Removal of Methylene Blue Dye by Using Eggshell Powder

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Graphical abstract

Abstract

Dyes contain carcinogenic materials which can cause serious hazards to aquatic life and the users of water. Textile industry is the main source of dye wastewater which results in environmental pollution. Many studies have been conducted to investigate the use of low cost adsorbent as an alternative technique for the adsorption of dye. The objective of this study is to determine the potential of eggshell powder as an adsorbent for methylene blue removal and find out the best operating conditions for the color adsorption at laboratory scale. The adsorption of cationic methylene blue from aqueous solution onto the eggshell powder was carried out by varying the operating parameters which were contact time, pH, dosage of eggshell powder and temperature in order to study their effect in adsorption capacity of eggshell powder. The results obtained showed that the best operating condition for removal of methylene blue was at pH 10 (78.98 %) and temperature 50°C (47.37 %) by using 2 g of eggshell powder (57.03 %) with 30 minutes equilibrium time (41.36 %). The kinetic studies indicated that pseudo-second-order model best described the adsorption process.

Keywords: Dye wastewater; textile industry; eggshell powder; methylene blue; adsorption

INTRODUCTION

Dyes have been used in many industries for coloration purpose. Textile and dying industries are two main sources of dye wastewater production. It is difficult to treat dye wastewater because of the synthetic and complex structure of dye. Dye is resistant to light, heat and biological degradation due to their molecular structure. Nowadays, more than 10000 types of dye are commercially available which are classified into anionic, cationic and non-ionic types (Eren and Acar, 2006).

Many physical and chemical methods including adsorption, coagulation, precipitation, anaerobic treatment, filtration and oxidation have been used for the treatment of dye wastewater. However, many of these treatment technologies are expensive, especially when treat a large amount of dye wastewater. Adsorption has become one of the most effective and comparatively low cost methods for the decolorization of textile wastewater (Annadurai, et al., 2002; Arami, et al., 2006). Several studies have been conducted by various researchers to develop the cheaper and effective alternative adsorbents for removal of dyes from wastewater. Reife and Freeman (1996) reported that activated carbon has been investigated extensively due to the effectiveness of color removal from different classes of dyes and now the most widely used as adsorbent for dyes.
Despite its prolific use in wastewater industries, carbon adsorbent still remains an expensive process due to the high cost and difficulty in the regeneration of spent activated carbon. In order to reduce the cost of wastewater treatment, various adsorbent materials such as poultry waste, agricultural waste and other natural waste have been investigated (Nuttawan & Nuttakan, 2006). The materials that have been widely used as the adsorbents for dye removal are orange peels, banana peels, apple peel and wood in many researches (Nader, et al., 2011). Adsorption method by using low cost adsorbents are the most potential technique for textile wastewater treatment due to their efficiency in removing of organic and mineral pollutants and economic considerations (Pereira et al., 2003).

Chicken eggshell is a waste material discarded from domestic sources such as poultries, homes, food manufacturers and restaurants (Fajobi et al., 2005). The porous nature of eggshell makes it an attractive material to be employed as an adsorbent. It was estimated each eggshell contain between 7000 and 17000 pores (Pramanpol and Nitayapat, 2006; Elkady et al., 2011). Several studies showed that eggshells and eggshell membrane may be used as an adsorbent for iron (Yedduou and Bensaouli, 2007), cadmium (Park et al., 2007; Kuh and Kim, 2000), chromium (Chojaacka, 2005; Park et al., 2007; Ghazy et al., 2008; Rajendran and Mensiya, 2011; Liu and Huang, 2011), lead (Arunlertaree et al., 2007; Park et al., 2007), arsenic (Oka et al., 2008), reactive dye (Pramanpol and Nitayapat, 2006; Ehrampoush et al., 2011; Elkady et al., 2011), cationic dye (Tsai et al., 2006), azo dye (Tao, 2011) and malathion (Elwakeel et al., 2010). It is potential material for the removal of reactive dyes from industrial wastewater. However, the application of discarded eggshells in the removal of reactive dyes by adsorption method still has received very little attention. Therefore, the objective of this study is to investigate the potential of the eggshell powder as an adsorbent towards the methylene blue dye.

2.0 MATERIALS AND METHODS

2.1 Instruments and Materials

The instruments used for this study were beakers, measuring cylinders, pipettes, volumetric flasks, conical flasks, heater, pH meter, blender, glass rod, dropper, 2ml sample tubes, spatula, thermometer, electronic weigh, UV–VIS spectrophotometer, stopwatch, magnetic stirrer, centrifuge and oven. The materials used are eggshell, distilled water, methylene blue dye, hydrochloric acid (HCl) and sodium hydroxide (NaOH).

2.2 Methods

2.2.1 Preparation of Eggshell Powder

Discarded eggshells were collected from University Technology Malaysia (UTM) cafeterias. To prevent decomposition, eggshells were washed under tap water first. After that, eggshells were boiled in water and dried at 105°C in an oven for 2 hours to remove the moisture (Elkady et al., 2011). Next, the dried eggshells were grinded by using a blender. Finally, the eggshell powder was formed and stored in a sealed bottle to be used as adsorbent in this study.

2.2.2 Preparation and Determination of Dye solution

In this experiment, dye solution was prepared by dissolving methylene blue powder in distilled water to prevent and minimize possible interference. The dye was stirred until it was completely dissolved. A stock solution of the dye was prepared by dissolving 1gram of dye in 1000 mL distilled water to make a stock solution of 1000 mg/L. Then, the experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration. Six standards of dye solution with different dye concentration which are 10, 20, 30, 40, 50 and 60 mg/L were prepared. A sample of distilled water was used as a blank (0 mg/L). The blank and the standards were introduced into the UV-visible spectrophotometer at a wavelength of 565 nm and the absorbance reading of the blank and each standard were recorded. The aqueous solutions of dye with concentration range 0-60 mg/L were used for calibration. A standard calibration graph with absorbance versus concentration was plotted which was in linear form. With the calibration curve, the concentration of the dye samples after reacted with eggshell powder was determined.

2.2.3 Effect of Contact Time

1.0 g of eggshell powder was added to 50 ml of dye solution with concentration of 50 mg/L at room temperature. The mixture was stirred continuously with a magnetic stirrer. The samples were then taken at time 5, 10, 15, 30, 45, 60, 75, 90, 105 and 120 minutes. The temperature and pH of the solution were kept constant at 27°C and pH 6, respectively. At the above mentioned time intervals, the dye samples were sucked by a dropper. After collecting all the samples, the samples were centrifuged for 5 minutes at the speed of 9000rpm and the concentration of dyes was determined with UV-VIS Spectrophotometer. The effect of contact time on color removal efficiency was investigated by observing the color changes of the dye solutions.

2.2.4 Effect of pH

The pH of 50 ml dye solution with concentration 50 mg/L was manipulated to study the performance of adsorbent in different pH (2, 4, 6, 8, 10). The samples were titrated with hydrochloric acid (HCl) or sodium hydroxide (NaOH) to the desired pH value. The samples were then mixed with 1.0 g of eggshell powder and stirred at constant temperature of 27°C for 30 minutes. After that, the dye samples were centrifuged for 5 minutes at the speed of 9000 rpm and the concentration of dyes was determined with UV-VIS Spectrophotometer.

2.2.5 Effect of Adsorbent Dosage

The adsorption studies was carried out at room temperature by mixing various amounts of eggshell powder (0.2 g, 0.6 g, 1.0 g, 1.5 g, 2.0 g) into 50 ml of five 50 mg/L dye solution respectively and stirred at room temperature for 30 minutes. After that, the dye samples were centrifuged for 5 minutes at the speed of 9000 rpm and the concentration of dyes was determined with UV-VIS Spectrophotometer. The pH of the solution was kept constant 10.

2.2.6 Effect of Temperature

The experiment was carried out by setting the temperature of 50 ml of dye solution with concentration 50 mg/L in the range of room temperature to 80°C in order to study the performance of adsorbent in different temperature. Five sets of 50 ml volumes of samples were prepared by mixing 1.0 g of eggshell powder and stirred for 30 minutes with difference temperature (27°C, 35°C, 50°C, 60°C, 80°C). After that, the dye samples were
In order to investigate the ability of eggshell powder to remove the amount of dye from its solution, the concentration of dye solution was determined with UV-VIS spectrophotometer at a wavelength of 565 nm. After the adsorption process had attained equilibrium, the samples were centrifuged and the residual concentration in the supernatant dye solution was introduced into UV-VIS Spectrophotometer. The absorbance was recorded to find the unknown dye concentration remaining after it has undergone the reaction. By determining the residual concentration of the dye samples, the percentage of dye removal and amount of dye adsorbed by the eggshells powder were calculated.

2.2.8 Adsorption Kinetics

Pseudo-First Order

The pseudo-first order rate generally expressed as follow:

\[
\frac{dq_t}{dt} = K_1 (q_e - q_t)
\]

where \( K_1 \) is the rate constant of pseudo-first order adsorption \((\text{min}^{-1})\) and \( q_e \) represents adsorption capacity. After definite integration at \( t=0 \) to \( t=t \) and \( q_e=0 \) to \( q=q_t \) as a boundary condition, equation (1) becomes equation (2) as follow:

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t
\]

where \( q_e \) and \( q_t \) are the adsorption capacity \((\text{mg/g})\) at equilibrium and at any time \( t \). The plot of \( \log (q_e - q) \) versus \( t \) must be linear relationship to determined the rate constant for different treatment condition. From the plot, the slope indicates \( K_1 \) value and intercept is \( \log q_e \) value respectively. The straight lines of the plot approach the applicability of the first-order rate expression.

Pseudo-Second Order

The pseudo-second order equation also based on the adsorption capacity on the solid phase. The pseudo-second order kinetic model is expressed as:

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

where \( K \) is the rate constant of pseudo-second order adsorption \((\text{g/mg.min})\). The straight line plot of \( t/q_t \) versus \( t \) will obtained rate parameter. As a result, \( 1/q_t \) indicates as the slope and \( 1/Kq_e^2 \) as the intercept.

The Intraparticle Diffusion Model

Usually the adsorbate species transported from the bulk solution into solid phase through intraparticle diffusion process.

Intraparticle diffusion is a kind of kinetic model express as follow:

\[
q_t = K_{dif} t^{1/2} + C
\]

where \( C \) is the intraparticle diffusion rate constant \((\text{mg/g.min}^{1/2})\). The \( q_t \) is a linearity correlation of \( t^{1/2} \) and rate constant \( K_{dif} \) from the slope of regression line. The linearity of the plot indicates the applicability of the experimental data as the intraparticle diffusion model.

3.0 RESULTS AND DISCUSSIONS

3.1 Effect of Contact Time

Figure 3.1 illustrates the effect of contact time towards dye removal percentage \( (%) \) and \( q \), amount of dye adsorbed per unit adsorbent weight \((\text{mg/g})\). Initially, methylene blue dye was removed rapidly in 5 minutes. The quantity of adsorbed dye molecules rose with time and started to attain an almost constant value around 30 minutes. When the contact time was increased to 5, 10, 15 and 30 minutes, the percentage of dye removal showed a slightly increased trend and became almost constant with 39.22%, 40.88%, 41.20% and 41.36% respectively. The amount of dye on adsorbent also showed the same trend with 0.98, 1.02, 1.03 and 1.03 mg/g respectively. However, the percentage of dye removal exhibited a slightly fluctuated and downward trend with time after 30 minutes ranging from 33% to 39%.

From the graph, it reveals that the rate of percent dye removal was higher at the beginning. This was probably due to larger surface area of the eggshell powder being available at the beginning for the adsorption of dye ions. As the contact time was increased, the active sites were decreased and remaining vacant sites of eggshell surface were difficult to be occupied due to repulsive forces between the molecules of the eggshell surface and the aqueous solution. The dye molecules which carried positive charged ions adsorbed on the adsorbent repelled with the unabsorbed dye molecules. As a consequent, it prevented the remaining molecules to move towards the eggshell structure. Apart from that, the small fluctuation in the amount of dye adsorbed might due to the weak physical adsorption of eggshell powder. This result was supported by Tsai et al., (2006) which is the basic dye methylene blue is very poorly adsorbed by both eggshells and their membranes.

3.2 Effect of pH

Figure 3.2 shows the effect of pH towards dye removal percentage \( (%) \) and \( q \), amount of dye adsorbed per unit adsorbent weight \((\text{mg/g})\). By increasing the pH of the aqueous solution, it led to the improvement of the dye adsorption efficiency. Dye solution with pH value 2, 4, 6, 8 and 10 were observed to have an elevated trend of dye removal percentages which were 0.47%, 5.11%, 35.18%, 69.75% and 78.98% respectively. On the other hand, \( q \) was increased tremendously from 0.01 mg/g to 1.97 mg/g as the pH value was increased from 2 to 10.

From the results, it is proven that the pH of an aqueous solution is the main parameter that affects the adsorption capability which is a function of hydrogen ions and hydroxyl ions concentrations. It was found that methylene blue was best adsorbed by eggshell powder in alkaline condition and quite difficult or almost unable to remove in acidic condition. This
may due to the effect of pH on the charge of reactive group within the eggshell which made it more effective to adsorb dye in alkaline pH. The adsorbent carried a lot of negative charges. In aqueous solution, the carbonate species were $\text{H}_2\text{CO}_3$, $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$. As the pH of the system increased, the numbers of negatively charged sites were increased with presence of $\text{OH}^-$ ions. The negatively charged sites on the adsorbent favor the adsorption of cationic dyes due to the electrostatic attraction. However, the low adsorption capacity of methylene blue at acidic pH might due to the presence of excess $\text{H}^+$ ions competing with positively charged cationic dye for the available adsorption sites. Moreover, calcium carbonate might dissolve to form calcium chloride, water and release carbon dioxide gas when a small quantity of HCl was added (Equation 3.1). As a result, it lost its adsorption capability.

$$\text{CaCO}_3 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad (3.1)$$

![Figure 3.1 Effect of contact time on adsorption efficiency](image1)

![Figure 3.2 Effect of pH on adsorption efficiency](image2)
3.3 Effect of Adsorbent Dosage

Figure 3.3 shows the effect of adsorbent dosage towards the dye removal percentage (%) and q, amount of dye adsorbed per unit adsorbent weight (mg/g). When the adsorbent dosage increased, the percentage of dye removal was also increased. From the result obtained, the dye removal was 0.01%, 31.12%, 35.18%, 49.31% and 57.03% at adsorbent dosage of 0.2 g, 0.6 g, 1.0 g, 1.5 g and 2.0 g respectively. Then, the adsorbed dye was increased from around 0.00 mg/g to the 1.43 mg/g by increasing the dosage from 0.2 g to 2.0 g.

The adsorption efficiency increased with adsorbent dosage because there were plenty of surface area and more adsorption sites available to interact with the dye molecules provided by the increased adsorbent dosage. In contrast, the low adsorption capability might due to the saturation of adsorption sites and hence cannot further adsorb the dye molecules.

![Figure 3.3 Effect of adsorbent dosage on adsorption efficiency](image)

3.4 Effect of Temperature

Figure 3.4 illustrates the effect of temperature towards the dye removal percentage (%) and q, amount of dye adsorbed per unit adsorbent weight (mg/g). The percentage of dye removal for temperature 27°C, 35°C, 50°C, 60°C and 80°C were 35.18%, 42.79%, 47.37%, 14.53% and 0.18% respectively. The q was elevated from 0.88 mg/g to 1.18 mg/g when the temperature was increased from 27°C to 50°C. After 50°C, it was followed by a steep drop of q from 1.18 mg/g until approximately 0.00 mg/g when the temperature was beyond 60°C.

The increased of adsorption temperature from 27°C to 50°C significantly enhanced the adsorption capacity of the methylene blue. At 50°C, the eggshell powder exhibited the best adsorption affinity with the dye molecules. This phenomenon indicated that the elevation of solution temperature to around 50°C can provide suitable driving force to raise the mobility of dye molecules. As a result, more dye molecules number get enough of energy to move towards the eggshell powder and undergone an interaction with its structure. Apart from that, the swelling effect within the internal surface of the eggshell powder due to elevated temperature enabled large amount of dye molecules to penetrate further into the eggshell structure. Nevertheless, the adsorption efficiency of eggshell powder was decline sharply from temperature 50°C to 80°C and even lost its adsorption ability with high temperature. Further elevated of solution temperature might damage the structure of the eggshell and lead to the failure of eggshell capability to act as an adsorbent.

3.5 Adsorption Kinetics

The adsorption kinetic data of methylene blue was analyzed using three kinetics models which are pseudo-first-order, pseudo-second-order and intra-particle diffusion. The best model was selected based on the linear regression correlation coefficient, R² values. The graphs of pseudo-first-order, pseudo-second-order and intra-particle diffusion for adsorption of methylene blue onto eggshell powder are shown in Figures 3.5 (a), 3.5 (b) and 3.5 (c) respectively.
Figure 3.4 Effect of temperature on adsorption efficiency

\[ y = 4 \times 10^{-6}x^4 - 0.000x^3 + 0.052x^2 - 1.461x + 15.19 \]
\[ R^2 = 1 \]

\[ y = 0.000x^4 - 0.031x^3 + 2.108x^2 - 58.45x + 607.7 \]
\[ R^2 = 1 \]
Pseudo-first-order, pseudo-second-order and intra-particle diffusion models were applied to fit the experimental data in order to examine the adsorption kinetics. The fitting results are shown in Table 3.1 to compare the kinetic parameters for adsorption of methylene blue onto eggshell powder with three different types of kinetic models.

For pseudo-first-order model, the $q_e$ calculated from the equation (2) differed from the experimental value of $q_e$. The theoretical $q_e$ value deviated far away from the corresponding experimental value which was 0.0389 mg/g and 1.0341 mg/g respectively. The linearity of log ($q_e - q_t$) versus time obtained was very low with correlation coefficient value of 0.6288. It clearly indicated that pseudo-first-order model was not adequate to describe the adsorption process of methylene blue onto eggshell powder. It suggested that this adsorption system was not a first-order reaction. However, the adsorption of methylene blue was well fitted with pseudo-second-order kinetic model. The correlation coefficient obtained was 1.0. The straight line in plot of $t/q_t$ versus $t$ in Figure 3.5 (a) shows the good agreement of experimental data with the pseudo-second-order kinetic model. The calculated $q_e$ value which was 1.044 mg/g also quite closed with the experimental value which was 1.034 mg/g. Hence, it proved that pseudo-second order model can well represent the experimental data in order to describe the adsorption kinetic of cationic dye onto the adsorbent surface.
For intra-particle diffusion, the linearity of the plot was not so high with $R^2$ of 0.6796. Apart from that, a plot of solute adsorbed on adsorbent versus the square root of the contact time also did not yield a straight line which passed through the origin. Therefore, the experimental results did not fit well with the intra-particle diffusion model.

Based on the analysis and comparison of the parameters obtained, the adsorption of methylene blue onto eggshell powder was well described by pseudo-second-order model with a high correlation coefficient. The experimental results were fitted better with pseudo-second-order model compared to the other two models. Pseudo-second-order kinetic model can describe the adsorption process of methylene blue onto eggshell powder with the rate of adsorption depending on the square of the dye concentration. In other words, the second order adsorption indicated that the rate of reaction was directly proportional to the square of the dye concentration.

<table>
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<th>Kinetic model</th>
<th>$q_e$ (exp) (mg/g)</th>
<th>$q_e$ (calc) (mg/g)</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$k_2$ (g/mg min)</th>
<th>$R^2$</th>
<th>$k_{id}$ (mg/g min$^{1/2}$)</th>
<th>$C_i$ (mg/g)</th>
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<td>Pseudo-first-order</td>
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<td>0.6288</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Pseudo-second-order</td>
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<td>1.0440</td>
<td>-</td>
<td>3.7145</td>
<td>1.0000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>0.6796</td>
<td>0.0148</td>
<td>0.9619</td>
</tr>
</tbody>
</table>

### 4.0 CONCLUSION

In conclusion, eggshell powder possess a good adsorption capability for methylene blue which is a cationic dye. The best operating conditions for eggshell powder to operate efficiently was at 30 minutes contact time, pH 10 and 50°C by using 2.0 g of eggshell powder in a 50 ml of methylene blue solution with concentration 50 mg/L. At pH 10, it could remove up to 78 % of dye solution. The experimental results were best described with pseudo-second-order kinetic model. The results show that eggshell powder is a potential adsorbent which is environmentally friendly for removal of basic dye wastewater.

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