Methylene Violet Dye Adsorption Using Onion Skins: Kinetics and Isotherm Studies

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Abstract. This study examined the use of Onion Skins, an inexpensive adsorbent material, for removing the Methyl Violet dye which represents the main objective by using batch adsorption process to investigate and understand the adsorption behaviour, the kinetics and the equilibrium isotherm using a low-cost adsorbent. The study included the influence of contact time and the dosage of adsorbent experiment. The Onion skins was dried, cleaned and crushed. Batch experiments were applied to study the contact time effect using dye with an initial fifty milligram per litter concentration, and different amounts (0.5, 1.0, 1.5, 2.0) gm of adsorbent were used to study the dosage effect. The batch experiment showed a good dye removal with 51.3% during the first 150 min and 54.03% using 1.0 gm of adsorbent. Three kinetics models were applied: Pseudofirst, pseudosecond order and adsorption model for intraparticle diffusion. Pseudosecond and intraparticle diffusion were highly fitted models with a correlation of 0.9998 and 0.9691 respectively. Isotherm study was applied using the Langmuir, Freundlich and BET model, Freundlich model was best fitted model with a correlation of 0.9945, which suggesting a multilayer adsorption.

Keywords: adsorbent; onion skin; biosorbent, isotherm.

1. Introduction
Synthetic dyes represent useful industrial products that have substituted natural dyes because production costs are low. The main category of these dyes is the triphenylmethane which is often employed in dying and textile manufactures, such as paper, plastic and food products [1]. Due to several steps included in pretreatment, dyeing, also finishing techniques, a huge quantity of wastewater is released, especially in textile manufactures [2]. Releasing of waste components into the ambience is a significant issue. in many areas of industry, dyes have been frequently used, like (clothing, tanning, food, photoelectrochemical) manufactures. The intense utilize organic dyes contributes to high waste life and stimulates the importance to explore ways to eliminate.in addition dispose all them [3]. Dyes generally have unreal source and complicated aromatic molecular constructions, creating biodegradation more steady and difficult. Nowadays, there are 10000 kind of dyes or more than this number widely available [4]. Some of them are known to be have to be mutagenic and carcinogenic aquatic species [5]. Increased heartrate, shock, vomiting, jaundice and tissue necrosis are caused by extreme contact with methylene violet [6]. The elimination of different coloured agents from hydrous wastes by environmental,
technical, and commercial parts of considerable importance [7]. Methylene violet is currently a cationic dye used in many industries, including textiles, colouring paper, paint, cosmetics pharmaceuticals, plastics, dyeing cottons and paper stock coating, among many dyes [8].

Methyl violet is a dye with a complex structure, high brilliant and intensity and is vastly used in the industry. Methyl Violet may be harmful by ingestion, inhalation and skin contact. Long term exposure can cause eye and skin damages [9]. The structure of Methyl violet is shown in Fig.1 [10]. Methyl violet dye is a mutagen and mitotic poison; hence, concerns exist regarding the ecological impact of the release of methyl violet into the environment. [11]

To eliminate colour from manufacture effluents, various methods have been approved [12]. These approaches like chemical, physical and biological have their own characteristics and limitations. Adsorption is known as to become more successful, less costly and technically easy for polluted water treatment among these processes [13]; [14]. A vast area of adsorbents for the elimination of dyes from wastewater from non-biodegradable contaminants [15]. Activated carbon is the most common and with its tremendous sorption capability for elimination a huge various dyes from wastewater, is a best option among all the proposed sorbent materials [16]. However, the high costs associated with the adsorption usage and re-generation of industrial activated carbon (CAC) have led researchers to look for more economical and other efficient adsorbents. Recently, many attempts have been made to examine the use of many forms of solid agricultural waste and by-product substances, like “ rice husk [6], cereal chaff [8], sawdust [17], pinecone biomass [18], fallen Platanus leaves [19], pinetree leaves [20], peach Gum [21], magneticorn straw [22], palm tree flower [23], cucumber” [24].

The main objective of this work is to investigate the removal of Methyl violet using a low-cost adsorbent under optimized conditions such as contact time and dosage of adsorbent, adsorption kinetics and isotherm of Methyl Violet on Onion skins from aqueous solution.

2. Mathematical models

2.1 Kinetics Models

The adsorption method control mechanism, such as the coefficient of mass transfer, diffusion or chemical reaction employed to identify kinetic models and understand the dynamic of adsorption process. Three different models were employed to examine the behavior MV dye adsorption method on skin of onion. The model of pseudofirst order recognized as Lagergren Eq. 1:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

(1)
Where \( q_e, q_t \) symbolize the adsorption capacity (mg/gm) at equilibrium, in addition for any time \( t \) (min), \( k_1 \) symbolize the kinetic rate constant of (Pseudofirst order (Lit./min) [25]).

Integrated form to the kinetic model of (Pseudosecond order) may be expressed in Eq. 2 as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

Where \( k_2 \) represent the kinetic rate constant of Pseudosecond order (gram per milligram. minute), also from the slope and the values of the intercept of \( q_e \) and \( k_2 \) may be evaluated [26].

As a specified kinetic model mentioned above could not recognize the mechanism of sorption, a third models used for diffusion mechanism by using model of intraparticle diffusion with equation is expressed in Eq. 3:

\[
q_t = k_p t^{1/2} + C
\]

Where \( q_t \) represents quantity at time \( t \) of adsorbed dye (mg/g), the thickness of the border layer is \( C \) (mg/g) is and the rate constant of intraparticle diffusion model (mg/g.min1/2) is \( k_p \) [27].

### 2.2 Isotherm Models

The adsorption isotherm regularly explains the adsorbate, adsorbent interactivity and the adsorption ability of the adsorbent may also be indicated. Three isotherm models: Langmuir, Freundlich and BET were studied to describe position of MV dye molecules in two phases (liquid, solid) and to detect a more appropriate model for the design process [28].

The Langmuir model presumes the adsorption process happen on the surface of adsorbent and the process occurs on monolayer adsorption. This model generally suitable for an explanation of chemisorption while (an ionic or covalent) bond is formed between both adsorbent and adsorbate. The Langmuir model’s linearized form may be expressed as:

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

Where: \( q_e \) represents adsorption capacity (mg/g) and \( C_e \) symbolizes the equilibrium concentration (mg/L), \( K_L \) known as Langmuir constant (L/mg), so \( q_m \) symbolizes the maximum capacity (mg/g) [29].

Freundlich isotherm explains reversible adsorption and is not constrained to the formation of the monolayer. Both (heterogeneous, homogeneous) surfaces and (chemical, physical) adsorption can be used. linearized equation of Freundlich may be expressed as:

\[
\log(q_e) = \frac{1}{n} \log(C_e) + \log K_F
\]

The constant \( K_F \) is associated with adsorbent capacity for the adsorbate and \( 1/n \) represent a function of the adsorption force and it indicate clearly attraction between adsorbate and the adsorbent. A value of \( n \) under unity indicates that operation is absolutely chemical [26]. BET model presumes that the molecular layers are adsorbed together with earlier molecules adsorbed, every layer when adsorbs based on the Langmuir models. equation of BET may be linearized as:
\[
\frac{C_v}{(C_v - C_e)q_m} = \left(\frac{K_B - 1}{K_B q_m}\right) \left(\frac{C_e}{C_v}\right) + \frac{1}{K_B q_m} \quad (6)
\]

Where \( q_m \) represents maximum ability (mg/g), \( C_v \) represents the adsorbate initial concentration (mg/L) and \( K_B \) is continuously connected to the energy of adsorbent and adsorbate interaction [30].

3. Materials and methods

3.1 Preparation of adsorbent

Onion skins were collected from local market and cleaned with tap water many times then with distilled water to eliminate the dust particles, also other impurities were separated. After that dried for 24 hr. to remove a moisture content. The dry onion skins are crashed and sieved to the 1.0 mm.

3.2. Preparation of dye solution

When dissolving 1.25 gram from Methylene Violet dye in one litter of distilled water, a stock solution of 1250 milligram per litter was set and the solution was then diluted to desirable concentrations.

4. Results and Discussion

4.1 Fouriertransform infrared spectroscopy analysis

To recognize the functional groups related to the adsorption process, FTIR spectra of unloaded adsorbent was noted in the section of 400 – 4000 cm\(^{-1}\) [31]. Figure 2 shows the FTIR analysis of Onion skin before adsorption, the peaks indicate the complicated structure of onion skin. The strong and broad peak between 3414 - 3303 cm\(^{-1}\) represents an alcohol group; the bond of 2920 cm\(^{-1}\) is related to existence of Sp3 Carbo-Hydrogen. Peak of 1735 refers to the aldehydes C=O, 1629 cm\(^{-1}\) stating to carbonyl set – C = O, 1516 cm\(^{-1}\), although 1427 and 1371 cm\(^{-1}\) linked with C - O in phenols and then – CH3, this means the aromatic rings.

4.2 Contact Time

Recognizing the equilibrium contact time is essential for adsorption process design and consider an important and effective parameter in batch process. Figure 3 shows the adsorption capacity of Methyl
Violet using the Onion skin as an adsorbent. Generally, the figure shows that rate of dye adsorption increased rapidly at the first 30 min of contact, then slowly increased to a certain level, 150 min. Any further contact time will not increase the adsorption uptake of dye molecule since the adsorption phase reached the equilibrium. This is mainly because of the fact that the availability of empty accessible active positions at the onion skin surface when the process of adsorption starts. At equilibrium, remaining saturated vacant site are difficult to be occupied [32]; [33].

4.3 Effect of dosage
The dosage of adsorption is a significant process factor to calculate the adsorbent capacity for a given dose of adsorbent [34]. Influence of the adsorbent quantity provides an advantage for the capability of a dye to be adsorbed at a little quantity of adsorbent. Different dosages of adsorbents were examined (0.5, 1.0, 1.5 and 2.0) gm, and added to 100 milliliters from MV dye solution about 50 milligram per litter concentration. From Fig. 4, the results showed that increasing the dosage to a certain amount increases the adsorption capacity, owing to the growth rate of active adsorption sites on the adsorbent’s surface area. Figure also showed that increasing the amount to 2.0 gm, decreases the adsorption capacity, this can be assigned to the fullness of active sites at the surface because of particulate interaction such as aggregation [35].

![Figure 3. Impact of contact time on ability for adsorption](image3)

![Figure 4. Impact on the adsorption capability of the adsorbent dose](image4)
4.4 Kinetics models

In order to evaluate the kinetic mechanism which controls the adsorption process, Fig. 5 - 7 illustrates the application of Pseudo (1st., 2nd.) order in addition to intraparticle diffusion models. Figure 6 shows that Pseudo-second order is best fitted model and suggesting that the chemical adsorption is the controlling step in adsorption process, while Figure 7 shows a good fitting of the adsorption method with model of intraparticle diffusion and showing that the process occurs in two stages: first stage can be due to external surface adsorption [28].
Figure 7. IntraParticle diffusion model

Table 1. The kinetics study parameters.

| Pseudo(1st. order) |       |
|-------------------|-------|
| $q_t$ (mg/g)      | 40.262|
| $k_1$ (1/minute)  | 6.9x10^{-4}|
| $R^2$             | 0.5933|

| Pseudo(2nd. order) |       |
|--------------------|-------|
| $q_e$ (mg/g)       | 4.319 |
| $k_2$ (g/mg.minute)| 0.038 |
| $R^2$              | 0.9998|

| Intra(particle diffusion) |       |
|---------------------------|-------|
| $k_p$ (mg/g.minute^{0.5}) | 0.0738|
| $C$ (mg/g)                | 3.2912|
| $R^2$                     | 0.9691|
4.5 Isotherm Models

Figures 8 – 10 show linear mode of the three models associated with adsorption isotherm of MV dye on to onion skin adsorbent. It may be observed that figures – show best fit with Freundlich and BET models respectively. Freundlich isotherm is appropriate for surfaces (homogeneous, heterogeneous) suggesting more than one layer adsorption [36],[37],[38].

Table (2) presents the Isotherm Parameters; value of (n) less than unity implying that technique of adsorption is a chemical adsorption.
5. Conclusions
In this study, it can be shown that the onion skin is a good adsorbent for the Methylene Violet dye. The model of Pseudo (second order) illustrated that, chemical adsorption is a controlling phase in this
process, while the Intra-particle diffusion shows a good fitting and occurs in two steps. The Freundlich and BET model showed that adsorption method occurs at the surfaces of (homogeneous and heterogeneous), additionally in multi-layer.

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