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Methylene Blue Adsorption by Using Eggshells in Synthetic Solution

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Abstract: The amount of methylene blue dye released into the textile industry's wastewater is increasing throughout the year, and this problem is concerning. There are many side effects of having dye released into the wastewater, such as eutrophication, which can be the source of algal blooms that affect the aquatic organisms because of the lack of oxygen in the water and the environment too. This research focuses on reducing the amount of methylene blue dye released into the wastewater by using the adsorption method and using the eggshells as the adsorbent. The batch study used different adsorbent dosages (0.2g, 0.4g, 0.6g, 0.8g and 1.0g) and different particle sizes of adsorbent (0.30mm, 0.60mm, 1.18mm, 2.36mm and 5.00mm). It is expected that the higher the adsorbent dosage used, the higher the dye removal efficiency and the smaller the particle size used, the higher the dye removal efficiency. This study's contribution to eggshells' methylene blue adsorption shall get a future assessment in a prospective wastewater treatment facility setting.

Keywords: Adsorption, Eggshells, Methylene Blue, Textile, Wastewater

1. Introduction

Water is a liquid that cascades from the clouds in rain, streams, lakes, and seas. Water plays a vital role in our ecosystem and environment. However, it has been polluted by chemicals and impurities that made it unsafe and dangerous for living things to consume. The discharge of dye from these industrial factories into natural streams has caused many significant problems, such as increasing the toxicity and chemical oxygen demand (COD) of the effluent. This phenomenon had significantly affected the aquatic environment impeding light penetration, precluding photosynthesis of marine flora, thus causing eutrophication that prevents the aquatic plants from photosynthesizing. Photosynthesizing is a process that provides oxygen in the water for aquatic livings. If this process could not occur, it would cause death to the aquatic plants because of the lack of oxygen.

In order to overcome this problem, many methods and applications have been introduced to remove those chemicals and impurities in the water. Adsorption appears to be the most effective and low-cost

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method, among other techniques [1]. Many adsorbents can be used, such as activated carbon, rice husk, and sawdust. However, to take cost, design, environmental-friendly, and suitable for a wide chemical range as the main criteria to be fulfilled; eggshells are highly efficient adsorbent that can remove pollutants in an aqueous solution [2]. Therefore, this research investigates the efficiency of removing methylene blue by synthesizing eggshells into powder form with different particle sizes and dosages.

1.1 Adsorption

Adsorption is a process where mass transfer from pollutants transforms from the liquid phase to solid adsorbent. It is one of the most widely used water and wastewater treatment methods because of its advantages, such as simple design, low price, easy maintenance, and high efficiency [3-4]. Adsorption also is widely-used to remove pollutants from the water treatment processes [5]. Adsorption is one of the cheapest and effective methods of getting rid of the dye that has caused harm to live organisms compared with other methods such as chemical treatment, oxidation, and advanced oxidation processes (AOPs), electrochemical methodology, and biological treatment [6]. Adsorption process as a surface method usually has a porous solid medium as the mixture of multi-component fluid either in liquid or gas form is pulled towards solid surface either in chemical or physical bonds. The solid porous medium provides high micropore volume that can lead to high adsorptive capacity. The porous solid medium has pores that are very small in size where they can adsorb molecules that should find their way to the micropore volume. The adsorption process depends on the adsorbent, so it should have an adequate adsorption capacity. Adsorbents with small pore size can allow the molecules to reach the adsorbent's interior, making the adsorbent suitable for a successful adsorption process [7-8].

1.2 Eggshells

Eggshells are waste that can be modified into other uses such as fertilizer, adsorbent, chicken feed, bird feed, and others, but the other eggshells leftover are being thrown into the dump. Eggshells are highly efficient adsorbent that can remove pollutants in an aqueous solution and have been used to remove the untreated wastewater released into the water by the factories. Eggshells are also proven to adsorb certain heavy metals and organic materials from wastewater effectively. Eggshells are constructed by three-layered structures: the cuticle on the outer surface, a spongy layer, and an inner lamellar. Eggshells have 7000 to 17000 pores, an intrinsic pore structure that can be used to adsorb chemicals and impurities in the water in a large quantity. The composition of the inner eggshell membrane, which is polysaccharides fibers and collagen such as protein, contains substituting group sites such as hydroxyl, amine, and sulfonic groups that can react with dyes, thus making eggshell serves good adsorption characteristics [9].

1.3 Dye

The dye is one of the hazardous pollutants often found in the wastewater that has been released without treatment by an irresponsible party. It is a chemical compound that has been used in many industries for colouration purposes, especially in the textile industry. There are over $7x10^5$ tonnes and 10,000 types of dye and pigments roughly produced every year, and it keeps increasing each year [10]. Generated dyes that have been released into the wastewater are toxic, non-biodegradable, and pollute the environment, especially aquatic life. The dye chosen in this study is Methylthioninium Chloride ($C_{16}H_{18}ClN_3S$), also known as methylene blue (MB), because of its well-known strong adsorption into solids. It is dark green when in crystal or powder form and becomes deep blue when it turns into a solution. It is also soluble in water, chloroform, and alcohol. Methylene blue is commonly used for dyeing cotton, wool, and silk. The molecular weight of the methylene blue is 373.9 g/mol.

2. Materials and Methods

Flowchart, as shown in **Figure 1**, shows the process that was done along with the research. It starts with collecting the literature reviews on the absorbent of methylene blue, which is eggshell. Then, the adsorbent and the synthetic solution were prepared. Lastly, the parameter analysis is conducted to achieve the objectives of this research.

In this study, the apparatuses, materials, and equipment used were beaker, measuring cylinder, spatula, glass rod, volumetric flask, filter tunnel, methylene blue, distilled water, eggshells, hot plate magnetic stirrer, mechanical sieve shaker, oven, analytical weight balance, and UV-Vis spectrophotometer.

Journals about eggshells, dyes, adsorbent dosage, and particle size were collected and reviewed.

↓

Preparation of adsorbent:

- Washed and dried under the sunlight.
- Dried in the oven to eliminate moisture
- Crushed by using mortar.
- Measure the particle size by using a mechanical sieve shaker.
- Measure the adsorbent dosage by using analytical weight balance.

↓

Preparation of synthetic solution:

- A stock solution was prepared by dissolving 1gram of methylene blue in 1000 mL distilled water to make a stock solution of 1000 mg/L.
- The stock solution was diluted into 10, 20, 30, 40, 50, 60 mg/L to obtain a calibration curve.
- The concentration of 50 mg/L was used as the sample for each parameter analysis.

↓

Parameter analysis:

UV-Vis Spectrophotometer was used to determine the methylene blue solution's absorbance at a wavelength of 565 nm.

Figure 1: Flowchart of present investigation

The eggshells were washed then dried under the sun and in the oven to eliminate moisture in eggshells, as shown in **Figure 2**. Based on the objective, there are two experiments will be done. Therefore, the eggshells are divided into two parts, i.e., for the adsorbent dosage and particle size experiment. The eggshells were weighed using analytical balance to get the necessary adsorbent dosage to be used in the adsorbent dosage experiment. **Figure 3** shows the eggshells crushed using a mortar and transferred into a mechanical sieve shaker to obtain the particle size needed for particle size experiments.

Figure 1: Adsorbents were dried in the oven

Figure 2: Adsorbents were sieved in the mechanical sieve shaker

The stock solution was prepared by dissolving 1 gram of methylene blue in 1000 mL distilled water to make a stock solution of 1000 mg/L as shown in **Figure 4** and diluted into 10, 20, 30, 40, 50, 60 mg/L to obtain calibration curve using UV-Vis Spectrophotometer. The concentration of 50 mg/L was used as the sample for each parameter analysis.

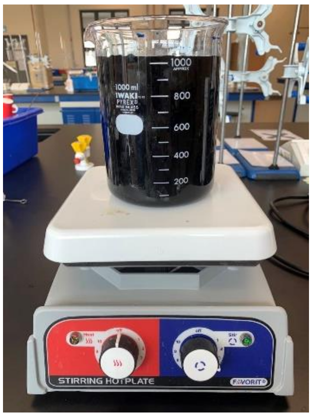

Figure 3: The preparation of stock solution

The parameters were analysed using UV-Vis Spectrophotometer to find the absorbance of methylene blue solution with wavelength of 565nm and the results obtained were recorded. The methylene blue adsorption capacity was obtained by using the general formula:

$$qe = \frac{V}{m}(Co - Ct) \qquad \text{Eq. 1}$$

where,

qe: the amount of methylene blue adsorbed at equilibrium per unit weight of sorbent (mg /g), Co, Ct: the dye concentrations before and after adsorption (mg /L). V: the solution volume (in liter (L)). m: the amount of sorbent (in gram (g)) used to experiment.

Meanwhile, the percent dye removal (%) was calculated by using equation:

$$E : \frac{Co - Ct}{Co} \times 100 \qquad \text{Eq. 2}$$

3. Results and Discussion

Two experiments were conducted to investigate the effectiveness of eggshells to absorb methylene blue. The independent variables are eggshells dosage (0.2g, 0.4g, 0.6g, 0.8g and 1.0g) with constant particle of 1.18mm and particle size of eggshells (0.30mm, 0.60mm, 1.18mm, 2.36mm and 5.00mm) with constant adsorbent dosage of 0.6g, while the volume and the concentration of the solution are constant which are 50ml and 50 mg/L respectively.

3.1 Calibration curve

The absorbency of methylene blue is vital to determine the percentage of methylene blue colour removal. Therefore, the absorbency of methylene blue was obtained first before conducting further experiments. **Figure 5** shows the calibration curve between methylene blue concentration and absorbance with correlation y = 0.0022 x where the regression linear (R^2) is 0.984.

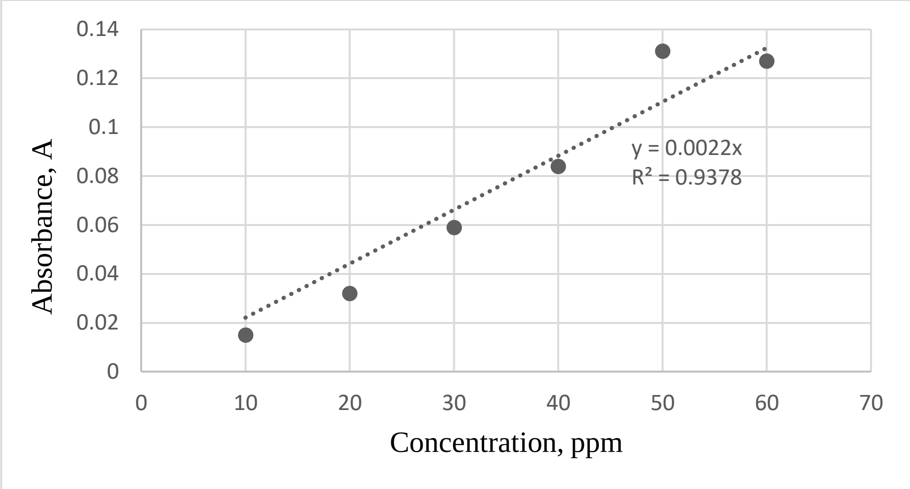

Figure 4: The calibration curve for methylene blue

3.2 Effect of adsorbent dosage

Table 1: The value of percentage removal by using different adsorbent dosage

Adsorbent dosage (g)	Adsorbance (A)	Percentage removal (%)
0.2	0.044	54.0
0.4	0.058	42.8
0.6	0.040	57.2
0.8	0.046	52.4
1.0	0.076	28.4

Based on **Table 1**, it can be seen the highest percentage removal is 57.2%, with the adsorbent dosage of 0.6g, and the lowest percentage removal is 28.4%, with the adsorbent dosage of 1.0g. It shows the optimum adsorbent dosage of eggshells to remove methylene blue is at 0.6g. It can also be seen that the trend result is rising. As stated by [11], the percentage removal increase as the adsorbent dosage increase before it reach a limit and become saturated.

Refering to the work of Deng *et al*., (2011), the decrease in percentage removal may cause by the splitting effect of concentration gradient between adsorbates with increasing adsorbent dosages that cause a decrease in amount of dye adsorbed onto unit weight of adsorbents [12]. Wang *et al*., (2017) also explained that the decrease in adsorption density with increase in adsorbent dosage is mainly due to unsaturation of adsorption sites through the adsorption reaction [3].

3.3 Effect of particle size

Table 2: The value of percentage removal by using different particle size

Particle size (mm)	Adsorbance (A)	Percentage removal (%)
0.30	0.0125	-10.8
0.60	0.0880	18.8
1.18	0.104	6.0
2.36	0.082	23.6
5.00	0.069	34.0

Table 2 shows that the percentage removal of methylene blue at a particle size of 0.30mm is -10.8. There is a possibility that the eggshells have became saturated because the particle was too small. Thus, the solution became more concentrated, and there was no methylene blue adsorbed. The highest percentage removal is at the particle size of 5.00mm, which is 34.0%, which means the particle size of 5.00mm is the optimum size for methylene blue adsorption. From Table 2, as the particle size decreases, the higher the methylene blue adsorbed.

The negative result for 0.3mm particle size might cause by the parallax error in the initial concentration. The synthetic solution became more concentrated, which was more than 50ppm and there might be a mistake where the initial concentration poured was over 50ppm. The result obtained fluctuated might be caused by the inaccuracy of the UV-Vis Spectrophotometer. Some fingerprints might present around the cuvette during the reading, so the instrument could not analyze the results accurately. Besides, Yu et al., (2003) explained that it might due to the interaction between particles, such as aggregation that came from high sorbent concentration [13]. Aggregation would result in a decrease in the sorbent's total surface area and an increase in diffusional path length.

4. Conclusion

In conclusion, eggshell possesses good adsorbent properties for its capability of removing methylene blue. The best conditions of eggshell in removing methylene blue is at 5.00mm of particle size by using 0.6g of eggshell in a 50ml of methylene blue solution with a concentration of 50 mg/L. At a 5.00mm particle size and 0.6g of eggshell, it could remove the methylene blue up to 57.2% and 34%, respectively. The experimental results show that the absorbance against adsorbent dosage does not decrease linearly; meanwhile, the graph of absorbance against particle size does not increase linearly as expected from the research hypotheses as both obtained results show contradictions from the expected results. The inaccuracy of the experimental results may occur due to random errors made during the experiment. A future investigation could be conducted on more parameters that affect the adsorption rate, such as temperature, contact time, and methylene blue pH.

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