Removal of malachite green oxalate from aqueous solution using sawdust as a biosorbent

by

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the requirements for the
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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July 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and the work contained herein have not been undertaken or done by specified sources or persons.

LE PHAN QUYNH LINH

ABSTRACT

Dyes are using in many industries such as textile, paper and ink, printing, pharmaceuticals, food industries…. They are highly visible contaminants and often toxic. Many dyes are stable to light and difficult to degrade, hence contaminants due to dyes pose to not only public health concern but also environmental problems. Due to the toxic nature of most dyes to human, plants and micro-organisms, colored waste water cannot be discharged without adequate treatment. Many methods to remove dye from industrial waste water are used such as biodegradation, coagulation-flocculation, adsorption, ozone treatment…. These methods are either not efficient or expensive.

This study deals with low cost, locally available bio-sorbents. The literatures are reviewed using rich sources of information from library books, special journals and papers and internet. By studying the references, the methodology to study potential of using biosorbents to remove Malachite Green Oxalate has been come out. There are four main experiments will be conducted including factors influence dye biosorption, equilibrium test, kinetic study and effect of different forms of sorbent on biosorption of dye.

The project can be the solution for current issue not only on colored waste water but also solid waste disposal. Since the bio-materials used are the waste from industries and agriculture. Furthermore, the result of this project can be used as reference for further study on biosorption using other types of biomaterial.

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Hopefully, the knowledge and findings gained from this project will be essential for us in the future.

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CHAPTER 1
INTRODUCTION

1.1. PROJECT BACK GROUND

Presently, it was estimated about 10,000 of different commercial dyes and pigments exist and over 7 x 10^5 tones are produced annually worldwide [1]. Dye are used in various industrial processes such as dyeing and printing, textile, paper and ink manufacturing, cosmetics, pharmaceuticals and food industries. Waste water generated by those processes containing a high concentration of colored organic which is highly visible, often toxic compounds. It is estimated that an average of 30% of applied reactive dyes end up in effluent in the alkaline dye bath because their hydrolyzed form has no affinity for textile fabrics. In some situations, the concentration may be as high as 800 mg/L [2]. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [3].

Dyes are classified according to structure including acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes which are either cationic or nonionic or anionic type. Anionic dyes are the direct, acid and reactive dyes. The highest rates of toxicity were found amongst basic and diazo direct dyes [4]. Many dyes are difficult to degrade. They are generally stable to light, oxidizing agents and are resistant to aerobic digestion [5]. Because of effect of dyes and color that discharged into rivers, water supply for public may not meet the drinking water quality standards. Dyes and their degradation products may be carcinogen and toxic if these effluents are treated inefficiently before discharging to the rivers or streams, they could bring negative impact to human health such as dysfunction of kidney, reproductive system, liver, brain and central nervous system [6]. Therefore, dye removal has become an important but challenging area of waste water treatment.

1.2. PROBLEM STATEMENT

"In China, about 1.6 billion tons of dye-containing wastewater is produced every year, but only a small proportion of this is recycled," says Juncheng Hu, who worked on the Chinese side of the project at the South-Central University for Nationalities in Wuhan (2009).

There are three ways to reduce pollution: use of new, less polluting technologies; effective treatment of effluent so that it conforms to specified discharge requirements; and recycling waste several times over before discharge [7]. The most popular method is to have effective treatment of effluent. Currently, there are many physical, chemical, and biological methods to remove dye from industry effluent such as: biodegradation, coagulation-flocculation, membrane separation, adsorption…. The advantages and disadvantages of some methods available are compared in table 1.

Table 1.1: Advantages and disadvantages of some of current dye removal methods [7]

Processes	**Advantages**	**Disadvantages**
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability of dyes
Coagulation–flocculation	Elimination of insoluble dyes	Production of sludge blocking filter
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Cost of activated carbon
Ozone treatment	Good de-colorization	No reduction of the COD
Electrochemical processes	Capacity of adaptation to different volumes and pollution loads	Iron hydroxide sludge
Reverse osmosis	Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure
Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from mono-valent salts. Treatment of high concentrations	-----
Ultrafiltration–microfiltration	Low pressure	Insufficient quality of the treated wastewater

Considering the pros and cons of dye removal methods and the persistence in nature and non biodegradable characteristics of dye, adsorption has been used. Among all the adsorption process the activated carbon has been shown to be one of the most efficient adsorbent for the removal of dyes from effluents. However, it is an expensive material except for easy regeneration, but this adds to the operational costs. The utilization of alternative low-cost materials with high adsorption activity to solve environmental problems has received considerable attention over the recent years. Adsorbents from agriculture by-products are particularly advantageous due to their low cost and high availability as starting materials. Furthermore, the waste is used for another purpose so that there will be less waste disposed to environment. That will improve the environmental issue which is the big problem in waste disposal to Malaysia as well as many other countries around the world. Many other materials, for example, sugarcane bagasse [1], rice hull [5], coffee husk [8], rice straw [9], degreased coffee bean [10], …. have been tested as adsorbent on remediation of contaminated water.

In this work, I am attempting to utilize sawdust, taken from a furniture workshop, as an alternative low-cost sorbent in the removal of malachite green from aqueous solutions. Malachite green is widely used in distilleries for coloring purposes. Malachite green has properties that make it difficult to remove from aqueous solutions and also toxic to major microorganisms. Though the use of this dye has been banned in several countries and not approved by US Food and Drug Administration, it is still being used in many parts of the world due to its low-cost, ready availability and efficacy and to lack of a proper alternative. Its use in the aquaculture practice in many countries, including Malaysia has not been regulated. Malachite green when discharged into received streams will affect the aquatic life and causes detrimental effects in liver, gill, kidney, intestine, gonads and pituitary gonadotrophic cells. Therefore, the treatment of effluent containing such dye is of interest due to its esthetic impacts on receiving waters. [11]

1.3. OBJECTIVES AND SCOPE OF STUDY

1.3.1 Objectives:

The main objectives of this project are:

- To define a biomaterial that can be used as an adsorbent in treating waste water from dyeing industries
- To characterize the selected bio-adsorbent before and after process
- To study effect of different operating condition on the performance of the adsorbent
- To modify the adsorbent to enhance the performance.

The bio-sorbent used needs to meet requirements listed below:

- Low cost materials such as agricultural waste or industrial waste,
- High adsorption capacity, and
- High availability.

1.3.2 Scopes of work

- Study factors that mainly influence the sorption of dye: pH, initial concentration of dye, initial dose of bio-sorbent, temperature of process, sorbent particle size, form of biomaterial (raw, treated chemically or thermally) to optimize the best condition of bio-sorption of certain dye and sorbent.
- Study the kinetic of bio-sorption of dye.
- Study the change in pH, dye concentration after sorption process.
- Compare sorption capacity of different biomaterials to have different alternatives sorbent can be used due to availability.

CHAPTER 2

LITERATURE REVIEW

In this study, there are three isotherm can be used for describing the experimental results, namely Freundlich isotherm, Langmuir isotherm and multilayer adsorption (MLA) isotherm.

2.1 FREUNDLICH ADSORPTION ISOTHERM

The Freundlich isotherm is used for non-ideal adsorption on heterogeneous surfaces. The heterogeneity arises from the presences of different functional groups on the surface, and the various absorbent-absorbate interactions

The Freundlich Adsorption Isotherm is mathematically expressed as [11]:

$$q_e = K_F C_e^{1/n} \tag{1}$$

where

Ce: the equilibrium concentration (mg/L),

q_e: the amount of dye adsorbed (mg/g),

K_F: Freundlich adsorption constant, and

1/n: a measure of the adsorption intensity.

2.2 LANGMIUR ADSORPTION ISOTHERM

The derivation of the Langmuir isotherm assumes ideal monolayer adsorption on a homogenous surface. It is expressed by [12]:

$$q_e = \frac{q_m K_a C_e}{1+ K_a C_e} \tag{2}$$

where

Ce: the equilibrium concentration (mg/L),

q_e: the amount of dye adsorbed (mg/g),

q_m: q_e for complete monolayer adsorption capacity (mg/g), and

K_a is the equilibrium adsorption constant (L/mg).

- *Assumptions in the Langmuir Model [13]*

Langmuir had to make several assumptions in order to derive an (admittedly over-simplified) adsorption expression:

- all surface sites have the same adsorption energy for the adsorbate (and a similar statement for the solvent)
- adsorption (of either solvent or adsorbate) at one site doesn't affect the availability of (block) the next site to adsorb solvent or adsorbate
- adsorption (of either solvent or adsorbate) at one site doesn't affect the energy of adsorption of the neighboring sites (as they adsorb either solvent or adsorbate)
- the activity of the adsorbate is directly proportional to its concentration (and a similar statement for the solvent)

These assumptions are not satisfied for many real-life cases. However, the simplified version gives insight into the dependence of surface coverage on concentration in solution. The driving force for adsorption on the surface is proportional to the concentration of the species in solution. The driving force for desorption from the surface is proportional to the fractional surface coverage of the species on the surface.

Basic forms of Langmuir sorption isotherm have reasonable agreement with a large number of experimental isotherms including those have different interfaces between the two phases. Therefore, the Langmuir sorption isotherm is most widely used for the sorption of a solute from a liquid solution assuming the sorption takes place at specific homogeneous sites within the sorbent. Furthermore, it also assumes that once a dye occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force times an area. The driving force is the concentration of the solution and the area is the amount of bare surface. If the fraction of covered surface is φ, the rate per unit of surface is:

$$r_a = k_a C(1 - \varphi) \tag{3}$$

Desorption from the surface is proportional to the amount of surface covered:

$$r_d = k_d \varphi \tag{4}$$

where k_a and k_d are the rate constants,
r_a the sorption rate, r_d the desorption rate,
C the concentration in the solution and
φ the fraction of the surface covered.

The two rates are equal at equilibrium and we find that:

$$\phi = \frac{k_a C_e}{k_d + k_a C_e} \tag{5}$$

and

$$K_a = \frac{k_a}{k_d} \tag{6}$$

Since q_e is proportional to φ:

$$\phi = \frac{q_e}{q_m} \tag{7}$$

The saturated monolayer sorption capacity, q_m, can be obtained. When φ approaches 1, then $q_e=q_m$.

The saturated monolayer isotherm can be represented as a linear form:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{8}$$

The above equation can be rearranged to the following:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \tag{9}$$

where:

- C_e is the equilibrium concentration (mmol/dm^3)
- q_e the amount of dye sorbed (mmol/g),
- q_m is q_e for a complete monolayer (mmol/g),
- K_a the sorption equilibrium constant (dm^3/mmol).

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/K_a q_m$.

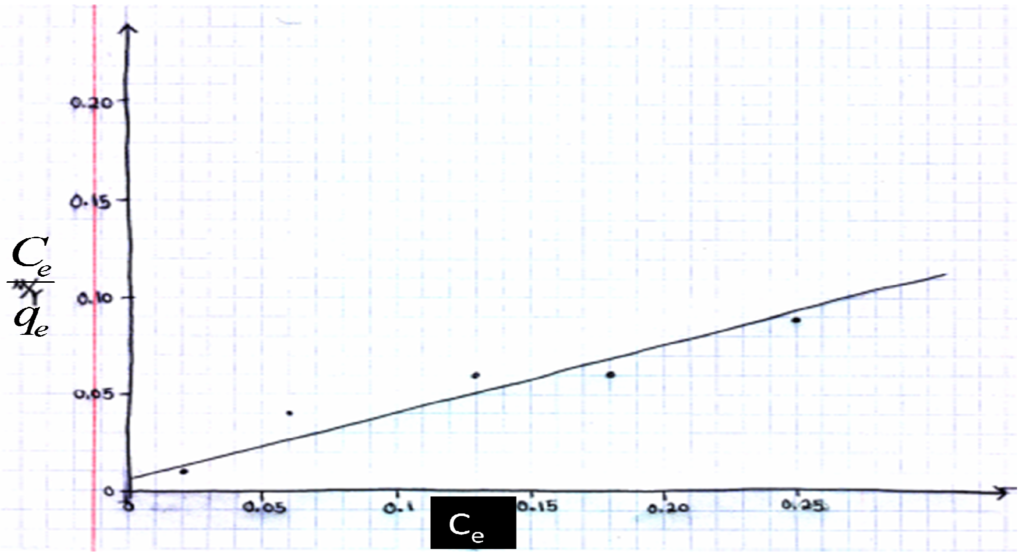


Figure 2.1: C_e/q_e versus C_e graph

2.3 MUTILAYER LANGMIUR ADSORPTION ISOTHERM

If the adsorption takes place in a multilayer equilibrium on a homogenous surface, the total multilayer adsorption capacity (Γ, mg/g) can be expressed by the following equation [10]:

$$\Gamma = \frac{\Gamma_m K_1 C_e[1-(K_2 C_e)^n]}{(1-K_2C_e)[1+(K_1-K_2)C_e]} \tag{10}$$

where

Γ_m: monolayer adsorption capacity (mg/g),

K_n : equilibrium adsorption constant of the *n*th layer (L/mg) and

C_e : equilibrium concentration of solution (mg/L).

In the case of multilayer adsorption, the amount of dye adsorbed in a subsequent layer must be smaller than that in the previous layer.

Therefore, the term $(K_2C_e)^n \approx 0$, and Eq. (1) can be simplified to:

$$\Gamma = \frac{\Gamma_m K_1 C_e}{(1-K_2C_e)[1+(K_1-K_2)C_e]} \tag{11}$$

It can be seen that for ideal monolayer adsorption K_2 will have a value of zero, and Eq. (10) will be reduced to the monolayer Langmuir isotherm of Eq. (11).

CHAPTER 3
METHODOLOGY / PROJECT WORK

3.1. MATERIALS

3.1.1 Dye solution – Malachite Green Oxalate

- Formula: $[(C_{23}H_{25}N_2)(C_2HO_4)]_2(C_2H_2O_4)$
- Structure:

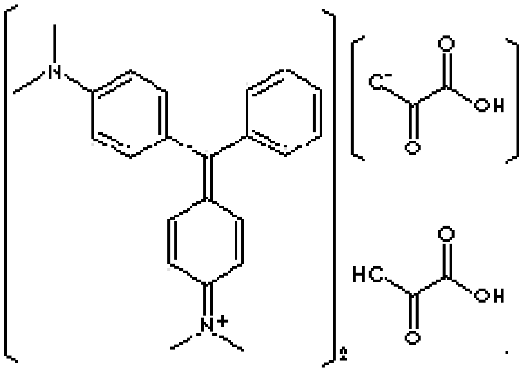
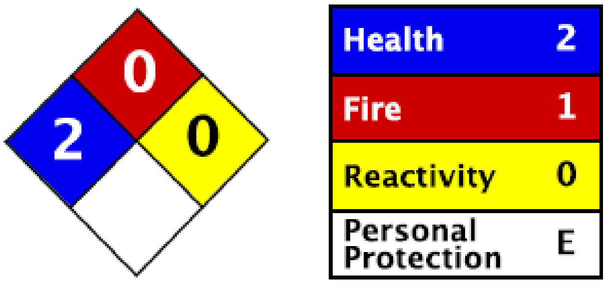


Figure 3.1: Molecular structure of Malachite Green Oxalate

- Molecular weight: 927.02
- Synonyms:
  - Bis[[4-[4-(dimethylamino)benzhydrylidene]cyclohexa-2,5-dien-1-ylidene] dimethylammonium] oxalate, dioxalate;
  - N,N,N',N'-Tetramethyl-4,4'-diaminotriphenylcarbenium oxalate;
  - C.I. 42000; Malachite green oxalate; Victoria Green B; Basic Green 4; Diamond Green B

Malachite green is a basic dye. Basic dyes are salts of the colored organic bases containing amino and amino groups and also combined with a colorless acid, such as hydrochloric or sulfuric. They are brilliant and most fluorescent among all synthetic dyes. Basic dyes are cationic which has positive electrical charge and are used for anionic fabrics which are negative-charge-bearing, such as wool, silk, nylon, and acrylics where bright dying is the prime consideration. Malachite green does not contain the mineral malachite; the name comes from the similarity of color. This chemical dye is primarily designed to be used as a dye for silk, leather, and paper. Malachite green stains background to the surrounding tissue blue-green. Malachite green is used as a pH Indicator between pH 0.2 (green) - 1.8 (blue-green).



Health	2
Fire	1
Reactivity	0
Personal Protection	E

Figure 3.2: Hazardous potential of Malachite Green Oxalate

MSDS of malachite green is shown in appendix A.

3.1.2 Bio-sorbents:

There are many bio-sorbents available in market and industries. Considering some criteria required in the objectives and availability in local factory, bio-sorbents that will be used in this study is sawdust.

3.2. PREPAREATION

3.2.1 Adsorbate

Dye is used without further purification. The dye stock solutions are prepared by dissolving 30mg of dye into 1L of distilled water to obtain 1L solution with concentration of 30mg/L. The experimental solutions can be obtained by diluting the dye stock solution in accurate proportions to have different initial concentration.

3.2.2 Absorbent

- Wash the collected biomaterial with tap water to remove soil and dust.
- Spray it with distilled water and then dry in an oven at 100^{o}C for 24h to obtain constant weight.
- Crush the material into powder, sieved to different particle size ranges of 45-63µm, 63-125 µm, 125-250 µm, 250-500 µm and 500 µm-1mm.

- Preserve in plastic boxes for further uses.

3.2.3 Characterization of the sorbent

The surface functional groups of the OPTF were detected by Fourier transform infrared (FTIR) spectroscope. In addition, Scanning electron microscopy (SEM) analysis is carried out for the sawdust to study the surface morphology before and after dye adsorption. Finally, the porosmetry test is also performed to study the surface area, pore distribution and porosity of the material.

3.3. EXPERIMENTS

3.3.1 Calibration curve

Before proceed with the main experiment, the calibration curve needs to be done. It is used as the reference for the concentration of dye solution.

Certain concentration of solution gives certain wave length. A series of solutions of a sample is prepared with different concentrations. The wave length of these solutions are measured and plotted versus solution concentration.

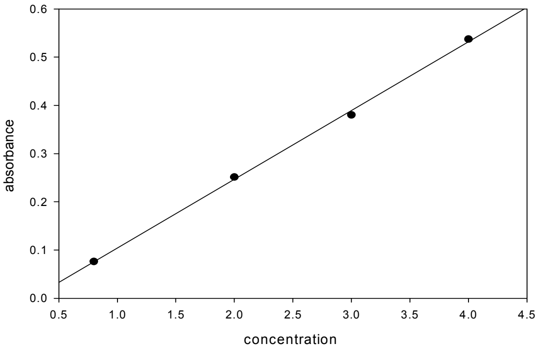


Figure 3.3: Sample of a possible calibration curve

A calibration curve is a valuable tool in finding the concentration of an unknown solution. Once the calibration curve is prepared, the corresponding concentration of solution as well as the amount of dye adsorbed is known.

3.3.2 Exp 1: Equilibrium isotherm

Batch equilibrium study is carried out by adding a fixed amount of 45-63μm sorbent (0.1g) into 250-mL Erlenmeyer flasks containing 100mL of 30ppm dye solution at pH 5. The flasks are agitated in an isothermal water-bath shaker at 130rpm and 40° C. Aqueous samples are taken from the solutions at 5, 10, 20, 30, 60, 90, 120, 150 and 180 mins.

Repeat the experiment with dye solution which has concentration of 20ppm and 10ppm.

The concentrations are analyzed using a double beam UV/vis spectrophotometer at 617.5 nm.

The amount of equilibrium adsorption, qe (mg/g), is calculated by:

$$q_e = (C_o - C_e)\frac{V}{W} \tag{12}$$

The removal efficiency is computed according to Eq. (13)

$$Removal\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{13}$$

where

C_o, C_e (mg/L): liquid-phase concentrations of dye at initial and equilibrium, respectively.
V is the volume of the solution (L), and
W is the mass of dry sorbent used (g).

3.3.3 Exp 2: Effect of sorbent size

The effect of sorbent size is study by agitating 0.1g of sawdust and 100mL of dye solution using water bath shaker at 130rpm and 40°C until equilibrium reaches. There will be 5 size ranges: 45-63μm, 63-125 μm, 125-250 μm, 250-500 μm and 500 μm-1mm considered. Solution pH used in this experiment is 5.

3.3.4 Exp 3: Effect of solution pH

Batch sorption experiment is carried out in water bath shaker at 130rpm and 40°C. 0.1g sorbent is put into 250-mL Erlenmeyer flasks containing 100mL of different initial pH.

The pH of the dye solution is varied from 3 – 9 by using acid – base combination NaOH (0.1M) and HCl (0.1M). The equilibrium time obtained from experiment 1 will be applied for this experiment. The pH which gives the best performance of absorption will be used for next experiment.

3.3.5 Exp 4: Effect of sorbent dosage

This experiment is taken place to find the optimal dose of sorbent for 100ml of 30ppm dye solution. The sample is agitated in bath shaker at 130rpm and 40°C. The sorbent doses used are 0.1, 0.2, 0.3 and 0.4g. Other parameters are taken from previous experiment.

3.3.6 Exp 5: Effect of solution concentration

100mL dye solutions that have concentration varied from 5-30ppm are contained in 250mL conical flasks with 0.1g of 45-63 µm sorbent in each flask. All sets are place in isothermal water bath shaker at 130rpm and 40°C. Contact time and pH are taken from the result of exp1 and 2, respectively.

3.3.7 Exp 6: Effect of temperature

Conduct the experiment in different temperature conditions in range of 30°C – 80°C using water bath shaker at 130rpm. 0.1g sorbent and 100mL solution is in 250mL flask. Apply result of previous experiments for other parameters.

CHAPTER 4

RESULT AND DISCUSSION

4.1. CALIBRATION CURVE

The calibration curve was obtained using UV-Vis. At first, the spectrum is run to get the maximum wave length of 617.5nm. Then, using photometric function to establish standard calibration curve between concentration and absorbance at λ_{max}=617.5nm. The calibration curve will be used to determine the concentration of unknown dye solution.

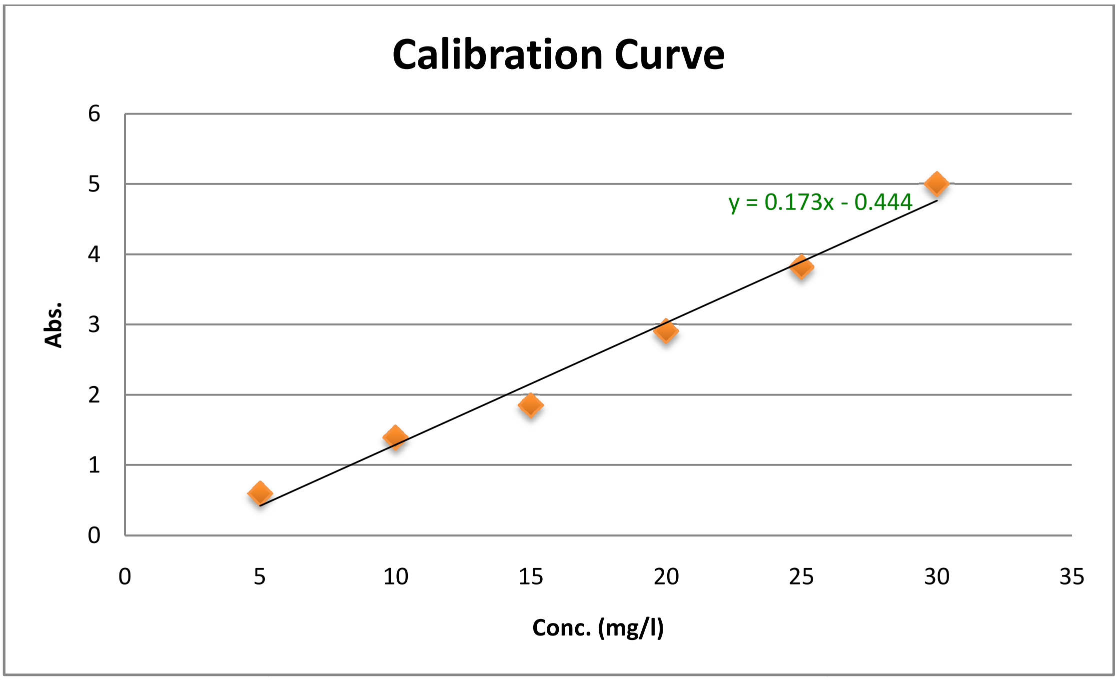


Figure 4.1: Calibration curve

4.2. CHARACTERISTICS OF ADSORPBENT

4.2.3 Scanning Electronic Microscopy (SEM) Analysis:

Figure 4.2 show the SEM micrographs of sawdust before dye adsorption. The sawdust exhibits cylinder-like, uneven and rough surface.

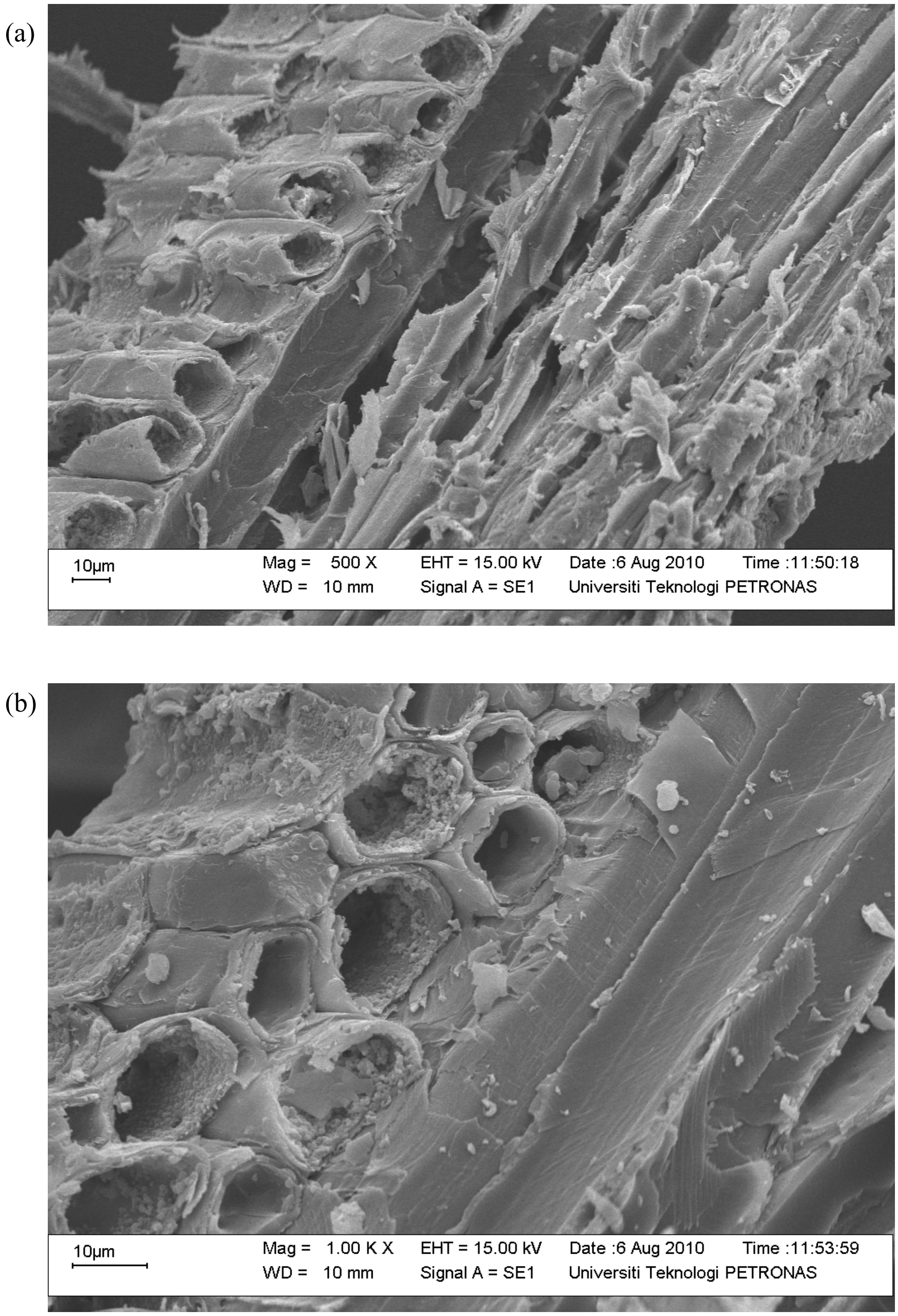


Figure 4.2 (a), (b): SEM micrographs of sawdust before dye adsorption with magnitude of 500x and 1000x respectively.

4.2.4 FTIR (Fourier Transform Infrared Spectroscopy) Analysis:

The purpose of FTIR spectrum is to know the functional groups of adsorbent surface before and after adsorption process. By studying that, the functional group(s) participating in the adsorption process can be indicated. The FTIR was done using FTIR – 8400s. In figure 4.3, FTIR spectrum of sawdust show peaks at range 3949.94 – 3705 (O-H stretching), 3500 – 3282.62 (N-H stretching), 2923.88 (C-H stretching), 1735.81 (C=O stretching), 1598.88 (N-H stretching), 1317.29 – 1035.70 (C-O), 896.84 (RR’C=CH_2) and 680.83 – 567.03 (Si-H rocking).

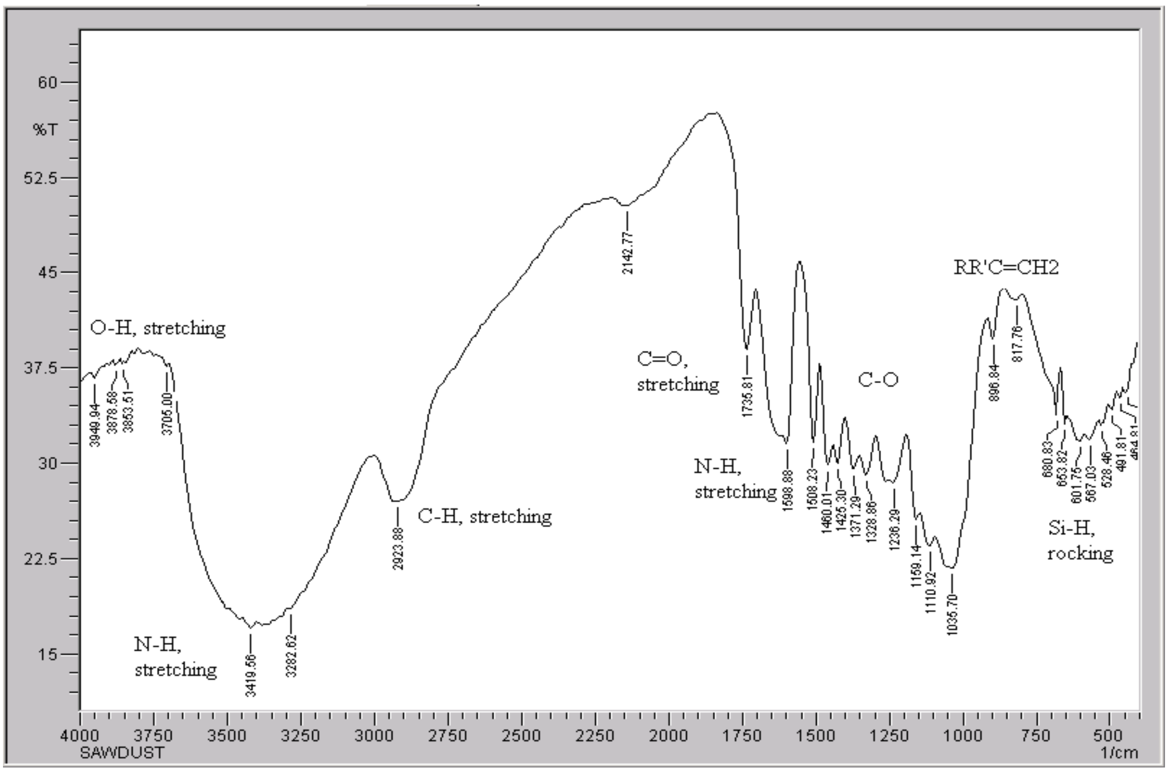


Figure 4.3: Functional group of sawdust surface

4.3. EQUILIBRIUM STUDY

In order to optimize the contact time of sawdust and dye in the solution, the samples are taken from the solutions at 5, 10, 20, 30, 60, 90, 120, 150 and 180 mins. The absorbance of samples is measured by UV-Vis and using the calibration curve, concentration of samples is defined. As the result, the adsorption process reaches equilibrium after 150mins.

Table 4.1: Data of equilibrium study

Time (mins)	**Absorbance**	**Concentration (ppm)**
5	3.702	23.897
10	3.519	22.844
20	3.022	19.976
30	2.584	17.452
60	2.292	15.771
90	1.895	13.481
120	1.642	12.025
150	1.5483	11.485
180	1.5476	11.481

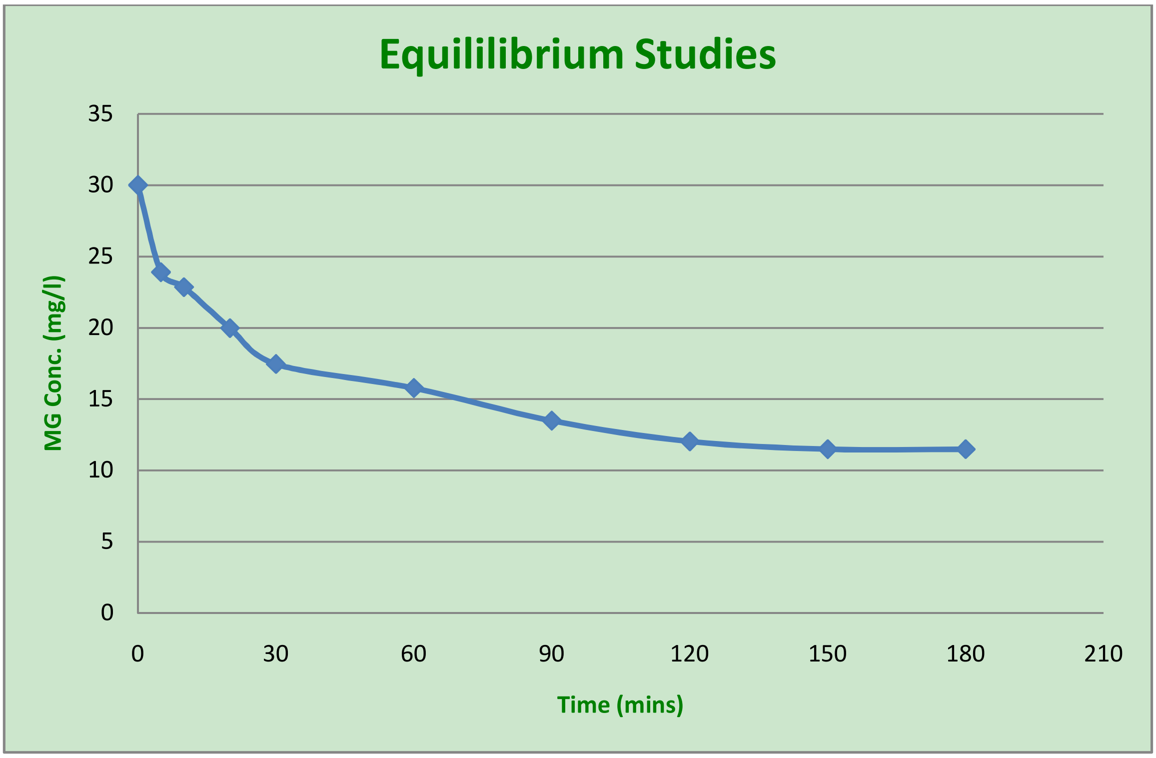


Figure 4.4: Equilibrium Curve

The removal efficiency is calculated using eq. 13 with $C_0 = 30$ppm and $C_e = 11.485$ppm:

$$The\ removal = \frac{30 - 11.485}{30} \times 100 = 61.7\%$$

Using eq. 12, the amount of dye adsorbed with:

$C_0 = 30$ppm

$C_e = 11.485$ ppm

$V = 0.1$L

$W = 0.1$g

$$q_e = \frac{(30 - 11.485) \times 0.1}{0.1} = 18.515 (mg/g)$$

The following experiments will be carried out in at least 2.5h to make sure that the equilibrium has been reached.

4.4. EFFECT OF ADSORBENT SIZE

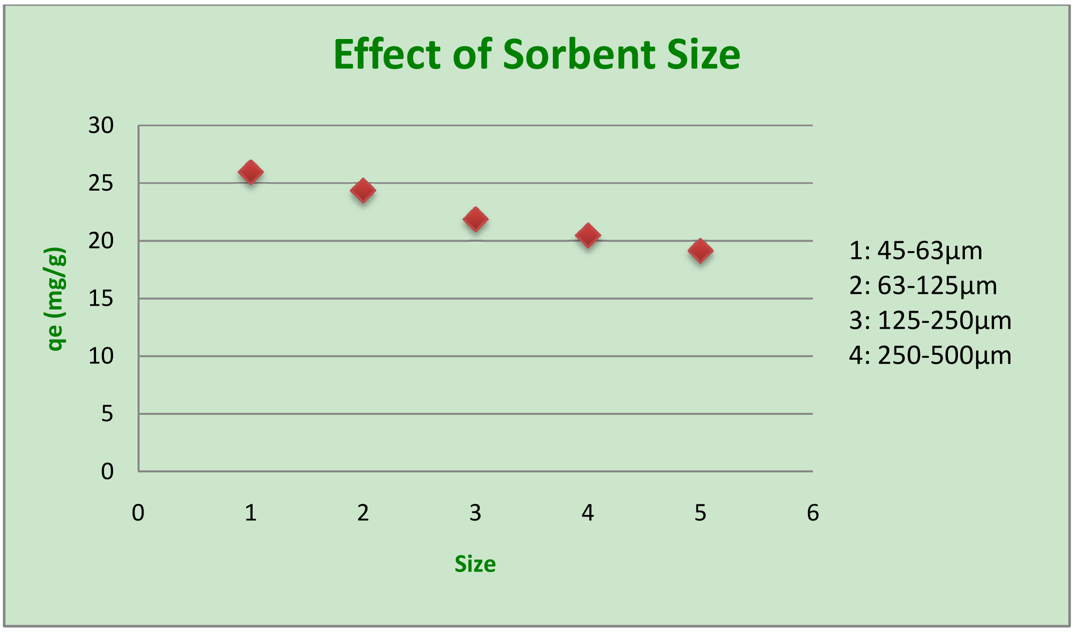


Figure 4.5: Effect of sorbent size on malachite green adsorption

According to equilibrium study, this experiment was taken place in 2.5h that equilibrium is reached. Four size ranges of sorbent were used which are 45-63µm, 63-125µm, 125-250µm, and 250-500µm.

From the graph in figure 4.5, it is shown that the smaller the size of sorbent is, the more dye is adsorbed. It can be explained based on the surface area. With same amount of sorbent, the smaller size means the more particles are. Therefore, there will be larger area for dye to attach to sorbent surface. The size of 45-63µm is the most effective in this study which remove 86.5% of dye in solution.

Using eq. 13:

$$The\ removal = \frac{30 - 4.046}{30} \times 100 = 86.5\%$$

4.5. EFFECT OF INITIAL pH

The experiment was done at 40^{O}C in the water bath with 130rpm shaker. The most effective size, 45-63µm was used in 100mL 30ppm solution. Seven (7) samples were prepared for pH varying from 3-9.

Malachite Green Oxalate is basic dye which releases dye cations in solution. The adsorption of this positively charged dye is influenced by the charge of sorbent surface. Therefore, solution pH has big influence to the adsorption of dye. The effect of intial pH of dye solution is presented in figure 4.6.

The result shows that availability of negatively charged groups is necessary for the adsorption of basic green. It is shown in the graph that the adsorption process is not favorable at pH less than 5 and the pH in wide range above 5 does not have significant effect on the adsorption. It is because of the presence of H_3O+ in highly acidic solution which has pH less than 5. In a system that H+ competes with dye cation, there will be less chance for dye to be adsorbed to the sawdust surface. In contrast, when the pH increases more negatively charge surface available thus facilitating greater amount of dye cation removal.

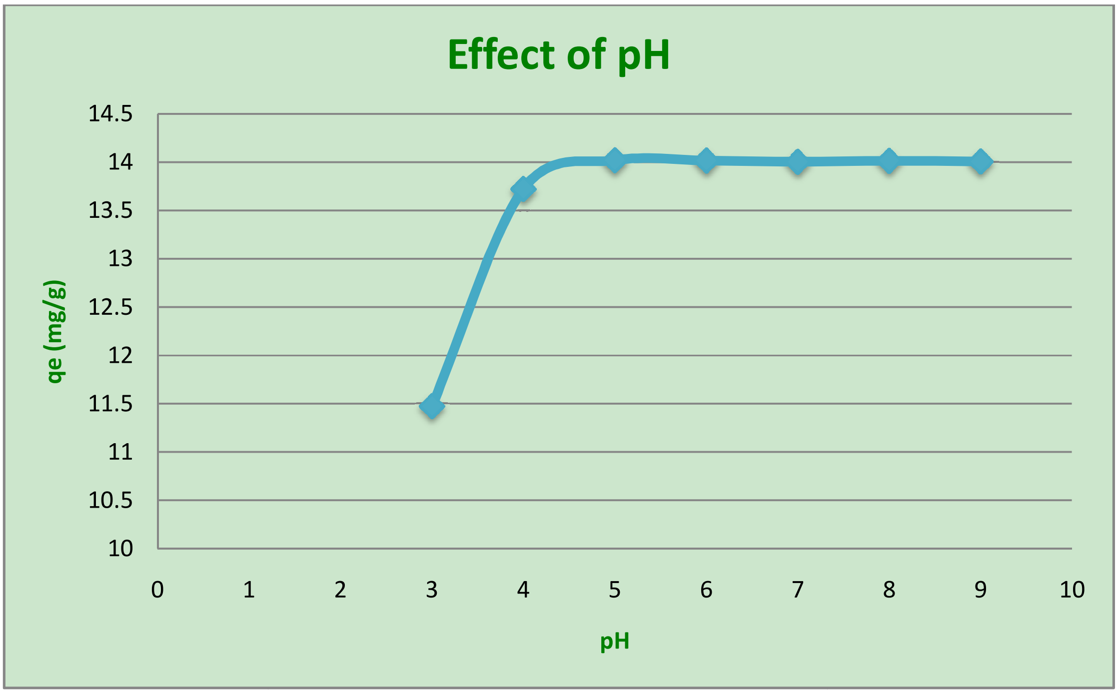


Figure 4.6: Effect of pH on adsorption process

4.6. EFFECT OF ADSORBENT DOSAGE

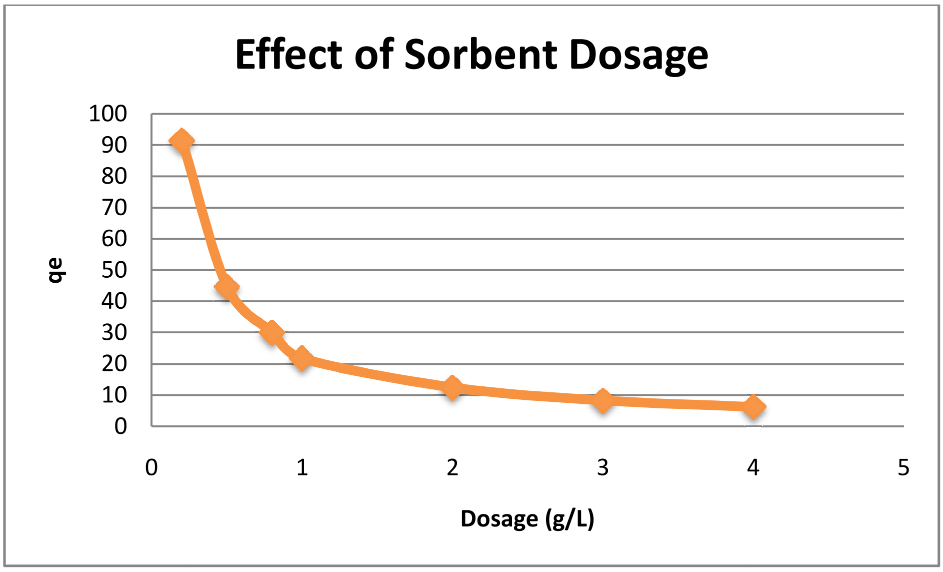


Figure 4.7: Effect of sorbent dose on adsorption process

The amount of sawdust was varied from 0.2, 0.5, 0.8 g/L and from 1 to 4 g/L using 30ppm dye solution. All samples were shaken at 130rpm in 40°C water bath. Concentration of each sample will be measured using UV-Vis after 2.5h.

The graph in figure 4.7 shows that the amount of dye decreased when the amount of sorbent increased. As the previous discussion is section 4.4, the more sorbent particle is, the larger surface area is which results in more dye will be adsorbed. However, the fact that more particles available in solution means less space for particles to move and absorb dye.

Further studies are recommended to find the optimal dose for basic green removal. The studies should be done with amount of sorbent smaller than 0.2g/L.

4.7. EFFECT OF OPERATING TEMPERATURE

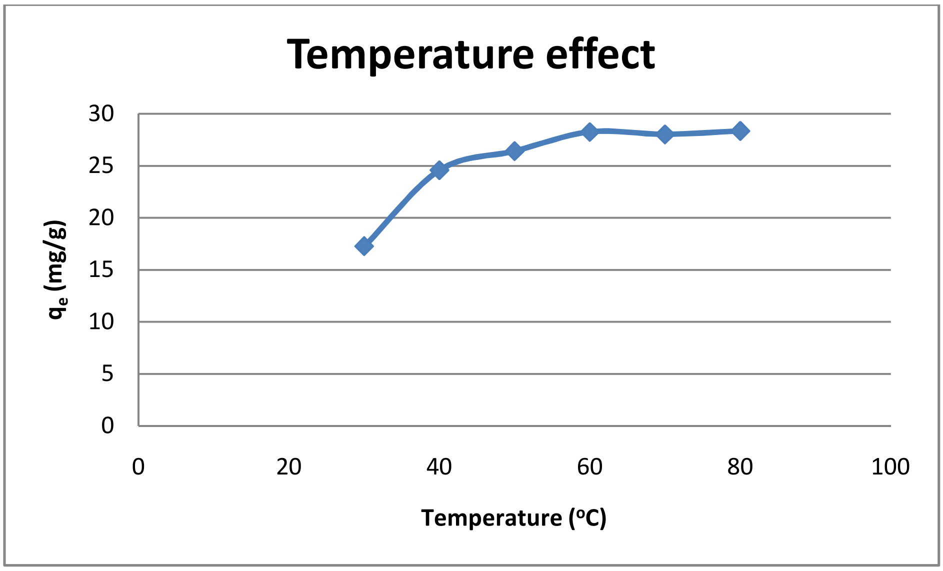


Figure 4.8: Effect of temperature on adsorption process

In practice, the effluent from textile factories is at high temperature. It can go up to 80°C. Therefore, to study the effect of temperature on adsorption of malachite green, batch sorption experiments were performed at desired temperature – 30, 40, 50, 60, 70 and 80°C using 1g/L of 45-63µm sorbent in 30ppm dye solutions. It is shown in figure

4.10 that the higher the temperature, the more dye is adsorbed. It is known that higher temperature provides higher energy for molecules. With higher energy, the molecules are more active and move faster. It increases the chance for dye molecules to be adsorbed into sorbent surface.

4.8. EFFECT OF SOLUTION CONCENTRATION

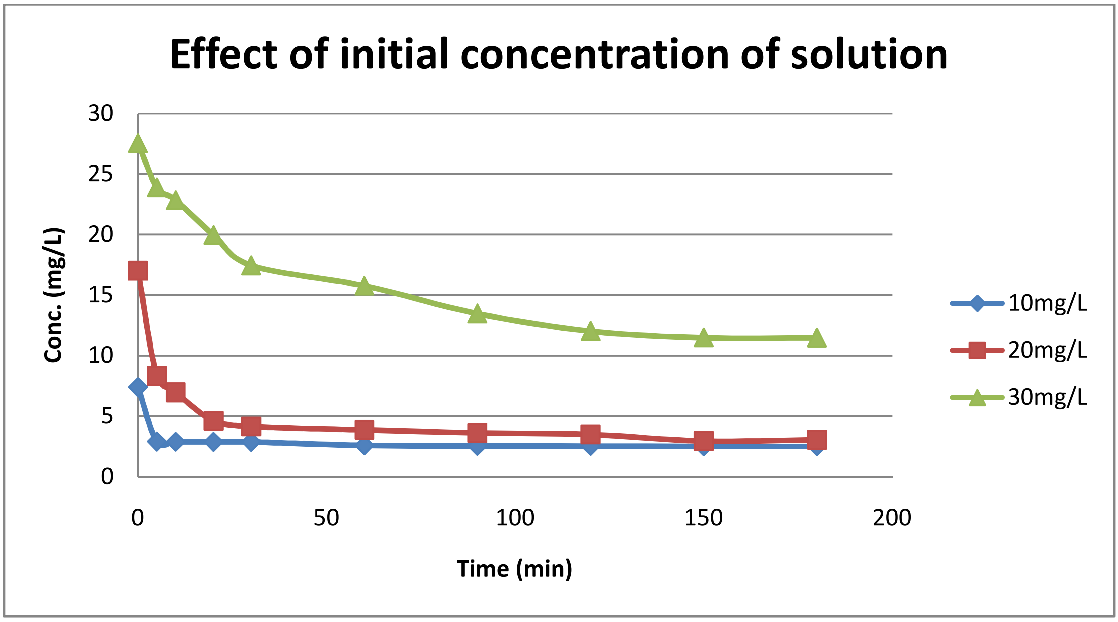


Figure 4.9: effect of initial concentration and contact time on malachite green adsorption.

In order to study the effect of initial concentration of dye in the solution on the rate of adsorption on sawdust, the experiments were conducted at different initial dye concentrations which are 10, 20 and 30ppm. Fixed adsorbent dose, 1g/L, was used at 40^{o}C. The result taken after 2.5h is shown in figure 4.8. At the beginning, the adsorption process took place rapidly, indicating a high affinity between malachite molecules and sawdust surface. The rate of adsorption tent to reduce, suggesting a gradually equilibrium. Finally, the saturation is reached, showing the equilibrium.

However, the contact time needed for equilibrium of 10ppm dye solution is shorter than the other which is 2h comparing to 2.5h.

Table 4.2: Effect of initial concentration on adsorption capability

q_o (ppm)	q_e (ppm)	% removal
10	2.503	66.1
20	2.942	82.7
30	13.481	58.4

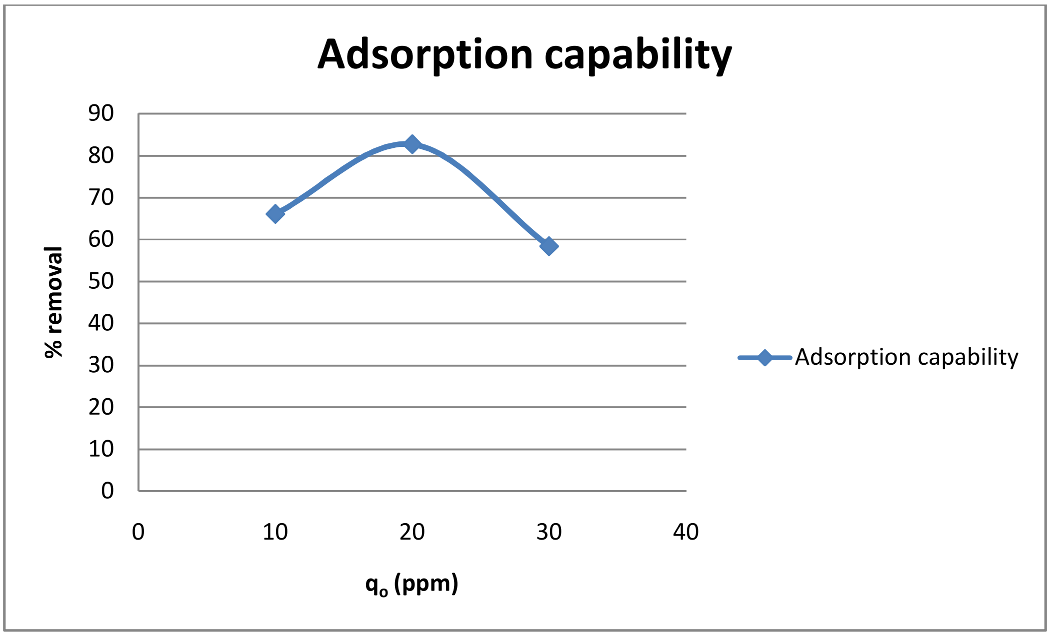


Figure 4.10: Effect of initial concentration on adsorption capability

As in table 4.2 and figure 4.9, 20ppm concentration shows the best adsorption capability of sawdust in condition of 40°C, 130rpm shaker, pH = 5 and 1g/L of 45-63µm sorbent. It is because there is an optimum condition for each concentration of solution where the adsorption capability of sorbent is maximized.

4.9. EQUILIBRIUM ISOTHERM

- ***The Freundlich isotherm***

The Freundlich Adsorption Isotherm is mathematically expressed as [11]:

$$q_e = K_F C_e^{1/n} \tag{1}$$

where

*C*e: the equilibrium concentration (mg/L),

q_e: the amount of dye adsorbed (mg/g),

K_F: Freundlich adsorption constant, and

1/n: a measure of the adsorption intensity.

Taking ln for both size of above equation:

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \tag{14}$$

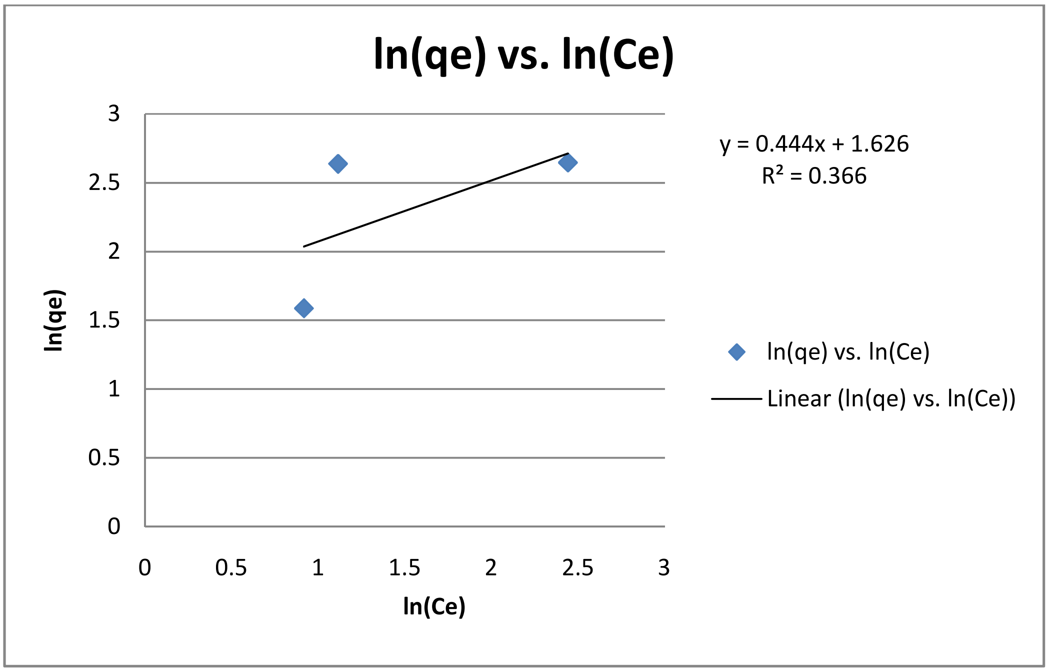


Figure 4.11: ln(qe) vs ln(Ce) using Freundlich isotherm

From the linear relation, K_f and n can be obtained:

- $lnK_f = 1.626$ => $K_f = 5.08\ (mg/g)(L/mg)^{1/n}$
- $1/n = 0.444$ => $n = 2.25$

- ***Langmuir isotherm***

The saturated monolayer isotherm can be represented as a linear form:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$$

The above equation can be rearranged to the following:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e$$

where:

- C_e is the equilibrium concentration (mol/dm^3)
- q_e the amount of dye sorbed (mol/g),
- q_m is q_e for a complete monolayer (mol/g),
- K_a the sorption equilibrium constant (dm^3/mol).

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/K_a q_m$.

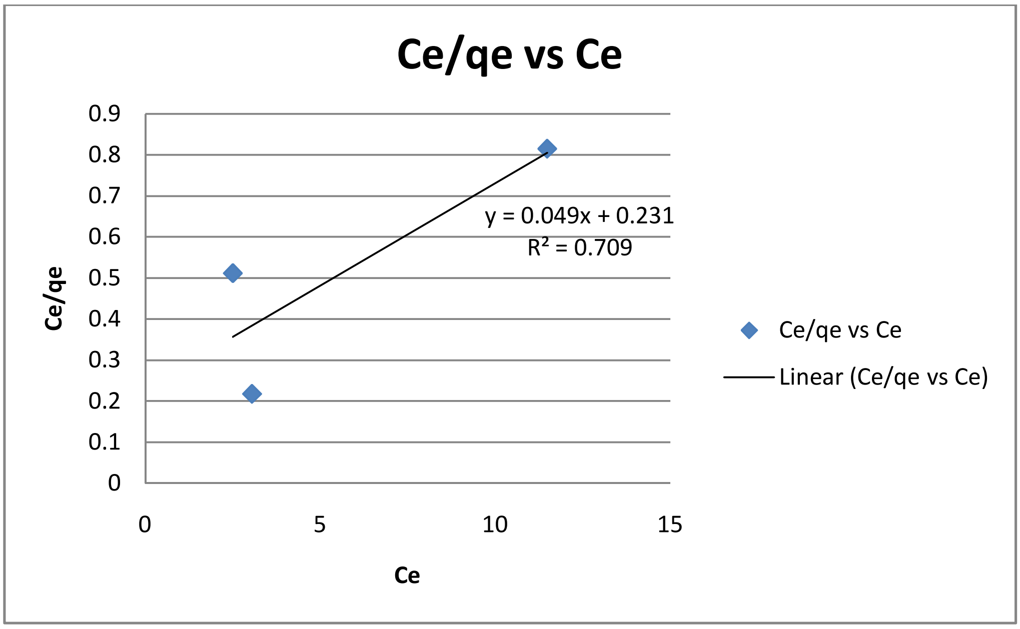


Figure 4.12: Ce/qe vs Ce using Langmuir isotherm

From the linear relation, K_a and q_m can be obtained:

- $1/q_m = 0.049$ => $q_m = 20.408$ mg/g
- $1/(K_a p_m) = 0.231$ => $K_a = 0.210$ L/mg

➢ ***Multilayer adsorption:***

If the adsorption takes place in a multilayer equilibrium on a homogenous surface, the total multilayer adsorption capacity (Γ, mg/g) can be expressed by the following equation [10]:

$$\Gamma = \frac{\Gamma_m K_1 C_e[1-(K_2 C_e)^n]}{(1-K_2C_e)[1+(K_1-K_2)C_e]}$$

where

Γ_m: monolayer adsorption capacity (mg/g),

K_n : equilibrium adsorption constant of the *n*th layer (L/mg) and

C_e : equilibrium concentration of solution (mg/L).

In the case of multilayer adsorption, the amount of dye adsorbed in a subsequent layer must be smaller than that in the previous layer.

Therefore, the term $(K_2C_e)^n \approx 0$, and Eq. (1) can be simplified to:

$$\Gamma = \frac{\Gamma_m K_1 C_e}{(1-K_2C_e)[1+(K_1-K_2)C_e]}$$

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_m K_1}\frac{1}{C_e} - \frac{K_2}{\Gamma_m K_1} + \frac{K_1 - K_2}{\Gamma_m K_1} - \frac{(K_1 - K_2)K_2 C_e}{\Gamma_m K_1}$$

$$\frac{C_e}{\Gamma} = \frac{1}{\Gamma_m K_1} + \frac{K_1 - 2K_2}{\Gamma_m K_1} C_e - \frac{(K_1 - K_2)K_2}{\Gamma_m K_1} C_e^2$$

Plot graph $\frac{C_e}{\Gamma}$ vs C_e

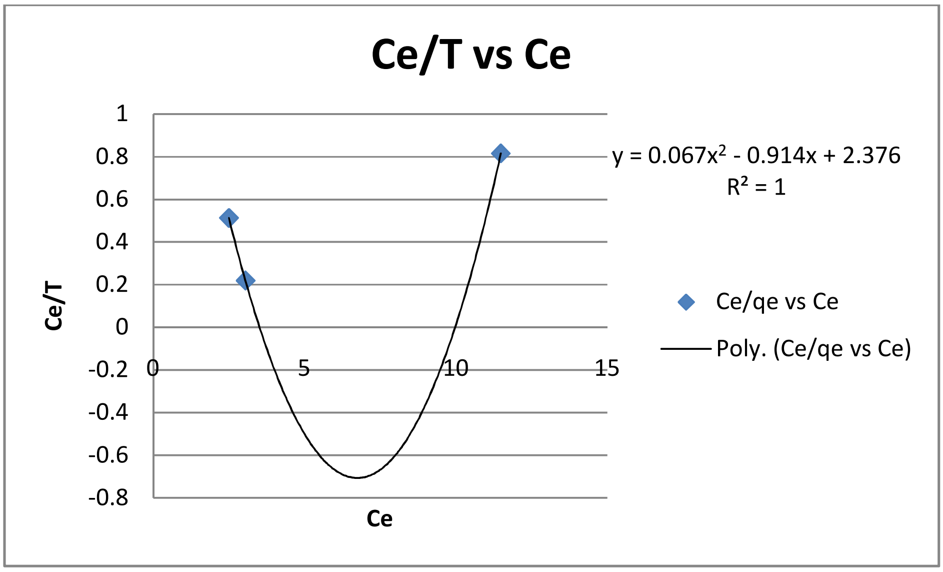


Figure 4.13: $\frac{C_e}{\Gamma}$ vs C_e using Multilayer adsorption

Γ_m, K_1, K_2 can be obtained from the graph in figure 4.12

$$-\frac{(K_1-K_2)K_2}{\Gamma_m K_1} = 0.067 \qquad (15)$$

$$\frac{K_1-2K_2}{\Gamma_m K_1} = -0.914 \qquad (16)$$

$$\frac{1}{\Gamma_m K_1} = 2.376 \qquad (17)$$

Subtitute eq(17) into eq(15) & (16):

(16) & (17) => $K_1 - 2K_2 = -0.385$

=> K1= 2K2-0.385 (18)

(15) & (17) => $(K_1 - K_2)K_2 = -0.028$ (19)

(18) & (19) => $K_2^2 - 0.385K_2 + 0.028 = 0$ (20)

Solving eq (20), $K_2 = 0.288$ or $K_2 = 0.097$

Table 4.3: Value of K1 and Γ_m

K_2	K_1	Γ_m	
0.288	0.191	0.08	Valid number
0.097	-0.191	-0.08	Invalid number

Because Γ_m is adsorption capacity, it cannot be a negative value. Therefore,

- $K_1 = 0.191$
- $K_2 = 0.288$
- $\Gamma_m = 0.08$

Table 4.4: Summary of isotherm constant for Malachite green adsorption on sawdust at 40°C

Freundlich isotherm model			Langmuir isotherm model			Multilayer adsorption model			
$K_{f,}$ (mg/g)(L/mg)$^{1/n}$	n	R^2	q_m (mg/g)	K_a (L/mg)	R^2	Γ_m(mg/g)	K_1 (L/mg)	K_2 (L/mg)	R^2
5.08	2.25	0.366	20.408	0.210	0.709	0.08	0.191	0.288	1

The fitting results, isotherm parameters, and the coefficient of determination, R^2, are shown is table. The determination coefficient, in case of multilayer adsorption R^2 value of 1 is higher compared to Langmuir (0.709) and Freundlich (0.366). This indicates that the adsorption of MG on OPTF takes place as a multilayer adsorption on a surface that is homogenous in adsorption affinity.

4.10. PERFORMANCE OF SAWDUST – COMPARISON WITH OTHER SORBENTS

Table 4.5 compares the adsorption capacity of different types of adsorbents used for removal of malachite green. The most important parameter to compare is the Langmuir q_m value since it is a measure of adsorption capacity of the adsorbent. The adsorption capacity of plywood sawdust (this project) is not high compared to other sorbent. The value of q_m taken is the research using acid rice straw is higher than others. It is suggested that malachite green should be removed using acid rice straw.

Furthermore, comparing q_m value of normal and acid treated rice straw, the adsorption capacity of rice straw increase after acid treatment. Therefore, further study using treated plywood sawdust in malachite green removal should be conducted.

Table 4.5: Comparison of adsorption capacities of various adsorbents for malachite green

Adsorbent	**q_m (mg/g)**	**T ($_o$C)**	**References**
Plywood sawdust	20.408	40	This study
Oil palm trunk fiber	149.35	30	[11]
Rice straw	94.34	30	[9]
Acid rice straw	256.41	30	[9]
Degreased coffee bean	36.2	35	[10]
Neem sawdust	4.23	35	[15]
Rattan sawdust	62.7±1.27	30	[16]
Treated ginger waste	84.03	30	[17]
	163.9	40	[17]
Dead leaves of plane tree	80.65	35	[18]

CHAPTER 5

CONCLUSION

The study has been conducted in two semesters in which, the first one was researching part and the second one was experimental work.

In last semester, it was shown the relevancy and feasibility of the project of removal dye from industrial waste water employing bio-sorption. The collection of material and paperwork for laboratory also has been done. Material used is sawdust due to the availability in the surrounding area of university. Sawdust after being collected was washed, dried, sieved and preserved.

The experiment has been started with the equilibrium study which shows that adsorption process of malachite green reaches equilibrium after 2.5h. The study on factor affecting the removal process of basic dye using sawdust indicates that it is unfavorable to carry out the adsorption process in high acidic solution which is pH lower than 5 due to the presence of H_3O+. The most effective size of sorbent in this study is 45-63µm which has the larger surface area for dye to be adsorbed. It is because of the presence of larger surface area of sorbent. These experiments were carried on at 40^oC in water bath with 130rpm shaker.

Temperature affects positively on the process when the operating temperature increase from 40^oC to 80^oC. The study on effect of initial concentration and contact time has proved that the rate of adsorption is higher with higher concentration. And the lower concentration solution reaches equilibrium faster.

It was found out that the experimental isotherm data can be fitted well to Langmuir multilayer adsorption equation. However, comparing the result of this study to others, plywood sawdust is not a good material used for removal of malachite green.

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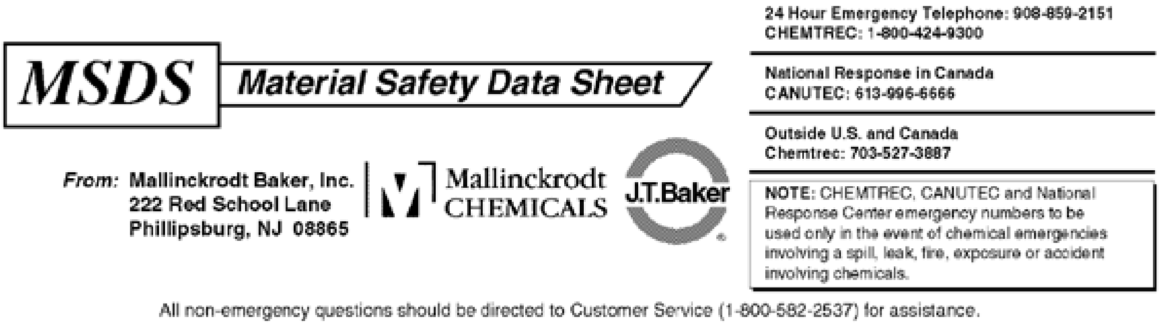
APPENDIX

MSDS OF MALACHITE GREEN OXALATE



MSDS Material Safety Data Sheet

From: Mallinckrodt Baker, Inc.
222 Red School Lane
Phillipsburg, NJ 08865

24 Hour Emergency Telephone: 908-859-2151
CHEMTREC: 1-800-424-9300

National Response in Canada
CANUTEC: 613-996-6666

Outside U.S. and Canada
Chemtrec: 703-527-3887

NOTE: CHEMTREC, CANUTEC and National Response Center emergency numbers to be used only in the event of chemical emergencies involving a spill, leak, fire, exposure or accident involving chemicals.

All non-emergency questions should be directed to Customer Service (1-800-582-2537) for assistance.

MALACHITE GREEN OXALATE

1. Product Identification

Synonyms: Malachite green oxalate certified
CAS No.: 2437-29-8
Molecular Weight: 927.10
Chemical Formula: C48H50N4O4.2HC2O4
Product Codes:

- J.T. Baker: P450
- Mallinckrodt: E107

2. Composition/Information on Ingredients

Ingredient	CAS No	Percent	Hazardous
Malachite Green Oxalate	2437-29-8	90 - 100%	Yes

3. Hazards Identification

Emergency Overview
WARNING! HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT.
SAF-T-DATA$^{(tm)}$ Ratings (Provided here for your convenience)

Health Rating: 3 - Severe (Poison)
Flammability Rating: 1 – Slight
Reactivity Rating: 1 – Slight
Contact Rating: 4 - Extreme (Corrosive)

Lab Protective Equip: GOGGLES & SHIELD; LAB COAT & APRON; VENT HOOD; PROPER GLOVES

Storage Color Code: White (Corrosive)

Potential Health Effects

Information on the human health effects from exposure to this substance is limited.

Inhalation: Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath.

Ingestion: Toxic by ingestion. Adverse health effects unknown. Causes irritation to the gastrointestinal tract. Symptoms may include nausea, vomiting and diarrhea.

Skin Contact: Causes irritation to skin. Symptoms include redness, itching, and pain.

Eye Contact: Causes irritation, redness, and pain.

Chronic Exposure: No information found.

Aggravation of Pre-existing Conditions: No information found.

4. First Aid Measures

Inhalation: Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Ingestion: Induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person. Get medical attention.

Skin Contact: Immediately flush skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse.

Eye Contact: Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

5. Fire Fighting Measures

Fire: Not considered to be a fire hazard.

Explosion: Not considered to be an explosion hazard.

Fire Extinguishing Media: Use any means suitable for extinguishing surrounding fire.

Special Information: In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode.

6. Accidental Release Measures

Ventilate area of leak or spill. Wear appropriate personal protective equipment as specified in Section 8. Spills: Sweep up and containerize for reclamation or disposal.

Vacuuming or wet sweeping may be used to avoid dust dispersal.

7. Handling and Storage

Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

8. Exposure Controls/Personal Protection

Airborne Exposure Limits: None established
Ventilation System:
A system of local and/or general exhaust is recommended to keep employee exposures as low as possible. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.
Personal Respirators (NIOSH Approved):
For conditions of use where exposure to dust or mist is apparent and engineering controls are not feasible, a particulate respirator (NIOSH type N95 or better filters) may be worn. If oil particles (e.g. lubricants, cutting fluids, glycerine, etc.) are present, use a NIOSH type R or P filter. For emergencies or instances where the exposure levels are not known, use a full-face positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.
Skin Protection: Wear impervious protective clothing, including boots, gloves, lab coat, apron or coveralls, as appropriate, to prevent skin contact.
Eye Protection: Use chemical safety goggles and/or full face shield where dusting or splashing of solutions is possible. Maintain eye wash fountain and quick-drench facilities in work area.

9. Physical and Chemical Properties

Appearance: Green crystalline solid.
Odor: Odorless.
Solubility: Very soluble in water.
Specific Gravity: No information found.
pH: No information found.
% Volatiles by volume @ 21C (70F): 0
Boiling Point: Not applicable.
Melting Point: 164C (327F)
Vapor Density (Air=1): No information found.
Vapor Pressure (mm Hg): No information found.
Evaporation Rate (BuAc=1): No information found.

10. Stability and Reactivity

Stability: Stable under ordinary conditions of use and storage.

Hazardous Decomposition Products: Burning may produce carbon monoxide, carbon dioxide, nitrogen oxides.
Hazardous Polymerization: Will not occur.
Incompatibilities: Strong oxidizers.
Conditions to Avoid: Incompatibles.

11. Toxicological Information

Oral rat LD50: 275 mg/kg. Irritation (std Draize, rabbit): eye = 76 mg/kg, severe. Investigated as a mutagen.

-----------------------------------\Cancer Lists\--

	---NTP Carcinogen---		
Ingredient	Known	Anticipated	IARC Category
Malachite Green Oxalate (2437-29-8)	No	No	None

12. Ecological Information

Environmental Fate: No information found.
Environmental Toxicity: No information found.

13. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be managed in an appropriate and approved waste disposal facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

14. Other Information

NFPA Ratings: Health: **2** Flammability: **0** Reactivity: **0**

Label Hazard Warning:
WARNING! HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT.

Label Precautions:
Avoid breathing dust.
Avoid contact with eyes, skin and clothing.
Keep container closed.
Use only with adequate ventilation.
Wash thoroughly after handling.
INTENDED FOR R & D USE ONLY.
NOT ON THE TSCA INVENTORY.

Label First Aid:

In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Wash clothing before reuse. If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. If swallowed, induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person. In all cases, get medical attention.

Product Use: Research and Development Use Only.

Revision Information: No Changes.

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