Recycling of Agriculture Wastes for Efficient Removal of Methyl Orange Dye Using Batch Adsorption Unit

Ihsan Habib Dakhil
Chemical Engineering Department, College of Engineering, Al-Muthanna University, Iraq
E-mail: em2ihsan@mu.edu.iq

Abstract. The main purpose of this study is to examine the ability of agriculture wastes without pretreatment such as date palm fibers (DPF), sawdust (SD), rice husk (RH) as low-cost adsorbents for removing of methyl orange dye (MO) from industrial wastewater. The operating parameters were designed under isothermal batch conditions to study the influence of pH (2-10), initial concentration of MO dye (100-500) mg/l, adsorbent dose (0.1-1) g/100 ml and contact time (10-150) min. The optimum conditions were pH = 2, the initial concentration of dye = 100 mg/l, the amount of adsorbent dose = 0.6 g/100ml and 120 min contact time. At these conditions, the maximum removal efficiency was 95%, 86% and 77% for DPF, SD, and RH, respectively. There are two advantages to this work, it can remove MO dye from wastewater and disposal of agricultural wastes. The equilibrium results were compared with the most common isotherm adsorption models, Langmuir and Freundlich models, to measure the conformity of results obtained. It was fitted with the two models with a high correlation coefficient ($R^2$) for all adsorbents.

Keywords. Recycling, Removal, Adsorption, Methyl orange, Agriculture wastes.

1. Introduction
A large amount of dyes is consumed in many industries such as textile, paper, leather, printing and plastic industries, therefore, discharge of dying effluents has increased in recent years and can cause allergies and skin irritation even its discharge in a small amount. Some of the researchers have been reported that dyes can cause carcinogenic for aquatic organisms [1]. There are many methods that have been reported for removal of dye effluents such as biological treatment [2], electrochemical degradation [3], photocatalytic decolorization [4, 5], and adsorption process [6, 7].

Adsorption processes have been shown to be an efficient and economical method for aqueous effluent treatment among wastewater treatment technologies since there are many studies had examined different adsorbents for these treatments. Activated carbon can be considered as one of the most effective materials which are used in the adsorption processes for the removal of dye pollutants from textile effluents. However, due to the high cost of activated carbon in the case of processing large amounts of contaminated water, which reflected negatively on the economic treatment considerations. In recent decades, many researchers have reported agricultural waste as low-cost materials for eliminating dye pollutants from industrial wastewater since these materials have no cost. Large numbers of agriculture waste are being examined to show the ability to remove various types of dye at different operating conditions such as banana peel [8], leaf powder [9], Citrullus lanatus rind [10], wheat bran [11].
The present work aimed to investigate the ability of agriculture wastes such as (DPF, SD, and RH) as eco-friendly adsorbents for the removal of MO dye from its aqueous solutions and to get optimum operating variables that give maximum removal capacity of dye also to exam the result data at optimum parameters with adsorption isotherm models. The main two advantages of this work are to reduce the cost of wastewater treatment and to disposal of the agricultural wastes in the environment.

2. Materials and Methods

2.1. Adsorbents Preparation

Date palm fibers (DPF) were collected from the agriculture fields of Al-Samawa city, Iraq. Sawdust (SD) were collected from local timber shops and rice husk (RH) were collected from the agriculture fields of Al-Najaf city, Iraq.

Each of the materials was washed in tap water several times, then in distillate water to remove dust particles and color. After that, the leaves were dried in an electric oven at 80°C for 10 hours, then crushed using a mechanical grinder and sieved through a mesh to obtain ranges of size 5-8 mm particles and kept it in a glass container for experimental tests.

2.2. Preparation of MO Dye

To prepare a standard concentration of MO dye of (1000 mg/L), it dissolved (1 g) of commercial reagent grade of this dye in a volume of 1 L of double distillate water. The initial concentration of the MO dye was studied through the range of (100, 200, 300, 400 and 500) mg/L. The desired concentrations were obtained by dilution of stock dye solution in distillate water. The pH of the solution was adjusted using drops of 0.01N NaOH and 0.01N HNO3. A digital pH meter was used to measure the acidity of test solution for the adsorption process.

3. Adsorption Experiments

All adsorption experiments were performed at a batch isothermal process at a constant temperature of 30 ± 1°C. The operating parameters were chosen based on the most common that affected on adsorption processes like pH, amount of adsorbents, initial concentrations of dye and contact time. The experimental work was designed to study the effect of each factor separately on removal efficiency by calculating the initial and final MO dye concentration before and after each run. The four parameters were examined over the ranges (2-10) of pH, (100-500) mg/l of initial MO dye concentrations, the adsorbent dosage (0.1-1) g per 100 ml of aqueous MO dye and the final parameter, contact time, was examined over the ranges of (10-150) min.

The batch adsorption technique was carried out to evaluate the effect of pH solution on the removal capacity by varying its values over the ranges (2-10) and fixing the other parameters. This effect was examined by adding (0.5 g) of adsorbent in the volume of dye solution (100 ml) at constant concentration of dye C0 = 250 mg/l and the contact time of 150 min with a constant stirrer speed at 150 rpm to maintain the equilibrium conditions. After getting the optimum pH value, the influence of the second parameter, initial MO dye concentration, was studied by changing the initial concentration of dye at different values (100-500) mg/l with fixing the other parameters. Then, the effect of adsorbent dose and contact time were examined over the range of (0.1-1) g and (10-150) min, respectively, with the fixing of other factors at the optimum values.

At different time intervals, 2ml of samples were drawn out of the adsorber using a syringe and then the samples were filtrated using filter paper. The concentrations of MO dye before and after the experiment were determined using UV/VIS spectrophotometer (Shimadzu, Japan) at wavelength λ = 478 nm. The percentage of removal efficiency (% R) for MO dye was calculated according to Equation (1)[12]:

\[
% R = \frac{C_0 - C_e}{C_0} \times 100
\]

The capacity of dye adsorbed at a specific time, qe (mg/g), after ending each run can calculate using Equation (2):
\[ q_e = \frac{V(C_o - C_e)}{W} \]  

where \( C_o \) is represented the initial concentration of MO dye before the experiment in unit (mg/l), whereas \( C_e \) is represented the concentrations of MO dye at equilibrium state after a specific contact time in unit (mg/l). \( V \) is represented the volume of an aqueous solution which is measured in a unit of (L) and the letter \( W \) is represented the weight of agriculture wastes (adsorbents) used in the unit of (g).

4. Results and Discussion

4.1. Effect of pH

The most effective factor in reducing textile pollutants from wastewater during the adsorption processes is the pH solution since its effect on the surface charge of the adsorbent. Figure 1 shows the effect of pH on reducing MO dye over the pH values (2, 4, 6, 8 and 10) with initial MO dye concentration \( C_o = 250 \text{ mg/L} \), adsorbent dose of 0.5 g/100 ml for 150 min of contact time. From this figure, it can be noticed clearly that the optimum removal capacity was obtained at pH value = 2 for all adsorbents after this period the removal capacity was continuously decreased till the pH value = 10. The removal efficiency was decreased from (84%-29%), (75%-20%) and (69%-14%) for DPF, SD, and RH, respectively. MO dye exits in a negative charge since it is an anionic dye. The high adsorption capacity of MO dye at the acidic levels of pH can be attributed to the electrostatic attraction force that generates between the negative charge of MO dye ions and the positive charge of the acidic solution. Whereas, the decrease in the removal efficiency at basic levels of pH can be attributed to the competition for the adsorption sites between hydroxyl ions that presence in the excess amount in the basic solution with the particles of MO dye anion which affected the adsorption capacity. Similar results of optimum pH values were also obtained for the removal of MO by chitosan powder [13], using wheat bran [11], and using of treated wheat straw [14].

4.2. Effect of Initial MO Dye Concentration

The initial MO dye concentrations that considered in this study have been dependent on the concentrations of textile effluents [15]. Figure 2 shows the influence of initial MO dye concentration on removal efficiency in the range of (100-500) mg/L at constant adsorbent dosage of 0.5 g/100 ml with optimum pH value at 2 for 150 min of contact time.

From Figure 2, it can be noticed that the removal efficiency of MO dye decreases from (94%-60%), (85%-49%) and (77%-40%) with increasing of initial dye concentrations over the range examined for DPF, SD, and RH, respectively. The high removal efficiency at low levels of initial dye concentrations may due to the existence of many empty sites on the surface of adsorbents, after increasing initial dye concentrations, the removal efficiency decreases. This result could be due to the accumulating of MO dye particles on the surface of the adsorbent which was affected by the ability of adsorbents to remove more dye molecules. This conclusion is similar to the finding of other researchers such as adsorption of MO dye on modified kaolinite [16] and on treated eggshell [17].

The first period of Figure 3 illustrates the rapid increase in the adsorption capacity of MO dye with the increasing of initial MO dye concentrations. It can be noticed a fast increase in adsorption capacity at the initial dye concentration over the range of 100-400 mg/l. After an initial MO dye concentration of 400 mg/l, the adsorption uptake slowly increased for all agriculture adsorbents used. The maximum adsorption capacities were (61 mg/g, 53 mg/g, and 47 mg/g) for DPF, SD, and RH, respectively. This result can be attributed to that the initial MO dye concentration generates a high driving force between the adsorbents surface and aqueous solution to overcome the mass transfer resistance of all the dye molecules [18].
4.3. Effect of Adsorbent Dose

The amount of adsorbent dose that used to treat textile wastewater affected the economics of the adsorption process. To illustrate the effect of adsorbent dosage on the removal efficiency, the batch experiments were carried out at the different range of adsorbent dose (0.1, 0.2, 0.4, 0.6, 0.8, 1) g/100ml with fixing optimum concentration of MO dye at 100 mg/L and optimum pH at 2 for 150 min of contact time. Figure 4 shows this effect, it can be noticed that the removal efficiency of MO dye increases with increasing adsorbent dose in the range of adsorbent dose (0.1 - 0.6)g for all three adsorbents examined and reaches equilibrium state at 0.6 g/100ml of MO dye solution, after that, the removal efficiency remained constant. This observation can be attributed that, with the increasing of adsorbent dose, there are more adsorbent sites that adsorbed dye molecules until saturation of these vacant sites by dye molecules that remained removal efficiency curve in an almost straight line. This result agrees with almost all previous researcher observations on different dye types such as removal of basic dyes onto teak leaf powder [19] and removal of textile dye on agriculture wastes [15].

4.4. Effect of Contact Time

The factor of mixing time through batch experiments can be considered an essential parameter when studying adsorption processes since it provides good contact between the adsorbate and the adsorbent molecules. This effect was studied in the range of (10-150) min with fixing the other parameters at the optimum values. The optimum conditions for other parameters were initial MO dye concentration=100 mg/L, the adsorbent dose = 0.6 g/100ml and pH at 2. Figure 5 illustrates clearly increasing of removal MO dye efficiency with increasing contact time for all three adsorbent types that examined and reach equilibrium at the time of 120 min with a maximum removal efficiency of (96%, 86% and 78%) for DPF, SD, and RH, respectively. After the optimum value of equilibrium contact time, the curves of removal efficiency are nearly continued in strength lines which indicated reaching saturation or equilibrium. This finding agrees with almost all the findings of researchers reported that equilibrium time for removal of MO dye on chitosan reached after 100 min [20]. By using activated carbon, the equilibrium time has been reached after 120 min [21] and after 180 min by using biochar prepared from chicken manure [22].
5. Adsorption Isotherms

The experimental data results were analyzed using Langmuir and Freundlich models. In this study, the adsorption models used to determine how to distribute and contact between MO dye molecules in the liquid phase and the adsorbents in the solid phase. The experimental result data at optimum values were analyzed using these models. The Langmuir isotherm model is a linear form equation that used for monolayer sorption onto the surface of the adsorbent. It can be expressed by Equation (3):

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o K_l C_e}$$  \hspace{1cm} (3)

where $q_e$ (mg/g) is the equilibrium adsorption capacity, $C_e$ is the remaining concentration at the end of each experiment. $k_l$ and $q_o$ are represented Langmuir constants that can be determined by linear plotting of $1/q_e$ against $1/C_e$ as illustrated in Figure 6. The intercept and slope of the linear plot are represented Langmuir constants.

The favorability of the Langmuir model was determined by calculating the factor of ($R_l$) which represents the type of isotherm adsorption of MB dye on agriculture wastes. The value of ($R_l < 0$) indicates to unfavorable, whereas the value of $R_l$ lies between (0-1) which indicates favorable, and linear for ($R_l > 1$). The $R_l$ is calculated by Equation (4):

$$R_l = \frac{1}{1 + K_f C_e}$$  \hspace{1cm} (4)

The estimated $R_l$ values at different MO dye concentrations for three adsorbents which were found in the favorability range of (0.077 – 0.016) for DPF, (0.244 – 0.060) for SD and (0.353 – 0.098) for RH which were confirmed the favorable adsorption of MO dye using agriculture wastes. Figure 7 shows clearly the favorability values of $R_l$ on all three adsorbents examined. Similar results for fitting with the Langmuir model were obtained from previous studies such as adsorption on rice husk and egussi peeling [1] and on biochar [22].

The values of $K_f$ and $n$ are determined by both the intercept and slope, respectively. Figure 8 illustrates the linear plot between $\ln q_e$ vs. $\ln C_e$ which obtained from the experimental results at initial MO dye concentrations with different three agriculture wastes.

The correlation coefficients ($R^2$) are measured as the best fit of experimental results with the adsorption models. The constants of the two models are tabulated in Table (1), it can be seen that the values of correlation factors for each model are close to one.
The second common isotherm adsorption model which can be used to adapt for heterogeneous adsorption processes is the Freundlich model. It can be represented by Equation (5):

\[ q_e = K_f \cdot C_e^{1/n} \]  

(5)

The constant \( K_f \) is represented adsorption capacity of agriculture wastes and \( n \) is represented the adsorption intensity. To clarify the relation between experimental results at optimum values with the Freundlich isotherm model, it can be written this model in linear form as Equation (6):

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

(6)

**Figure 5.** Effect of contact time on removal efficiency.  
**Figure 6.** Langmuir isotherm of adsorption of MO dye on agriculture wastes.  
**Figure 7.** The separation factor for MO dye on agriculture wastes.  
**Figure 8.** Freundlich isotherm of adsorption of MO dye on agriculture wastes.
Table 1. Isotherm model constants and correlation coefficients.

| Adsorbents | Model            | \( q_0 \) (mg/g) | \( K_l \) (l/mg) | \( R^2 \) | Model            | \( K_f \) | n   | \( R^2 \) |
|------------|------------------|-------------------|------------------|----------|------------------|---------|-----|----------|
| DPF        | Langmuir isotherm | 48.79             | 0.1197           | 0.9887   |                  |         |     |          |
| SD         |                  | 50.52             | 0.03095          | 0.9979   | Freundlich isotherm | 6.22    | 2.65 | 0.95     |
| RH         |                  | 48.76             | 0.01827          | 0.9848   |                  | 5.1     | 2.67 | 0.91     |

6. Conclusions
The results of this work showed a good ability of agriculture wastes for the purification of industrial wastewater that contains MO dye. Since these materials available in a large amount, it has proven eco-friendly materials for this treatment. The most influential factor in the adsorption of MO dye on agriculture adsorbents tested was the acidity (pH) of the solution. The optimum value of pH solution that gives maximum removal efficiency was found to be 2. A high percent removal efficiency of MO dye was happened at decreasing initial dye concentration and increasing contact time. It was clearly found that the removal efficiency of DPF > SD > RH. The maximum adsorption capacities at equilibrium contact time were (61 mg/g, 53mg/g, and 47 mg/g) for DPF, SD, and RH, respectively. The equilibrium results of experimental work were analyzed isothermally using Langmuir and Freundlich models and found it's matched very well with two models with high value of correlation coefficients (R²).

References
[1] Tchuifon D, Anagho S, Njanja E, Ghogomu J, Ndifor-Angwafor N and Kamgaing T 2014 Equilibrium and Kinetic Modelling of Methyl Orange Adsorption from Aqueous Solution Using Rice Husk and Egussi Peeling International Journal of Chemical Sciences 12
[2] Lodha B and Chaudhari S 2007 Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions Journal of Hazardous Materials 148 459-66
[3] Fan L, Zhou Y, Yang W, Chen G and Yang F 2008 Electrochemical degradation of aqueous solution of Amaranth azo dye on ACF under potentiostatic model Dyes and Pigments 76 440-6
[4] Ali A H and Dakhil I H 2012 Photocatalytic Decolorization of Methyl Red dye under Solar Light Jornal of Kerbala University 10
[5] Taher I A, Dakhil I H, Kubba Z and Ali A H 2009 Degradation High Concentration of Eosin Yellowish Dye in Heterogeneous Catalyst Solution
[6] Garg V, Gupta R, Yadav A B and Kumar R 2003 Dye removal from aqueous solution by adsorption on treated sawdust Bioresource Technology 89 121-4
[7] Dakhil I H 2015 Adsorption of Lead from Industrial Effluents using Rice Husk International Journal of Engineering and Management Research (IJEMR) 5 109-16
[8] Annadurai G, Juang R-S and Lee D-J 2002 Use of Cellulose-Based Wastes for Adsorption of Dyes from Aqueous Solutions Journal of Hazardous Materials 92 263-74
[9] Ponnumasi V, Vikram S and Srivastava S 2008 Guava (Psidium guajava) Leaf Powder: Novel Adsorbent for Removal of Methylene Blue from Aqueous Solutions Journal of Hazardous Materials 152 276-86
[10] Bharathi K and Ramesh S 2013 Removal of dyes using agricultural waste as low-cost adsorbents: a review Applied Water Science 3 773-90
[11] Alzaydien A S 2015 Adsorption Behavior of Methyl Orange onto Wheat Bran: Role of Surface and pH Oriental Journal of Chemistry 31 643-51
[12] Dakhil I H 2013 Adsorption of Chromium (VI) from Aqueous Solutions using Low Cost Adsorbent: Equilibrium and Regeneration Studies Journal of Engineering 19 1395-406
[13] Shashikala M, Nagapadma.M, Vishnu.P and Gohain K 2014 Adsorption Studies On The Removal Of Methylorange Dye From Aqueous Solution Using Chitosan Powder JEST-M 3 6
[14] Aliabadi H M, Saberikhah E, Pirbazari A E, Khakpour R and Alipour H 2018 Triethoxysilylpropylamine Modified Alkali Treated Wheat Straw: An Efficient Adsorbent For Methyl Orange Adsorption Cellulose Chemistry and Technology 52 129-40
[15] Dakhil I H 2016 A comparative Study for Removal of Dyes from Textile Effluents by Low Cost Adsorbents Mesop. Environ. J, Special Issue A 1-9
[16] Sejie F P and Nadiye-Tabbiruka M S 2016 Removal of Methyl Orange (MO) from Water by Adsorption onto Modified Local Clay (Kaolinite) Physical Chemistry 6 39-48
[17] Belay K and Hayelom A 2014 Removal of methyl orange from aqueous solutions using thermally treated egg shell (locally available and low cost biosorbent) Chemistry and Materials Research 6 31-41
[18] Haddadian Z, Shavandi M A, Abidin Z Z, Fakhru’l-razi A and Ismail M H S 2013 Removal of methyl orange from aqueous solutions using dragon fruit (Hylocereusundatus) foliage Chemical Science Transactions 2 900-10
[19] Mishra Y, Sowmya V and Shanthakumar S 2015 Adsorption Studies Of Basic Dyes Onto Teak (Tectona Grandis) Leaf Powder Journal of Urban and Environmental Engineering 9
[20] Saha T K, Bhoumik N C, Karmaker S, Ahmed M G, Ichikawa H and Fukumori Y 2010 Adsorption of Methyl Orange onto Chitosan from Aqueous Solution Journal of Water Resource and Protection 2 898
[21] Ghosh G, Chakraborty T, Zaman S, Nahar M and Kabir A 2020 Removal of Methyl Orange Dye from Aqueous Solution by a Low-Cost Activated Carbon Prepared from Mahagoni (Swietenia mahagoni) Bark Pollution 6 171-84
[22] Yu J, Zhang X, Wang D and Li P 2018 Adsorption of Methyl Orange Dye onto Biochar Adsorbent Prepared from Chicken Manure Water Science and Technology 77 1303-12
[23] Dakhil I H 2015 Effect of Adding Zinc Oxide on Waste Rubber Tire Powder for Increasing Adsorption of Cadmium (II) from Wastewater The Iraqi Journal For Mechanical And Material Engineering 416-27
[24] Dakhil L I H 2016 Removal of Kerosene from Wastewater Using Locally Sawdust. In: Proceeding of 1st International Conference of Southern Technical University/Iraq. p 17