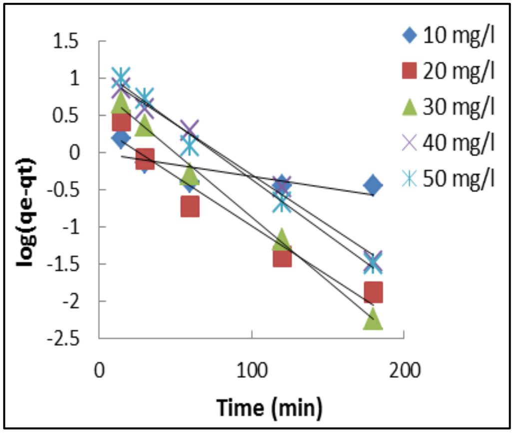

Fig.10, Pseudo-first-order kinetics for adsorption of MV dye onto bean peel adsorbent

The values of $K_1$ and $q_e$ were determined from the slope and the intercept of the plot, respectively, and are tabulated in table (4) along with the corresponding correlation coefficients.

Table 4, kinetic parameters and correlation coefficients for adsorption of MV dye onto BPA at different initial concentrations of MV dye (0.1 g adsorbent, 25°C and pH 7).

| $C_o$ (mg/l) | $q_{e,exp}$ (mg/g) | Pseudo first-order | | | Pseudo second-order | | |
|---|---|---|---|---|---|---|---|
| | | $q_{e,Cal}$(mg/g) | $K_1$ (min$^{-1}$) | $R_1^2$ | $q_{e,Cal}$(mg/g) | $K_2$ (g/mg.min) | $R_2^2$ |
| 10 | 4.100 | 1.009 | 0.0074 | 0.614 | 3.879 | 0.0504 | 0.999 |
| 20 | 7.688 | 3.752 | 0.0440 | 0.986 | 8.000 | 0.0205 | 0.999 |
| 30 | 9.896 | 7.019 | 0.0497 | 0.854 | 10.593 | 0.0089 | 0.996 |
| 40 | 13.885 | 13.646 | 0.0359 | 0.978 | 15.291 | 0.0038 | 0.999 |
| 50 | 17.941 | 17.104 | 0.0504 | 0.981 | 19.417 | 0.0042 | 0.996 |

### 2- Pseudo-Second-Order Kinetic Model

The second-order Lagergren model was presented by Ho and McKay [38]. The linear form of this model is expressed by

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad \ldots (8)$$

where $K_2$ is the rate constant of the pseudo-second-order model (g/mg.min). The experimental data obtained for the adsorption of the MV dye onto the BPA were fitted to Eq.8, by plotting t/$q_t$ versus t, as shown in Fig. (11).

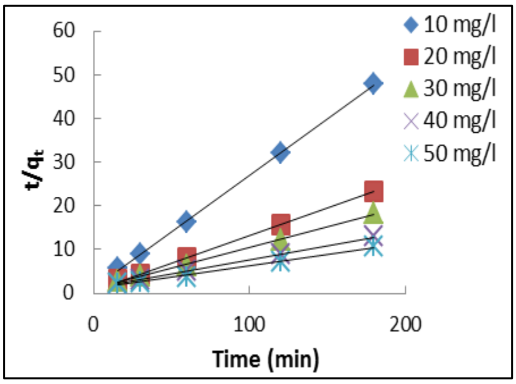

Fig. 11, Pseudo-second-order kinetics for adsorption of MV dye onto BPA

The plot should be linear with a slope of $1/q_e$ and an intercept of $1/K_2q_e^2$. The values of $K_2$ and $q_e$ are calculated from the slope and the intercept of Fig. (11) and are listed in Table 4along with the corresponding correlation coefficient.

As seen in table (4), the correlation coefficients of the pseudo-first-order kinetics model ($R_1^2$) were found to be in the range from 0.61 to 0.986. Therefore, this model did not fit well with the experimental data of the adsorption.

Additionally, it was found that at low concentrations, the calculated $q_e$ values do not agree with the experimental $q_e$ values. However, there is an agreement at higher concentrations. This confirms that the adsorption of the MV dye onto the BPA does not follow pseudo-first-order kinetics at low concentrations.

The same observation was reported by [32].

The pseudo-second-order model is used to investigate whether the rate-limiting step controlling the adsorption process is surface adsorption involving a chemical reaction (chemisorption) [39, 40]. Fits of the experimental data to this model indicate that adsorption is controlled by a chemical reaction if the following conditions are met [41]:

- The rate constant $k_2$ should be constant for different initial concentrations of adsorbate.
- The rate constant $k_2$ should be constant with particle size.
- The rate constant $k_2$ is sometimes independent of the agitation speed.

If any of the above conditions are not satisfied, then the adsorption process is not controlled by chemisorption even if the experimental data are well-fitted to the pseudo-second-order kinetics model.

As observed from table (4), the values of the correlation coefficient, $R_2^2$, of the pseudo-second-order kinetics were found to be in the range of 0.996 to 0.999, which is greater than that of the first-order model.

Additionally, it can be observed from table (4) that there is an agreement between the experimental and the calculated $q_e$ values for the pseudo-second-order kinetics model for all concentrations. These observations indicate that the adsorption of the MV dye onto the BPA follows pseudo-second-order kinetics, which may be due to chemisorptions.

However, from table (4), the values of the rate constant $k_2$ are not constant overall initial concentrations of the MV dye. This change in $k_2$ values with initial concentration confirms that the rate-limiting step is not chemisorption even though the experimental data give good fits to the kinetic model.

## Adsorption Mechanism

One of the kinetics models used to determine the mechanism of adsorption is the intraparticle diffusion model.

## Intraparticle Diffusion Model

Intraparticle diffusion model was described by Weber and Morris [42]. The linear form of this model is represented by

$$q_t = K_{id} t^{1/2} + C \qquad \dots (9)$$

where $K_{id}$ is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and C is the intercept, indicating the boundary layer effect. A plot of $q_t$ against $t^{1/2}$ should give a straight line with the slope $K_d$ and the intercept C. Intraparticle diffusion is considered as the rate-determining step if the plot is linear and the intercept C is zero [34]. If the intercept C is not zero, then external diffusion is involved in the adsorption process in addition to intraparticle diffusion. Fig. (12) shows the plot of $q_t$ against $t^{1/2}$ for the adsorption of the MV dye onto the BPA at different concentrations.

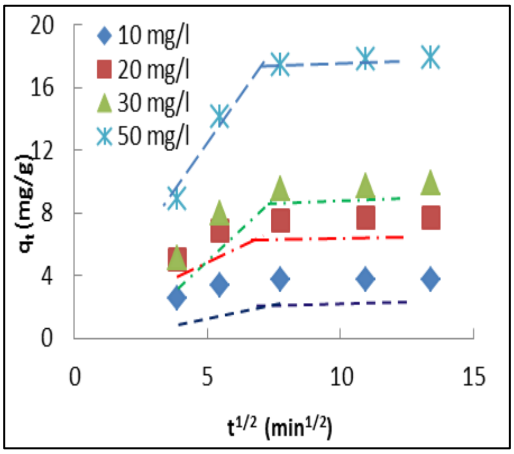

Fig. 12, Intraparticle diffusion kinetics for adsorption of MV dye onto BPA at different initial concentration of MV dye (0.1 g adsorbent, 25°C and pH 7).

Table 5, Intraparticle diffusion coefficient kinetics parameters for the adsorption of MV dye onto BPA at different MV dye concentrations (0.1 g adsorbent, 25°C and pH 7)

| Conc | 1st linear line | | | | | 2nd linear line | | |
|---|---|---|---|---|---|---|---|---|
| | $K_d$ (m/g.min$^{1/2}$) | C (mg/g) | R² | | | $K_d$ (m/g.min$^{1/2}$) | C (mg/g) | R² |
| 10 | 0.2809 | 1.6156 | 0.886 | | | 0.0103 | 3.6225 | 0.8995 |
| 20 | 0.7688 | 1.8788 | 0.8279 | | | 0.0306 | 7.289 | 0.8916 |
| 30 | 0.9223 | 2.2928 | 0.9897 | | | 0.0978 | 8.6224 | 0.9549 |
| 40 | 1.3921 | 2.4637 | 1.000 | | | 0.1087 | 12.396 | 0.9943 |
| 50 | 1.879 | 3.0622 | 0.9677 | | | 0.116 | 16.457 | 0.8955 |

This figure shows that the plots consist of double linear portions. This observation indicates that the adsorption process follows two stages of mass transfer. The initial linear portion of the plot covering the time range between 15 to 30 min is attributed to boundary layer diffusion (external mass transfer) [43].

Conversely, the second linear portion after 30 min is due to intraparticle diffusion or pore diffusion. The linearity of the plots confirms that intraparticle diffusion plays an important role in the adsorption process, but none of the plots in Fig. (12) pass through the origin. This indicates that intraparticle diffusion is not the rate-controlling step. It is concluded that external mass transfer (boundary layer diffusion) may be the rate-controlling step. This is in agreement with the results reported in the literature [12, 14, 22] for the adsorption of dyes by an agricultural material. The values of $K_{id}$ and C were obtained from the slope and the intercept of the double linear plots of Fig. (12), respectively. These values are listed in Table 5.

## Adsorption Thermodynamic

In environmental engineering practice, thermodynamic parameters must be considered in order to determine the nature of the adsorption process. These thermodynamic parameters, such as the change in Gibbs free energy ($\Delta G^o$) (kJ/mol), change in enthalpy of adsorption ($\Delta H^o$) (kJ/mol) and change in entropy ($\Delta S^o$) (J/mol.K),were calculated using the following equations [17, 27].

$$\Delta G^o = -RT \ln K_c \qquad \ldots (10)$$

where T is the absolute temperature in Kelvin, R is the gas constant and $K_c$ is the adsorption equilibrium constant, which was calculated using the following equation [17, 21, 12].

$$K_c = \frac{C_{Solid}}{C_{Liquid}} = \frac{q_e}{C_e} \qquad \ldots (11)$$

where $q_e$ and $C_e$ are the equilibrium concentrations of the MV dye in the solid phase (adsorbent) (mg/g) and in the liquid phase (dye solution) (mg/l). The enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) were calculated using the Van’t Hoff equation, as follows

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R}\frac{1}{T} \qquad \ldots (12)$$

where $\Delta G = \Delta H - T\Delta S$

Eq. (11) was applied to the experimental data of the adsorption of the MV dye onto the BPA, to calculate $K_c$ at different temperatures (25, 40, 50 and 60°C) and at different concentrations of MV dye (10, 20 and 50 mg/l). The plot of $\ln K_c$ versus 1/T (Eq.12) gives a straight line, as shown in Fig. (13).

Table 6, Thermodynamic parameters for the adsorption of MV dye onto BPA

| Conc. mg/l | ΔH kJ/mol | ΔS J/mol.K | ΔG kJ/mol | ΔG kJ/mol | ΔG kJ/mol | ΔG kJ/mol | $K_c$ | $K_c$ | $K_c$ | $K_c$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 298 | 313 | 323 | 333 | 298 | 313 | 323 | 333 |
| 5 | -3.705 | -10.981 | -0.417 | -0.301 | -0.149 | -0.038 | 1.18 | 1.12 | 1.06 | 1.01 |
| 10 | -3.216 | -9.034 | -0.49 | -0.43 | -0.32 | -0.17 | 1.22 | 1.18 | 1.13 | 1.06 |
| 20 | -3.056 | -7.606 | -0.79 | -0.69 | -0.57 | -0.54 | 1.38 | 1.30 | 1.24 | 1.21 |
| 50 | -2.867 | -6.334 | -0.96 | -0.92 | -0.82 | -0.74 | 1.47 | 1.42 | 1.36 | 1.31 |

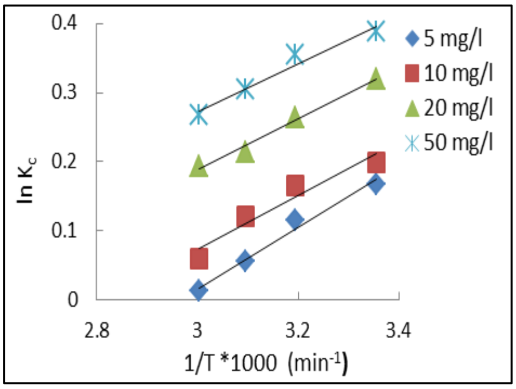

Fig. 13, the Van't Hoff plot for adsorption of MV dye onto BPA at different initial concentrations of MV dye (0.1 g adsorbent and pH 7)

The Gibbs free energy change ($\Delta G^o$) was calculated from Eqs.(10) and (11). The enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) were calculated from the slope and the intercept, respectively, of the plot in Fig. (13). The values of the parameters at different temperatures and concentrations are listed in table (6).

The negative values of $\Delta G^o$ shown in table (6) confirm that the adsorption of the MV dye onto the BPA is thermodynamically favoured, and the adsorption process is spontaneous under the experimental conditions. Additionally, the value of $\Delta G^o$ increases with increasing temperature, indicating that the degree of spontaneity increases at higher temperatures. The negative values of $\Delta S^o$ indicate the decrease in the disorder of the system. The negative values of $\Delta H^o$ indicate that the adsorption process is exothermic. The absolute value of $\Delta H^o$ may be used to determine whether the nature of adsorption is chemical or physical. For chemical sorption, the values of $\Delta H^o$ range from 83 to 830 kJ/mol while for physical sorption, they range from 8 to 25 kJ/mol [34]. As seen in table (6), their absolute values were less than 8 kJ/mol. This suggests that the adsorption process may be physical in nature. Additionally, the small values of $\Delta H^o$ confirm that the adsorption of the MV dye onto the BPA occurs by physical adsorption. It was suggested in previous work that if the $\Delta H^o$ values are less than 40 kJ/mol, then the adsorption process should be considered as physisorption [27, 44].

## Conclusions

1- BPA shows good effectiveness for the removal of MV dye from aqueous solutions in the presently reported conditions.

2- It was found that a pH value of 7 provides the best removal under the present conditions.

3- The percentage removal of MV dye (% R) increases significantly by increasing the dose and the size of the adsorbent (BPA), It was found under the present conditions that 0.1 g adsorbent is the best dose, resulting in the best percentage removal (71%) and best capacity (10.5 mg/g).

4- The amount of dye adsorbed increases with the increase in the contact time and reaches equilibrium after approximately 120 min. Additionally, it increases with the increase in the initial MV dye concentration.

5- The adsorption isotherm data of the MV dye fit well to the Freundlich isotherm. Therefore, the adsorption occurs by a physical process as well as multilayer sorption on the heterogeneous surface.

6- The maximum adsorption capacity ($q_{e,max}$) is calculated from the Langmuir model and found to be 84.034 mg/g .

7- The n value is greater than unity (n > 1) from the Freundlich isotherm and 0 < RL < 1 from the Langmuir isotherm, indicating that the adsorption of the MV dye onto the BPA is favourable.

8- The pseudo-second-order kinetic model provides a good description of the kinetic experimental data for MV dye adsorption onto BPA, and the experimental value of the adsorption capacity, $q_{e,exp}$, is very close to the calculated value, $q_{e,cal}$.

9- The fitting of the experimental data with the pseudo-second-order kinetics model indicates that the adsorption process is chemisorption. However, the values of the rate constant $k_2$are not constant for all initial concentrations of the MV dye.This confirms that the rate-limiting step is not chemisorptions, even though the experimental data gives provide a good fit to the kinetic model.

10- The application of the intraparticle diffusion model to the adsorption data indicates that the adsorption process is initially controlled by boundary layer diffusion and, finally, by intraparticle diffusion. However, boundary layer adsorption is the rate-limiting step.

11- The negative values of $\Delta H^o$ and $\Delta G^o$ indicate that the adsorption process is exothermic, thermodynamically favoured and spontaneous in nature. Additionally, the negative values of $\Delta S^o$ indicate the decrease in the disorder of the system.The small values of $\Delta H^o$ indicate that the adsorption process is physical in nature.

## Acknowledgements

I thank Prof. Thamer, the head of the Chemical Engineering Department/ University of Technology in Iraq, for providing the space and facilities needed to complete the requirements of my research. Additionally, my deep thanks to Prof. Adel O. Sharif from the University of Surrey in the UK, for providing me with some modern literature related to my research.

## Nomenclature

| | | |
|---|---|---|
| BPA | Bean peel adsorbent | |
| $b$ | Langmuir equilibrium constant | l/mg |
| $C$ | Intraparticle diffusion constant | mg/g |
| $C_e$ | Equilibrium liquid-phase dye concentration | mg/l |
| FTIR | Fourier transform infrared | |
| $C_o$ | Initial dye concentration | mg/l |
| $\Delta G^o$ | Gibbs Free energy change of adsorption | kJ/mol |
| $\Delta H^o$ | Enthalpy change of adsorption | kJ/mol |
| $K_1$ | The rate constant of the pseudo-first order model | $min^{-1}$ |
| $K_2$ | The rate constant of the pseudo-second order model | g/mg.min |
| $K_c$ | Thermodynamic equilibrium constant | l/g |
| $k_f$ | Freundlich constant related to adsorption capacity | $(mg/g)(l/mg)^{1/2}$ |
| $K_{id}$ | Intraparticle diffusion rate constant | mg/g min1/2 |
| MV | Methyl violet | |
| n | Freundlich constant related to adsorption intensity | |
| $q_e$ | Equilibrium solid-phase dye concentration | mg/g |
| $q_t$ | the intraparticle diffusion rate constant | |
| $q_{max}$ | Maximum capacity (mg/g) | |
| $R$ | Universal gas constant | 8.314 J/mol.K |
| $R_L$ | Dimensionless constant-separation factor | |
| $R^2$ | Correlation coefficient | |
| $\Delta S^o$ | Entropy change of adsorption | J/mol.K |
| T | Temperature | K |
| t | Time | min |
| V | Dye solution volume | l |
| W | Weight of the BPA | g |
| α | Temkin isotherm constant | l/g |
| β | Temkin constants related to the heat of adsorption | J/mol |

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