Cairo University

ADSORPTION OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTION USING DATE PITS

By

YARA ABDELRAHMAN ZAKARIA AMMAR

A Thesis Submitted to the
Faculty of Engineering at Cairo University
In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
In
CHEMICAL ENGINEERING

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Title of Thesis:
Adsorption of malachite green dye from aqueous solution using date pits.

Key Words:
Date pits; Malachite green dye; Adsorption isotherm; Kinetics; Thermodynamic.

Summary:
The aim of the present work is the use of low cost adsorbent such as date pits for the removal of malachite green (MG) dye from aqueous solution. The effect of parameters such as contact time, initial dye concentrations, pH, adsorbent dosage and temperature were performed for MG dye by batch adsorption studies. The optimum operating conditions of adsorption of MG were obtained as contact time 30 min, adsorbent dose of 0.1 g and pH 5. Fitting equilibrium data to Langmuir, Freundlich and Temkin isotherms showed that Freundlich model was more suitable to describe MG. The kinetic studies showed that the adsorption of MG followed pseudo-second-order model. Thermodynamic parameters for MG were calculated. The surface characteristics, pore structure, bonding behavior of the samples are characterized by nitrogen adsorption/desorption (BET), scanning electron microscope (SEM), The Energy Dispersive X-ray analysis (EDX) and Fourier transform infrared spectrometer (FTIR). A single stage batch adsorber was designed for adsorption of MG by DP based on the optimum isotherm.

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Table of Contents

List of Tables .... **iii**

List of Figures .... **iv**

List of Abbreviations .... **vii**

Abstract .... **viii**

CHAPTER 1: Introduction **1**

CHAPTER 2: Literature Survey **3**

2.1. Dyes 3

2.1.1. Classification of dyes 3

2.2. Harmful effects of dyes 7

2.3. Malachite green 8

2.3.1. Physical and chemical properties of malachite green 9

2.3.2. Uses of malachite green 10

2.3.3. Harmful Effects of malachite green 10

2.3.4. Adsorption of malachite green 10

2.4. Methods for the separation and elimination of dyes from waste water 11

2.4.1. Physical treatment methods 12

2.4.2. Chemical treatment methods 14

2.4.3. Biological treatment methods 17

2.5. Adsorption process 17

2.5.1. Adsorption isotherm 18

2.5.2. Kinetic studies 19

2.5.3. Adsorbent for dye removal 20

2.6. Overview on date pits 22

2.6.1. Chemical composition of date pits 23

2.6.2. Industrial uses of date pits 27

2.6.3. Application of date pits as adsorbent 27

CHAPTER 3: Experimental Work **33**

3.1. Instruments 33

3.2. Materials 35

3.3. Experimental procedure 35

CHAPTER 4: Results and Dicussion **40**

4.1. Characterization of adsorbent 40

4.1.1. Scanning electron microscopy ... 40
4.1.2. The energy dispersive X-ray analysis ... 40
4.1.3. BET analysis ... 41
4.1.4. FT-IR analysis ... 42
4.2. Factors affecting adsorption ... 44
4.2.1. Effect of contact time ... 44
4.2.2. Effect of initial dye concentration ... 44
4.2.3. Effect of pH ... 46
4.2.4. Effect of adsorbent dosage ... 47
4.2.5. Effect of temperature ... 48
4.3. Adsorption isotherms ... 49
4.3.1. Langmuir isotherm ... 50
4.3.2. Freundlich isotherm ... 50
4.3.3. Temkin isotherm ... 51
4.4. Adsorption kinetics ... 52
4.4.1. Pseudo-first-order model ... 52
4.4.2. pseudo-second-order model ... 53
4.5. Thermodynamic parameters ... 54
4.6. Process design ... 55
CHAPTER 5: **Conclusions and Recommendations** ... **58**
5.1. Conclusions ... 58
5.2. Recommendations ... 58
References ... 59

List of Tables

Table 2.1: Classification of dyes according to their application ……..……………… 6
Table 2.2: Physical properties of malachite green ……………………….……….. 9
Table 2.1: Classification of dyes according to their application………………………. 6
Table 2.2: Physical properties of malachite green…………………………………….. 9
Table 2.3: Adsorption capacities of various adsorbents used for MG removal…..…. 11
Table 2.4: Advantages and disadvantages of physical treatment methods …………... 14
Table 2.5: Advantages and disadvantages of chemical treatment methods..…….…… 16
Table 2.6: Advantages and disadvantages of biological treatment methods.………... 17
Table 2.7: Chemical composition of date pits ……………………………….….. 23
Table 4.1: Brunauer-Emmett-Teller data for date pits ..…………………………....... 42
Table 4.2: The principle bands in the FTIR spectra of DP before and after adsorption of MG……………………………………………..…………………………….... 44
Table 4.3: Effect of time on MG adsorption by DP, dosage 0.1g, natural pH and room temperature………………………………………………...……………..... 46
Table 4.4: Effect of initial dye concentration on MG adsorption by DP, dosage 0.1g, 30 min contact time, natural pH and room temperature……………………………..... 47
Table 4.5. Effect of pH on MG adsorption by DP, dosage 0.1g, 30 min contact time, room temperature……………………………………………………………….... 48
Table 4.6: Effect of dosage on MG adsorption by DP, 30 min contact time, pH 5 and room temperature.………………..…………………………………………......... 49
Table 4.7: Effect of temperature on MG adsorption by DP, dosage 0.1g, 30 min contact time, pH 5……………………..………………………………………........... 50
Table 4.8: Adsorption isotherm parameters for MG adsorption onto DP …………….… 53
Table 4.9: Adsorption rate constants of pseudo-first-order kinetics and pseudo-second-order kinetics at different initial MG dye concentrations……………….......... 55
Table 4.10: Thermodynamic parameters for MG adsorption onto DP ……...……….. 56

List of Figures

Figure 2.1: Acid red 74………...………………………………………………..... 3
Figure 2.2: Disperse blue 60………………..……………………………………. 4
Figure 2.3: Tyrian purple ………………………………………………………... 4
Figure 2.4: Malachite green ………………………...…………………………… 5
Figure 2.5: copper phthalocyanine …………...………………………………….. 5
Figure 2.6: The presumed form of Sulphur dye …………………………………. 6
Figure 2.7: Chemical structure of malachite green (MG)………………………...… 9
Figure 2.8: Classification of low-cost adsorbents ………..………………………… 21
Figure 2.9: Schematic representation of hydrogen bonding between nitrogen atoms of hydroxyl groups and methylene blue on the date pits surface, cellulose unit, and electrostatic attraction between methylene blue and the date Pits surfaces, cellulose ……………..……………………………………………………. 29
Figure 2.10: Binding mechanism of the Date pits, lignin and cellulose, respectively with Cd^{2+} and Cu^{2+}…………………………………………………..... 30
Figure 3.1: Scanning Electron Microscope (SEM) & Energy Dispersive X-Ray Analysis EDX…………………………………………………………………..... 34
Figure 3.2: Fourier Transform Infrared spectroscopy (FTIR)…………………..….. 35
Figure 4.1.a: SEM of DP before adsorption of MG dye …………..…………….. 41
Figure 4.1.b: SEM of DP after adsorption of MG dye …………..…..………….. 41
Figure 4.2.a: EDX images of DP before adsorption of MG dye………………..... 42
Figure 4.2.b: EDX images of DP after adsorption of MG dye………..……….... 42
Figure 4.3: Brunauer-Emmett-Teller data for date pits……................................ 43
Figure 4.4.a: FTIR of the DP before adsorption of MG dye.……………………. 44
Figure 4.4.b: FTIR of the DP after adsorption of MG dye………………………. 44
Figure 4.5: Effect of contact time on the adsorption of MG dye on DP, dosage 0.1g, natural pH and room temperature. ……………………………..………. 45
Figure 4.6: Effect of initial MG dye concentration onto DP, dosage 0.1g, 30 min contact time, natural pH and room temperature………..……………………. 46
Figure 4.7: Effect of pH on the adsorption of MG onto DP, dosage 0.1g, 30 min contact time, room temperature……………………………………………….. 47
Figure 4.8: Effect of DP dose on MG dye removal, 30 min contact time, pH 5 and room temperature………………………………………………………………. 48
Figure 4.9: Effect of temperature on MG dye removal by DP, dosage 0.1g, 30 min contact time, pH 5. ………………………………………………….………. 49
Figure 4.10: Equilibrium isotherms for adsorption of MG dye from aqueous solutions onto the DP……………………………………………………………….. 51
Figure 4.11: Langmuir isotherm for adsorption of MG on DP…………………... 51
Figure 4.12: Freundlich isotherm for adsorption of MG on DP…………………. 52
Figure 4.13: Temkin isotherm for adsorption of MG on DP.……………………. 52
Figure 4.14: Pseudo first-order kinetics models of MG onto DP.………………. 54
Figure 4.15: Pseudo second-order kinetics models of MG onto DP.……………. 54

Figure 4.16: Thermodynamic fittings of MG onto DP…………………….……. 55
Figure 4.17: A single-stage batch absorber design………………………….… 56
Figure 4.18: Volume of effluent treated versus mass of DP for different percentage removal of 100 mg/l MG dye concentration………………………… 57
Figure 4.19: Volume of effluent treated versus mass of DP for 85% removal at different initial MG dye concentrations………………………………………….. 58

List of Abbreviations

BET:	Brunauer-Emmett-Teller
C_e:	Equilibrium concentration
C_f:	Final concentrations
C_i:	Initial concentration
$C_{o:}$	Initial concentration
C_t:	The concentrations at time t
DP:	Date pits
EDX:	Energy Dispersive X-ray analysis
FTIR:	Fourier transform infrared spectroscopy
ΔG:	The free energy change
ΔH:	The change in enthalpy
K:	Equilibrium constant
K_1:	Pseudo first order rate constant
K_2:	Pseudo second order rate constant
K_F:	Freundlich constant
K_L:	Langmuir constant
K_T:	Temkin constant
M:	The mass of dry adsorbent
MG:	Malachite green
n:	Heterogeneity factor
q_e:	Adsorption capacity at equilibrium.
q_m:	Maximum adsorption capacity
q_t:	Adsorption capacity at time t
R:	Universal gas constant
ΔS:	The change in entropy
SEM:	Scanning electron microscope
T:	The absolute temperature
V:	Volume of solution

Abstract

Presence of dyes in the aquatic systems has become a critical environmental problem. Concerning the economical point of view, the use of low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing textile dyes from wastewater. This study explores the feasibility of using date pits (DP), an agricultural waste as an adsorbent, for removal of malachite green dye (MG) from aqueous solution.

Batch adsorption experiments were carried out for the adsorption of the dye molecule from aqueous solution onto the DP at constant room temperature $25^{o}C$ and agitation speed 240 rpm. Variation effect of different parameters like solution pH, adsorbent dose, contact time, temperature and the initial concentration of the dye were studied. UV/Vis spectrophotometer technique was used for the measurement of concentration of dye before and after adsorption.

Experimental results revealed that optimal adsorption took place at an acidic solution pH. The effective solution pH, adsorbent dose and contact time on the dye removal efficiency were found to be 5, 0.1 g of date pits/ 50 ml of dye solution and 30 min, respectively for the adsorption studies. Fitting equilibrium data to Langmuir, Freundlich and Temkin isotherms showed that Freundlich model is an appropriate model to explain the adsorption isotherm. Adsorption kinetics were determined using pseudo first order and pseudo second order models and it was found that the adsorption process follows pseudo second order model. The thermodynamic calculations indicated the exothermic and spontaneous character of adsorption of MG dye on DP.

The characterization of the DP before and after adsorption was accomplished by FTIR, SEM, BET and EDX measurements. The FTIR results showed various functional groups, i.e., hydroxyl and carboxyl, which were identified as potential adsorption sites responsible for binding malachite green to adsorbent. SEM analysis showed the active sites available for adsorption on the adsorbent surface. The specific surface area of DP was determined as 1.1324 m^2/g, obtained by the BET nitrogen gas adsorption measurements. EDX spectroscopy used for demonstrated that the surfaces of the sorbents contain various elements. A single stage batch adsorber was designed for adsorption of MG dye by DP based on the optimum isotherm. Generally the results indicate that DP may be used as a low cost adsorbent, alternative for treatment of effluents containing malachite green dye in water.

Chapter 1: Introduction

Industrial effluents are one of the main causes of environmental pollution because the effluents discharged from dyeing industries are highly colored, having a large amount of suspended organic solids [1]. Synthetic dyes are widely used in various industries, such as leather, paper, plastic, printing, textile and cosmetics, and their colored products. This dyes directed discharge to the nearest water sources such as lakes, rivers and seas. Most commercial dyes are chemically stable and are so difficult to remove from wastewater [2]. Wastewater-containing dye discharged into water bodies causes deterioration in water quality and may also have a significant impact on human health because of carcinogenic, toxic, and mutagenic effects of some dyes or their metabolites [3].

Although many adsorbents have been reported for removing some common dyes [4 -15], such as methyl orange, methylene blue (MB), malachite green (MG) and rhodamine B, it is still a challenge to search for adsorbents that are more effective, because the water-treatment industry requires highly effective, eco-friendly and low-cost adsorbents that are available in tonnage quantities. Malachite green (MG) is an organic compound that is classified as a basic dye used in the dyestuff industry and has been used traditionally as a dye for materials such as leather, silk and paper as well as in distilleries [16]. In addition, MG is also used as a fungicide, antiseptic and antibacterial in the aquaculture industry to control fish parasites and disease [17]. The products formed after the degradation of MG are unsafe having carcinogenic potential [18]. However, this dye has emerged as a controversial antimicrobial and has been banned for aquaculture use because it is highly cytotoxic to mammalian cells and acts as a tumor-enhancing substance, thereby posing significant risk to human health but also is a major cause of creating tumor in liver [19]. Therefore, the removal of malachite green from wastewater before discharge into receiving waters is very important to prevent environmental pollution in aquatic ecosystems.

Various physical, chemical and biological treatment methods have been used for the removal of dyeing effluents, such as advanced oxidation, combined chemical and biochemical process, adsorption membrane filtration, aerobic and anaerobic digestion [5, 9, 11]. Chemical treatment using flocculating agents or coagulating to remove dyes is not efficient for highly soluble dyes [20]. On the other hand, biological treatment is incapable of removing dyes from effluents on a continuous basis, whereas physical treatments such as precipitation, electrochemical destruction [21], membrane filtration, ion exchange, irradiation, and ozonation [22] have been used to treat dye-containing wastewater. Most of these processes are expensive and lead to the generation of sludge or formation of by-products [23]. Because of being inefficient and expensive, most of these processes are not used on large scale [24]. Considering the cost, effectiveness and environmental impact of these processes, adsorption is a more competitive treatment process for dye removal because of its simplicity, high efficiency and wide-ranging availability [9, 10].

So people try to develop cheaper and more effective adsorbents to remove dyes and find an alternative method from different starting materials such as bagasse pith [25], saw dust [26], rice husk [27,28], fly ash [29], melon husk [30], potato peel [31], hen feather [32], polar leaf [33], date pits [34], walnut shell [35], clay [36], papaya seed [37], Trapa bispinosa's peel and fruit [38], and pine cone powder [39].

Dates are fruits of palm trees known to the middle east region. This tree is adapted to dry climate and its fruit was the main source of energy for humans and animals. Date fruit flesh of most varieties contains high sugars (61–84 %), ash (2–4 %), low protein contents (2–4 %) and 0.1–0.5 % fats, and appreciable amount of potassium [40]. Date pits are a co-product of the date industry which represents about 10–15 % of the fruit and for a lot of years was used as animal feed [41, 34]. The average composition of the date seeds is about 6 % proteins, 1.5 % ash, 11 % fats, 52 % dietary fiber, and contains considerable amount (3.5 – 4.5 g/ 100 g) of phenolics [42, 43]. DP can be a low-cost source of dietary fiber and antioxidants [44].

The aim of this work is the use of date pits as low cost adsorbent for the removal of malachite green dye from aqueous solution. The effect of parameters such as contact time, initial dye concentration, pH, adsorbent dosage and temperature were performed in batch experiments. Adsorption isotherm, kinetic studies, thermodynamic parameters and single stage adsorber design were carried out. Therefore, effective methods for the removal of MG have been searched for in many laboratories.

Chapter 2: literature survey

2.1. Dyes

In former times, dyes were gained from mineral sources with the exception of some very expensive organic dyes from natural sources, such as of carmine from the Cochineal insect, purpur from the mollusk Murex spp and scarlet from the Kermes insect. Current time, dyes are not only obtained from the natural sources but also there are synthetic dyes. Dyes are used in a lot of industries such as paper, leather and textile. Dye is a synthetic or natural colouring material, even if insoluble or soluble, that impart its colour to a material by staining [45].

The world-use of reactive dyes increased from 60.000 tons in 1988 to 178.000 to 182.000 tons in 2011. Today, more than 10,000 different dyes are produced annually for different applications. However, 90% of the textile products are used at the level of 100 tonnes per annum or less, making for the huge variety of dyes used in the textile industry [46].

2.1.1. Classification of dyes

Dyes can be classified according to their application and their chemical structure. In term of chemical structure, dyes can be organic or inorganic compounds, both groups can be subdivided into synthetic and natural compounds. According to the dyeing method, dyes can be divided into direct, anionic or disperse dyes, here based on their application [47].

2.1.1.1. Dye Classification Based on the Chemical Structure of the Dye

2.1.1.1.1. Azo compounds

Azo compounds have the azo bond (two nitrogen atoms double bonded to each other: N=N) (Fig ٢.١). Each nitrogen atom is bound to another group, that most often is an aryl group. There are dyes with one, two, three and even four azo groups in the molecule. The aromatic rings usually have nitro, sulphate, hydroxyl or chloro groups attached, either to increase the solubility of the dye in water or to enhance its interactions with the substrate. Today, azo dyes are widely used because of their cost effectiveness and good performance [48].

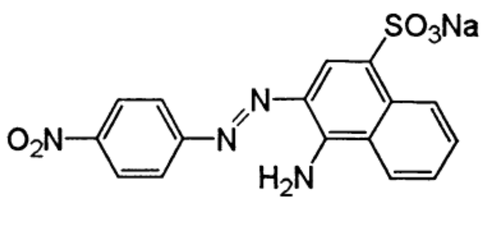

Fig ٢.١ Acid red 74.