Optimization of Malachite green removal using activated carbon derived from coconut shell

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Abstract. The textile industry is a sub-industry that contributes to our country's economy, and as a result, it is expanding on a daily basis. The processes that are involved in the textile industry are fibre production, spinning, twisting, weaving, knitting, scorching and dyeing, which involve colours or dyes. The combination of processes and products causes waste from the textile industry to contain a wide range of pollutants. The presence of even trace amounts of dye in water (less than 1 ppm) is highly visible and will affect water transparency and gas (carbon dioxide, oxygen) solubility in water bodies where waste is discharged. Dyes are usually resistant to conventional biodegradation. Therefore, adsorption is an effective alternative for dye removal treatment. Therefore, a study has been conducted to find a low-cost raw material for an alternative method of treating textile wastewater. In this study, the capability of activated carbon derived from coconut shells to remove malachite green dye was investigated. Three parameters were studied, such as activated carbon with different chemical impregnation and carbonization time, contact time and initial concentrations of dye. From the results acquired, 99.9% of malachite green dye was removed by the activated carbon impregnated with phosphoric acid solution of 5 minutes carbonization time. The optimum contact time and initial concentration of dye were 1 hour and 10 mg/L, respectively. Therefore, this result can contribute to some knowledge of using low-cost raw material impregnation with some chemicals to remediate textile wastewater.

1. Introduction
Wastewater from the textile industry can contain a variety of pollutants, for example, dyes. Pretreatment, dyeing, printing, and finishing are the main steps in the dyeing and printing process of the textile industry [1]. The main component used to make textiles is color, which is easily recognized in waste water and must be removed or treated before being discharged into a body of water. The effluents generated from industrial activities contribute to most sources of natural water pollution. This will cause huge problems in terms of waste water management or treatment and can continuously lead to direct source pollution problems which not only increase the high cost of treatment, but also introduce a variety of chemical pollutants and microbial contaminants to the water sources. The presence of dye in water is highly visible and will affect water transparency and gas (carbon dioxide, oxygen) solubility in the water bodies where the waste water is discharged [2]. Once the gas solubility is affected, it will affect the dissolved oxygen (DO) too.

Nowadays, there are many types of technologies that are used to remove contaminants from water sources, such as filtration, adsorption, chemical precipitation and ion-exchange. The most commonly used adsorbent for dye removal is activated carbon, which is also known as activated charcoal. It contains small, low-volume pores that increase the surface area, which can allow an efficient adsorption
process and chemical reactions. Activated carbon has the capability to adsorb a broad range of adsorbents efficiently. The main material needed to produce activated carbon is any organic material with a high carbon content, such as coal, wood, peat and coconut shells. The raw material, which is carbon-based, is transformed into activated carbon by thermal decomposition in a furnace using a certain heat and duration. Basically, there are two different processes for the preparation of activated carbon, the so-called physical or thermal and chemical activation [3]. Activated carbons are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, gases, potable water and wastewater [4].

The major problem occurred is the existing activated carbons in the market are very expensive [5]. This issue make people tried to use activated carbon that originated from low cost material such as bamboo [6], rubber wood sawdust [7] and coffee residue [8]. By using this agriculture waste, an efficient and cheap activated carbon can be alternative to expensive-existing activated carbon [9]. This study determine the efficiency of activated carbon from coconut shells to remove malachite green in synthetic textile waste water.

2. Materials and Methods

2.1 Materials

Coconut shells were obtained from a local supplier. The coconut shell was smashed into small pieces using a hammer and was rinsed with tap water. Then it was dried in the oven for 2 hours at 150°C. Next, the dried coconut shell was ground using a blender. After that, the coconut shell was sieved using a 2.00 mm siever. Then it was covered and stored at room temperature. The activation process was conducted with the impregnation ratio of 2:1 (dry weight of activating agent in ml /dry weight of precursor in grams). A granulated coconut shell was used to make 8 conical flasks. 4 conical flasks were filled with 25% zinc chloride and the remaining conical flasks with 25% phosphoric acid. The granulated coconut shell was stirred until it was mixed well and soaked overnight so that the activating agent could be fully absorbed. Aluminum foil was used to completely cover the mixture. The mixture was carbonized under an inert atmosphere in a muffle furnace. The mixtures were heated for 5 minutes, 10 minutes, 30 minutes, and 1 hour at different times. The temperature used to heat the mixtures was fixed at 400°C.

For preparation of synthetic textile wastewater, malachite green powder (1g) was mixed with 1000 ml of distilled water to prepare a 1000 ppm stock solution. The stock solution was then kept in the reagent bottle before being diluted to the selected concentrations.

2.2 Effect of different activating agent to remove malachite green

The Malachite green solution (25 ml, 10 ppm) was mixed with prepared activated carbon in a conical flask. The initial reading of the dye solution was recorded using a UV-Vis Spectrometer. The conical flask was covered with parafilm and was put into the mechanical shaker for an hour at 100 rpm. These steps were repeated using activated carbon prepared for 10 minutes, 30 minutes and 1 hour of activation time for both activating agents (zinc chloride and phosphoric acid). The activated carbon with the highest rate of removal acquired was used for the subsequent experiment.

2.3 Effect of contact time to remove malachite green

The Malachite green solution (25 ml, 10 ppm) was mixed with 0.5g of the activated carbon that has the highest rate of removal from previous parameters in a conical flask. The initial reading of the dye solution was recorded. The conical flask was covered with parafilm and was put into the mechanical shaker for half an hour at 100 rpm. These steps were repeated using 2 hours and 3 hours of contact time. The most optimum contact time acquired was used for the next parameter.

2.4 Effect of concentration of dye solution to remove malachite green

The Malachite green solution (25 ml, 25 ppm) was mixed with 0.5 g of the activated carbon that has the highest rate of removal in a conical flask. The conical flask was covered with parafilm and was put into
the mechanical shaker within the best time contact acquired from previous parameters. The mechanical shaker was set at 100 rpm. After that, the solution was filtered, and a final reading was taken. These steps were repeated using a 50 ppm dye solution.

2.5 Determination of malachite green removal
The percentage of dye removal was determined using Equation 1:

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\frac{\text{Initial concentration of dye} - \text{Final concentration of dye}}{\text{Initial concentration of dye}} \times 100
\]

3. Results and Discussion
3.1 Effect of different activating agent to remove malachite green
In this study, there were 2 types of activating agents, which were zinc chloride and phosphoric acid, and different sets of activating times, which were 5 minutes, 10 minutes, 30 minutes and 60 minutes. Figure 1 shows the effect of different types of activating agent (zinc chloride and phosphoric acid) on the removal of malachite green in an aqueous solution. From the results acquired, phosphoric acid is the best activating agent for coconut shell derived activated carbon. It has been demonstrated that activated carbon activated with phosphoric acid requires only 5 minutes of activation time to remove 99.9% of 10 ppm dye solutions. The other batch of activated carbon, activated by phosphoric acid but with different activation times (10 minutes, 30 minutes and 1 hour), also achieved 99% and above. So the fact that using chemical activation can reduce energy costs as the temperature and time needed is less, was proven in this experiment. [10] concluded chemical activation shows significant advantages, including low pyrolysis temperature, short processing time, high carbon yield and large specific surface area as well as controllable porous structure.

The use of zinc chloride as an activating agent is also possible for producing activated carbon from coconut shells, but it is not as efficient as phosphoric acid. The activated carbon of zinc chloride with a 5 minute activation time can only achieve an 87.87% removal of the dye from the 10 ppm solutions. The other batch of activated carbon by zinc chloride but with different activation times (10 minutes, 30 minutes and 1 hour) achieved 99% but still not as efficient as activated carbon by phosphoric acid which achieved 99.9%. So that means the activated carbon by zinc chloride, might need more activation time to remove the dye from the solutions. The coconut shell is a very hard material, so it requires a strong activating agent to decompose its structure. Because phosphoric acid is a more powerful activating agent, it can weaken the structure of the coconut shell while also producing carbon with a higher surface area and micro porosity. These characteristics are important for activated carbon to achieve a higher rate of dye removal.
The activation duration has a significant effect on the development of the network of carbon porous. The activation time should provide sufficient time to eliminate remaining moisture content in the raw material to produce excellent activated carbons. The activation time also was the time to eliminate most of the volatile components that will interrupt the development of porous in the precursor. Longer durations of activation cause enlargement of pores at the expense of the surface area [11]. These traits increase the rate of removal of dye from the synthetic waste water as the adsorption rate also increased.

The control of activation time is of economic interest since the shorter time needed will contribute to less energy consumption. It also reduces the cost of energy used (electricity). Yield also appeared to be dependent on the activation duration as it dropped upon reaching an optimum point. Low activation time resulted in an incomplete burn-off, thus resulting in higher yields.

There were different sets of activation times which were 5 minutes, 10 minutes, 30 minutes and 1 hour used to produce the activated carbons derived from coconut shell. These different sets of activation times are used to determine the most optimum activation time to produce the activated carbons. The temperature of the activation process was fixed to 400°C as this temperature was found to be the optimum temperature for coconut shell precursor.

The one-way ANOVA for percentage of dye removal versus activating time was tabulated in Table 1. The result shows that there are no significant mean different in dye removal with different time sets at the level of significance of 0.05. The Turkey test analysis was not conducted due to the ANOVA result of no significant mean difference in activating agent on dye removal at four different times of 5, 10, 30, and 60 minutes. Therefore, it is enough to descriptively discuss this finding using Figure 1.

![Figure 1. Effect of different activating agent to remove malachite green.](image)

**Table 1.** The one-way ANOVA for percentage of dye removal versus activation time.

| Source         | Df | Sum square | Mean square | F-value | P-value |
|----------------|----|------------|-------------|---------|---------|
| Activated carbon | 3  | 50.76      | 16.92       | 0.93    | 0.503   |
| Error          | 4  | 72.51      | 18.13       |         |         |
| Total          | 7  | 123.27     |             |         |         |

The results visualized in Figure 1 show that the best activation time was dependent on the type of activating agents. As for the phosphoric acid activating agent, the most optimum activation time required was 5 minutes. This batch of activated carbon has the highest percentage of dye removal, which was
99.9%. The other batch of activated carbon with 10 minutes, 30 minutes and 1 hour activation time also achieved a high percentage of dye removal, 99.67%, 99.45% and 99.54% respectively.

The results also show that for activated carbon with zinc chloride as activating agent, the activation time needed was higher to produce the optimum activated carbon. The most optimum activation time required was 30 minutes and 1 hour. This batch of the activated carbon achieved 99.87% of dye removal. The other batch of activated carbon with 5 minutes and 10 minutes activation time achieved 87.87% and 99.81% respectively.

The one-way ANOVA of percentage of dye removal versus types of activating agents was tabulated in Table 2. The result shows that there are no significant mean different in percentage of dye removal for different types of activating agents at the level of significance of 0.05. This means, there are no effects of dye removal using four different types of activated carbon. Therefore, analysis using the Turkey test was not conducted.

Table 2. The one-way ANOVA of percentage of dye removal versus types of activating agents.

| Source          | Df | Sum square | Mean square | F-value | P-value |
|-----------------|----|------------|-------------|---------|---------|
| Activated carbon | 1  | 15.51      | 15.51       | 0.86    | 0.389   |
| Error           | 6  | 107.67     | 17.96       |         |         |
| Total           | 7  | 123.27     |             |         |         |

3.2 Effect of contact time

Figure 2 shows the percentage of dye removal is the highest when the contact time (dye solution mixed with activated carbon in the shaker) was 1 hour. The colour of the dye solution changed from light blue to colourless. The result also shows that the percentage of dye removal is the lowest when the contact time (dye solution mixed with activated carbon in the shaker) was 3 hours but the dye solution still changed from light blue to colourless.

![Figure 2. Effect of contact time.](image)

The adsorption of dye is highly dependent on the initial concentration. At lower concentrations, the ratio of the initial number of dye molecules to the available surface area, subsequently the fractional adsorption becomes independent of initial concentrations. However, at high concentrations, the available sites of adsorption become fewer, hence the percentage of dye removal is dependent on the initial concentrations [12]. Therefore, the contact time required was varied. The less contact time needed, the higher the efficiency of the activated carbon. This means that the activated carbon is excellent at
adsorbing the dye to its surface area in a short time. The activated carbon with high surface area and high pores development needed a shorter time to remove dye from the synthetic waste water. The results from this experiment show that the most optimum contact time needed was 1 hour. The percentage of dye removal achieved was 99.9%. This is because the time allocated was sufficient enough for the adsorption process for dye solutions with initial concentrations of 10 ppm.

The remaining contact times which were 30 minutes, 2 hours and 3 hours achieved 99.77%, 99.8% and 99.6% respectively. The batch with 30 minute contact time achieved a lower percentage of dye removal because the time allocated was not sufficient for the dye molecules to adsorb to the activated carbon surface. The remaining batch with higher contact time achieved a low percentage of dye removal because the activated carbon had become saturated and was not capable of adsorbing the dye molecules anymore.

The one-way ANOVA for percentage of dye removal versus contact time was tabulated in Table 3. The result shows that there are significant mean different in percentage of dye removal in different contact times at the level of significance 0.05. This result supports the descriptive results in Figure 2. Further investigation using the Turkey test reveals that the different mean of dye removal was between one and three hours of time.

| Source               | Df | Sum square | Mean square | F-value | P-value |
|----------------------|----|------------|-------------|---------|---------|
| Activated carbon    | 3  | 0.11594    | 0.038646    | 13.50   | 0.015   |
| Error               | 4  | 0.01145    | 0.002862    |         |         |
| Total               | 7  | 0.12739    |             |         |         |

3.3 Effect of concentration

Figure 3 shows that the percentage of dye removal is highest when a dye with a concentration of 10 ppm is used. The colour also changed from light blue to colourless. The result also shows that the percentage of dye removal was lowest when 25 ppm dye was used. However, the colour still changed from light blue to colourless.

The adsorption of dye is highly dependent on the initial concentration (ppm). At lower concentrations, the ratio of the initial number of dye molecules to the available surface area, subsequently the fractional adsorption becomes independent of initial concentrations. However, at high concentrations, the available adsorption sites become fewer, and thus the percentage of dye removal is proportional to the initial concentrations [12].

The less contact time is needed, the higher the efficiency of the activated carbon. This means that the activated carbon is excellent at adsorbing the dye to its surface area in a short time [13]. The activated carbon with high surface area and high pore development needs a shorter time to remove the dye from the synthetic waste water.
Figure 3. Effect of dye concentrations.

The results from this experiment show that the most optimum contact time needed was 1 hour. The percentage of dye removal achieved was 99.9%. This is because the time allocated was sufficient enough for the adsorption process for dye solutions with initial concentrations of 10 ppm.

The remaining contact times which were 30 minutes, 2 hours and 3 hours achieved 99.77%, 99.8% and 99.6% respectively. The batch with 30 minute contact time achieved a lower percentage of dye removal because the time allocated was not sufficient for the dye molecules to adsorb to the activated carbon surface [14]. The remaining batch with higher contact time achieved a low percentage of dye removal because the activated carbon had become saturated and was not capable of adsorbing the dye molecules anymore.

Table 4 shows the result of one-way ANOVA for percentage of dye removal versus dye concentrations. It clearly shows that there are significant mean different in percentage of dye removal; in different concentration set in the experiment at level of significance 0.05. This result supports the initial descriptive results that are shown in Figure 3.

### Table 4. The one-way ANOVA for percentage of dye removal versus dye concentrations.

| Source            | Df | Sum square | Mean square | F-value | P-value |
|-------------------|----|------------|-------------|---------|---------|
| Activated carbon  | 2  | 0.986033   | 0.493017    | 1173.73 | 0.000   |
| Error             | 3  | 0.001300   | 0.000433    |         |         |
| Total             | 5  | 0.987333   |             |         |         |

4. Conclusion

This research was done to produce activated carbon derived from agricultural waste that is cheap and recyclable. The coconut shell is abundant in Malaysia and also in other countries. Hence, it is convenient to use the coconut shell to produce activated carbon. The activating agents used, zinc chloride and phosphoric acid, enhanced the porosity of the activated carbon, hence increasing the surface of binding sites. From the results acquired, 99.9% of malachite green dye was removed by the activated carbon impregnated with phosphoric acid solution of 5 minute carbonization time. The optimum contact time and initial concentration of dye was 1 hour and 10 mg/L respectively.
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