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# Removal of Methylene Blue Using Used Paper Powder

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Abstract

Methylene blue removal by adsorption method had been done in batch method using adsorbent of used paper powder. Adsorption parameters covering adsorbent doses, contact times, pH, adsorbate concentrations and adsorption isotherm as well as desorption study of the absorbed methylene blue were evaluated. The results showed the highest adsorption of methylene blue was obtained at an optimum adsorbent dose, for 30 min at pH > 9. The maximum adsorption capacity of 30.77 mg/g was obtained with Langmuir isotherm model. While the effective methylene blue desorption on the used paper powder adsorbent was obtained c.a. 0.27 mg/g at pH 1.

## 1. Introduction

The increasing concerns on environmental conservation in recent years, pollutant removal is of concern to the public and the research area. Dyes, a component in textile, paper, plastics, food and cosmetics industries, are a major pollutant in water [1]. Methylene blue is one of the most commonly used cationic dye for cotton, wood and silk dyeing [2]. It has some negative effects for human beings such as respiratory disorders, and can cause nausea, vomiting, diarrhea, and gastritis [3]. Untreated waste of methylene blue can pollute the environment, therefore the waste should be treated from environment [4]. One of the commonly used methods is adsorption because it is very effective in handling various pollutants with easy procedures [5]. However, commonly used adsorbents, such as activated carbon [6], still have some disadvantages. In addition to their effectiveness, many of these adsorbents are expensive and difficult to post handling that causes additional pollution. Therefore, in recent years, bio sorbents made from natural ingredients developed such as cellulose, chitosan, starch and lignin, are developed. Many of the modified cellulose adsorbents proved regenerable and reusable over a number of adsorption/desorption cycles [7]. Cellulose has active sites such as hydroxyl groups (-OH) which can easily bind with cationic compounds [8]. The adsorption method using cellulose bio sorbent has been used in several studies, among others by Kusumaningsih *et.al.* [9] using reeds to adsorb Remazol Yellow FG, Mardiah and Fathoni [10] using used newspaper to adsorb Cu (II) and Fe (II), and Bulut and Aydin [11] using wheat bran to adsorb methylene blue. In this study, considering used printing paper mainly consists of cellulose, it was used as adsorbent for methylene blue adsorption without further cellulose isolation, so that the preparation was simple and concise. Several adsorption parameters were investigated as well as desorption study. The desorption was aimed to recover the adsorbed methylene blue and possibly reused as a dye again.

## 2. Materials and Methods

### 2.1. Materials

Materials used in this work were Methylene blue (Merck), NaOH (Merck), M HCl (Merck), aquadest, used papers of A4 70g.

### 2.2. Instruments

Instruments used covered the Stirrer (IKA) with magnetic bar, analytical balance (Mettler), pH meter

(Hana), FT-IR Spectrophotometer (Shimadzu 1280), UV-Vis Spectrophotometer (Shimadzu series prestige 21).

### 2.3. Preparation 1000 mg/L Methylene blue solution

Preparation of 1000 mg/L methylene blue as the mother liquor was done by weighing 1.0 g of methylene blue, put into a beaker and dissolved with distilled water. Then the solution was soaked into volumetric flask (1 L) and filled up the solution with distilled water. Afterwards, by dilution the mother liquor was done to prepare the more diluted methylene blue solution concentrations.

### 2.4. Adsorbent preparation

Adsorbent for this work was prepared by cutting the used papers into pieces using scissors after selecting the parts with no ink (to avoid the ink disturbance to the adsorption process later). Then the cut papers were put into a blender to get fine powder. To homogenize the powder, it was sieved with 100 mesh filter and used without further treatment.

### 2.5. Adsorption study

#### 2.5.1. Effect of adsorbent dose

The adsorption of methylene blue experiment was conducted at pH 6 using 0.100 g adsorbent, 30 mg/L adsorbate and stirring speed of 200 rpm. Then to know the effect of adsorbent dose the adsorbent was varied (0.0025, 0.005, 0.0075, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 g). After the adsorption process the mixture of adsorbate and adsorbent was separated by filtering. The unabsorbed methylene blue concentration was measured using UV-Vis spectrophotometer. The methylene blue adsorbed used paper powder was dried at ambient atmosphere and used for further works (characterization and desorption study).

#### 2.5.2. Effect of contact time

The procedure was same as 2.5.1 with contact time was varied (5, 8, 12, 15, 30, 60, 90, 120 min).

#### 2.5.3. Effect of pH

The pH of the each of methylene blue solution before adsorption process was adjusted by drops of 0.1 M HCl (Merck) or 0.1M NaOH (Merck) solution to get the pH of 3, 5, 7, 9, and 11. The other procedure was similar as 2.5.1.

#### 2.5.4. Effect of adsorbate concentration

The procedure was similar as above (2.5.1) but the adsorbate concentration was varied (20, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200, 300, 500 mg/L).

### 2.6. Desorption study

The desorption study was done by immersing 1.0 g dried methylene blue adsorbed adsorbent with 10 mL HCl at different pH. The adsorbed methylene blue used paper powder was selected from the optimum condition of adsorption process. The dissolved methylene blue concentration was measured using UV-Vis spectrophotometer.

### 2.7. Characterization of methylene blue adsorbed used paper powder

Characterization of the used paper powder before and after contacted with methylene blue were examined using FT-IR Spectrophotometer (Shimadzu 1280). The sample preparation for the examination used a usual KBr pellet procedure.

### 2.8. Measurement of methylene blue concentration

The absorbance of the unabsorbed methylene blue solutions on the used paper powder were determined by using UV -Vis Spectrophotometer (Shimadzu series prestige 21) at the maximum wavelength of 658.6 nm. Furthermore, the measured absorbance was plotted at a standard curve to get the methylene blue concentrations. The standard curve is obtained by measuring the absorbance of a series of standard solutions and plotted with correlation as A *vs.* C. The straight line of standard curve follows the Lamber Beer Law, A = a.b.C (where A, a and C are absorbance, absorption coefficient, and concentration of measured solution (mg/L), respectively).

## 3. Result and Discussion

### 3.1. Effect of Adsorbent Dose on Adsorption of Methylene blue

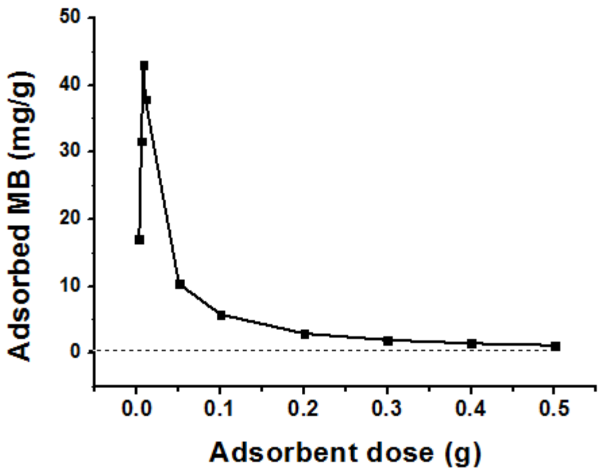


**Figure 1.** Effect of adsorbent dose on the methylene blue (MB) adsorption.

The effect of adsorbent dose variation to the methylene blue adsorption is shown in Figure1. From the figure can be seen the adsorbed methylene blue increases sharply until the adsorbent dose of 0.0075 g due to the more available active sites used for the adsorption. However, the sharp decrease occurs after that until the absorbent dose of 0.05 g and then, the changes are almost constant over 0.1g absorbent dose. This could be with more increased dose of adsorbent; the adsorbed methylene blue did not increase significantly because the adsorbate used was almost all adsorbed. In addition, high dose of adsorbent can also cause aggregation and agglomeration. The interaction among particles can decrease the surface area of the adsorbent and increase the diffusion distance [12].

### 3.2. Effect of Contact Time

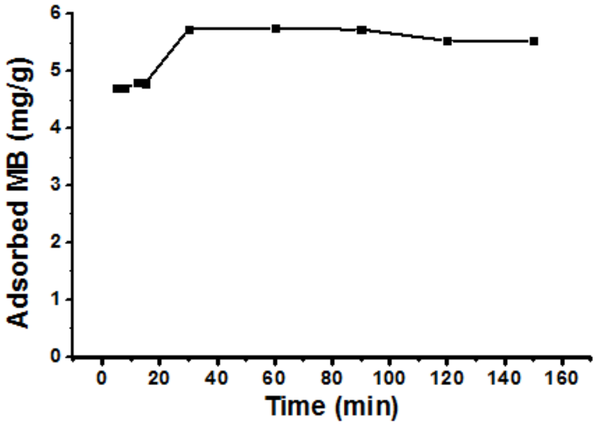


**Figure 2.** Effect of contact time on methylene blue (MB) adsorption.

Figure 2 shows that adsorption is rapid in the first 30 min, indicating a high affinity between the methylene blue molecule and the cellulose surface as the main component of the paper [13]. The adsorption increases significantly from 4.79 to 5.73 mg/g at the time from 15 to 30 minutes. At 30 to 90 min, the adsorption tends to be constant. In such circumstances the active sites are saturated and have reached the equilibrium between the dye molecules in the adsorbent. The increased duration of contact time over 120 min causes some adsorbate molecules released from active site of the adsorbent [14].

### 3.3. Effect of pH on Methylene Blue Adsorption

The effect of pH value on methylene blue adsorption can be seen in Figure 3. The figure shows the methylene blue adsorption increases significantly at pH 3.0-5.0, and the adsorption slightly increased at pH 7.0-11.0. The lowest adsorption of 5.13 mg/g was obtained at pH 3 and the highest adsorption of 5.88 was achieved at pH 9 and 11.The methylene blue dye will change its structure under various conditions of pH as shown in Figure 4, however, according to Kundu *et.al.* [15] there was no shift of maximum wavelength of methylene blue either at acidic or basic condition. The increase of adsorption at pH from 3 to 11 seems favorable to the adsorption process of methylene blue on the used paper powder. The increase of positive charges ($H^+$ ions) at lower pH made the surface of the used paper powder adsorbent become positively charged, thus they competed with dye cations causing the adsorption decrease significantly. Nevertheless, at higher pH the negative charged surface of the used paper adsorbent was more available and affected the increase of the methylene blue adsorption.

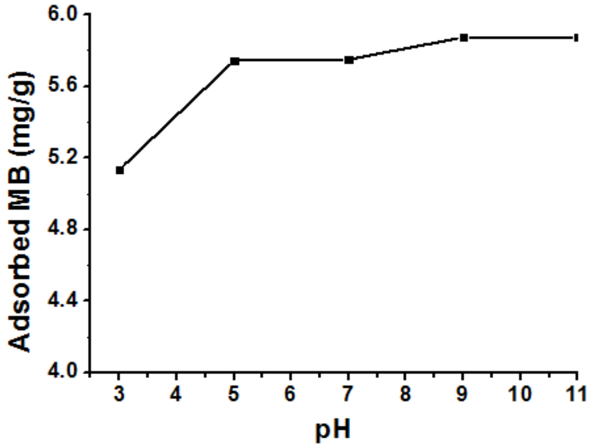


**Figure 3.** Effect of pH on methylene blue adsorption

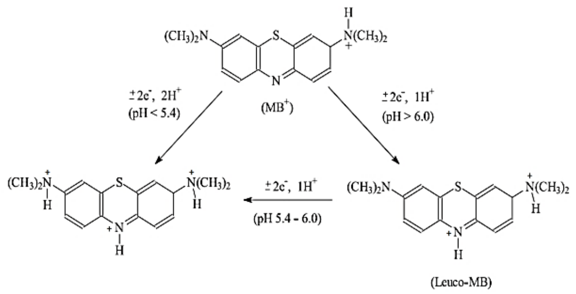


**Figure 4.** The structure of methylene blue in variations of pH conditions [16].

### 3.4. Effect of Initial Adsorbate Concentration

The results indicate that the adsorption decreases as the initial concentration of methylene blue increases as shown in Figure 5. At lower concentrations, many dye particles interact with the adsorbent, resulting in a better adsorption [17]. The adsorbate concentration of 20 to 500 mg/L decreases the adsorption from 94 to 45%. At a higher concentration, the sites present in the adsorbent have been saturated or have been covered by the dye so that the adsorption percentage does not increase [18].

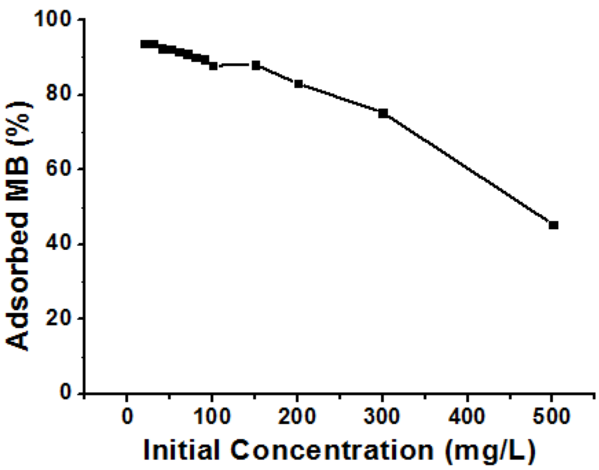


**Figure 5.** Effect of initial concentration of methylene blue on the percentage of methylene blue adsorption.

### 3.5. Adsorption of Langmuir Isotherm

Isothermal adsorption is a relation showing the adsorbent distribution between the adsorbed phases on the surface of the adsorbent with the equilibrium phase at a certain temperature [19].The Langmuir isotherm equation model is:

$$q = \frac{QbC}{1+bC} \qquad (1)$$

Where q is the mass of the adsorbate adsorbed per unit mass of adsorbent (mg/g), Q is maximum adsorption capacity (mg/g), C is the concentration of the adsorbate in solution and b is the equilibrium constant. The Langmuir adsorption model can be expressed in a linear form:

$$\frac{C}{q} = \frac{1}{Qb} + \frac{C}{Q} \qquad (2)$$

Where Q and b are constants and the values are obtained by plotting the C/q graph as a function of C. The equation is a straight line with $\frac{1}{Q}$ and $\frac{1}{Qb}$ are as slope and interception, respectively.

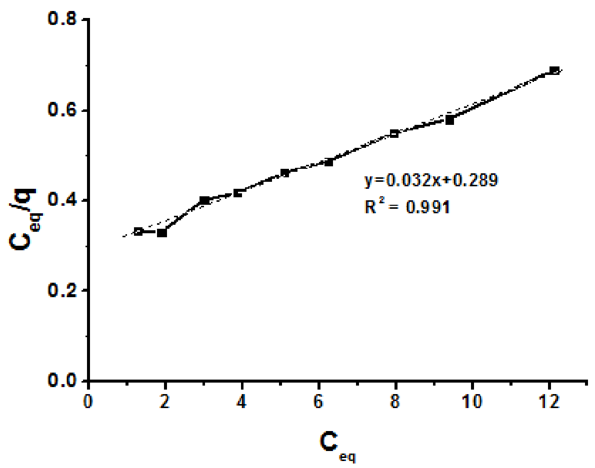


**Figure 6.** Linear form of Langmuir isotherm of methylene blue (MB) adsorption on used paper powder.

From Figure 6 shows the graph of Langmuir isotherm of methylene blue adsorption on used paper powder found the slope ($\frac{1}{Q}$) and the intercept ($\frac{1}{Qb}$) values are 0.0325 and 0.2897, respectively, with $R^2$ = 0.9919. The maximum adsorption capacity (Q) of methylene blue on the used paper powder, therefore, was found 30.77 mg/g. Langmuir's isothermal model forms a monolayer coating showing that the active site of the adsorbent can adsorb only one adsorbate molecule [11]. Comparison of the maximum monolayer adsorption of methylene blue onto various adsorbents can be seen in the Table 2. The table shows that this work has the highest maximum adsorption capacity. Nevertheless, there is still a room to improve this work by pretreatment the powder to remove the chemicals in the adsorbent other than cellulose. Since natural adsorbents from garlic peel and rice husk have better adsorption capacities than this work namely, 82.64 and 40.50 mg/g, respectively [20, 21].

**Table 2.** Comparison of the maximum monolayer adsorption of methylene blue onto various adsorbents.

| Adsorbents | Maximum monolayer adsorption capacity (mg/g) | Ref. |
|---|---|---|
| Used paper powder | 30.77 | This work |
| Raw beech sawdust | 9.78 | [22] |
| Activated rice husk | 0.21 | [23] |
| Jute processing waste | 22.47 | [24] |

### 3.6. Methylene blue Desorption Process

Methylene blue desorption was carried out by immersing the used paper of the adsorption process, in hydrochloric acid solution. The exchange of $H^+$ ions from hydrochloric acid with cationic methylene blue makes the methylene blue leaving out of the adsorbent sites and forms a methylene blue monomer. The $H^+$ ions of the acid bind $OH^-$ group of cellulose (as the main component of the adsorbent).

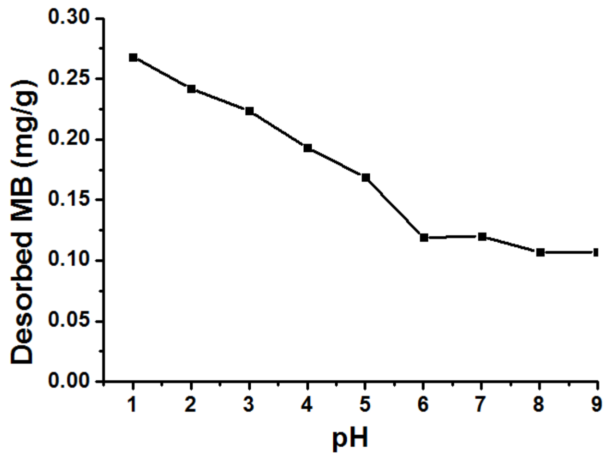


**Figure 7.** Effect of pH on the methylene blue (MB) desorption process

The effective methylene blue desorption was obtained with the highest desorption c.a. 0.27 mg/g (Figure 7) at pH 1 because the more $H^+$ can replace the methylene blue on the used paper powder adsorbent to form its own monomer. Meanwhile, as the less $H^+$ available in the solution at pH 6 and above the desorption of methylene blue was only 0.1 mg/g.

### 3.7. Adsorbent Characterization

Figure 8 depicts FTIR spectra of the used paper powder before and after used as adsorbent of methylene blue. The figure shows the absorption at a wave number of 3350.7 $cm^{-1}$ showing the shifting vibration of the hydroxyl group (-OH). The wave number of 2901.3 $cm^{-1}$ shows the presence of the -CH vibration of the alkyl group which is the framework of the cellulose structure [25]. Wave numbers of 1640 and 1430 $cm^{-1}$ denote an alkyl group (C-C). Also amplified by the ether group (C-O) which is a stretching vibration lies within the fingerprint region at the wave number of 1282-1035 $cm^{-1}$, which is the link of the carbon chain in the cellulose compound [26].

The appearance of cellulose in the spectra because the used (printing) paper mainly comprises 90% of cellulose and hemicelluloses [27].

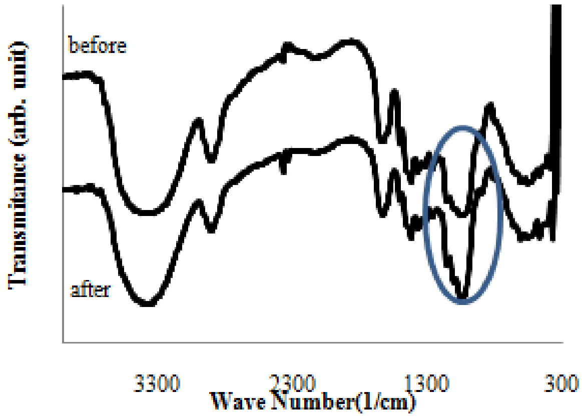


**Figure 8.** FTIR spectra of the used paper powder before and after used as adsorbent of methylene blue.

After adsorption with methylene blue there is a new band at the wavenumber of 1111.0 $cm^{-1}$ derived from the aromatic C-N vibration of the methylene blue. The presence of a new peak that emerges after adsorption indicates that methylene blue has been adsorbed on the cellulose of the used paper.

The surface functional group of the adsorbent is an active site that will interact directly with the adsorbate in the adsorption process. This active site depends on surface structure and composition [28].

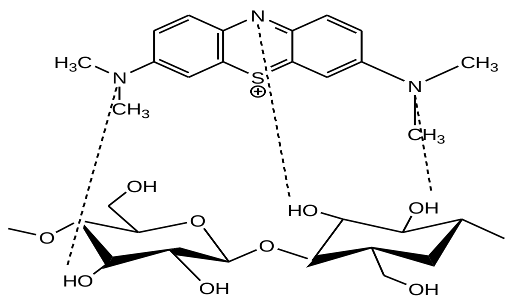

**Figure 9.** Cellulose interaction with methylene blue [29].

The mechanism of interaction between cellulose and methylene blue can be seen in Figure 9. Paper consists of a cellulose matrix that has an active site (OH), this active site has an important role for the adsorption process. With the presence of hydroxyl groups, cellulose is able to form hydrogen bonds both inter- and intramolecular [10].

## 4. Conclusion

The used paper can be used as adsorbent for removal of methylene blue. The highest adsorption of methylene blue was obtained at an optimum adsorbent dose, for 30 min at pH >9. The maximum adsorption capacity of 30.77 mg/g was obtained with Langmuir isotherm model. While the uptake of methylene blue by desorption process of the methylene blue adsorbed used paper powder was 0.27 mg/g at pH 1.

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