Removal of methylene blue using magnetic multi-walled carbon nanotubes: process optimization study

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**Abstract.** Adsorption is the most common methods used in industry for the removal of dye. In this study, magnetic multi-walled carbon nanotubes (MMWCNTs) was served as adsorbent for the removal of methylene blue (MB). Statistical optimization of the MB removal efficiency via response surface methodology coupled with central composite design was performed and reported. It was observed that all three experimental parameters: adsorption temperature (25-50°C), MB concentration (10-50 ppm) and MMWCNTs dosage (0.01-0.05 g/20mL) were significant in the removal of MB. The optimized conditions of 99.21 % MB removal efficiency can be achieved at adsorption temperature of 38°C, MB concentration of 23 ppm and MMWCNTs dosage of 0.033 g/20mL. The verification of the prediction was performed with 3 repeated experiments and the results were found to be in good agreement with the experimental data with only 0.21 % error.

**1. Introduction** Water is the most important source of life on Earth. However, water contamination has become a global issue due to the tremendous increase in human population and rapid pace of industrialization [1]. Dyes which are heavily used in textiles, cosmetics, paper, and food industries have worsened the situation as the effluents were not always treated [2]. As one of the most common colorant used, methylene blue (MB) is toxic and carcinogenic which may cause mutation, cancer, and dermatological diseases upon contact [3]. Therefore, it is of utmost importance to remove the dye prior to discharge to ensure minimal harm to the environment, especially to aquatic life.

Multiple techniques including adsorption, membrane separation, coagulation/flocculation, biological treatment, chemical oxidation, and ion exchange have been developed to tackle such issue. Among these techniques, adsorption is the most common methods due to its low operating cost, high efficiency, ease of operation, availability of the wide range of adsorbents and consistent performance in the removal of contaminate from the source [4]. Hence, in this study, magnetic multi-walled carbon nanotubes (MMWCNTs), consisted of multi-walled carbon nanotubes (MWCNTs) and iron oxide (Fe₃O₄) were synthesized to serve as adsorbent for the removal of MB.

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The aims of this study were to evaluate the effect of various process parameters which included temperature (25-50°C), MB concentration (10-50 ppm) and MMWCNTs dosage (0.01-0.05 g/20mL) in the removal of MB. These parameters were then optimized by employing response surface methodology (RSM) coupled with central composite design (CCD).

2. Materials and Methods

2.1. Materials
The multi-walled carbon nanotubes were purchased from Shen Zhen nanotechnologies Port Co. (China). Magnetite nano-colloid iron oxide Fe₃O₄ (20-30 nm) was supplied by NanoAmor (USA). Concentrated HNO₃ (60-70%) was supplied from J.T. Baker (Germany). MB was purchased from Sigma-Aldrich (Malaysia). All materials were used without further purification or alteration.

2.2 Functionalization of WMCNTs
1 g of pristine MWCNTs were weighted and dispersed in 100 mL of concentrated HNO₃ under ultrasonication for 30 minutes. After 30 minutes, the mixture was refluxed at 80°C for 8 hours under continuous stirring using magnetic stirrer. These treated MWCNTs were filtered and washed with excess distill water until the pH of the effluence was neutral. These MWCNTs were then dried in oven at 100°C for 18 hours. These functionalized MWCNTs were denoted as c-MWCNTs.

2.3 Synthesis of MMWCNTs by doping of c-MWCNTs with iron oxide, Fe₃O₄
The ratio of c-MWCNTs to Fe₃O₄ was fixed at 1.5:1 in the synthesis of MMWCNTs. A solution of Fe₃O₄ with 2 ppm concentration was prepared by dispersing 0.2 g of Fe₃O₄ into 100 mL distilled water. The mixture was sonicated for 5 minutes to achieve homogeneous dispersion. After the sonication, 7 mL of the Fe₃O₄ solution was pipetted into the centrifuge bottle with 30 mL of deionized (DI) water. The mixture pH was then adjusted to 4.5 - 4.6 as the doping process is most efficient within this pH range. After the pH was adjusted, 21 mg of the c-MWCNTs was weighted and dispersed into the centrifuge bottle and sealed with parafilm. The mixture was then sonicated for another 5 minutes. After that, the mixture was rotated using a rotating mixer for overnight (16 hours) to obtain the well-mixed c-MWCNTs and Fe₃O₄ nanoparticle. These magnetic composites were denoted as MMWCNTs. Next, these MMWCNTs were collected by applying a magnetic field using a magetic bar for 30 minutes and rinsed with DI water repeatedly. Lastly, these MMWCNTs were filtered and then dried in oven for 12 hours at 100°C.

2.4 Design of Experiment (DOE)
RSM coupled with CCD was performed to design the experiment work and to elucidate the MMWCNTs adsorption performance using Design Expert version 11.0.4 software (STAT-EASE Inc., USA). The process parameters selected and their respective ranges of investigation for this study were temperature (25-50°C), MB concentration (10-50 ppm) and MMWCNTs dosage (0.01-0.05 g/20 mL) while the MB removal efficiency was selected as the response, as presented in table 1. A total of 20 experiments were generated based on the selected ranges and these responses were categorized into 8 factorial points, 6 axial points and 6 replicates at the centers as calculated from equation (1) [5]:

\[ N = 2^n + 2n + n_c = 2^3 + (2 \times 3) + 6 = 20 \]  

Where N was the total number of experiments needed, n was the number of independent variables and \( n_c \) was the replicate number of the central point.
In a typical adsorption test, a pre-weighted amount of MMWCNTs was dispersed in 20 mL of the pre-determined concentration of MB solution in a 20 mL of scintillation vial. The mixture was then allowed to shake for 1 hour under the pre-determined temperature at a constant speed of 180 rpm. After 1 hour, the MMWCNTs suspended in the mixture was subjected to magnetic field for 30 minutes to separate the adsorbents from the medium. Then, the MB concentration after the adsorption was analyzed using UV-Vis spectrophotometer. The removal efficiency of MB was then calculated by using equation (2):

$$R = \frac{C_0 - C_e}{C_0} \times 100\%$$  \hspace{1cm} (2)

Where R was the removal efficiency of MB (%), $C_0$ was the initial concentration of MB (mg/L) and $C_e$ was the final concentration of MB (mg/L).

3. Results and Discussion

3.1 Development of Regression Model
All of the obtained results were analyzed using analysis of variance (ANOVA) and a regression model was developed based on the ANOVA result. After eliminating the insignificant terms with p-value greater than 0.05, the ANOVA analysis table (as presented in table 2) and the most accurate regression model equation (quadratic polynomial equation) was developed, as shown in equation (3). As shown in table 2, the model F-value was 128.12 and p-value < 0.0001 for the MB removal which proved that the developed model was significant. Besides that, high $R^2$ value (0.9879) showed that sample variation of 98.79% for MB removal was attributed to the independent variables and only 1.21% of the entire variation was not predicted by the empirical model [6]. Moreover, small difference (0.0513) between adjusted $R^2$ and predicted $R^2$ also proved that predicted $R^2$ of 0.9289 was in reasonable agreement with the adjusted $R^2$ of 0.9820 [7].

$$MB\ removal\ efficiency\ (\%) , (R1) = 93.07 + 2.81A - 10.21B + 10.52C + 3.05AB + 7.65BC - 3.30B^2 - 3.97C^2$$ \hspace{1cm} (3)

Where A was the adsorption temperature, B was the MB concentration and C was the MMWCNTs dosage.

3.2 Effect of single process parameter
All the three process parameters studied, temperature (A), MB concentration (B) and MMWCNTs dosage (C) were found to significantly affect the MB removal efficiency as all their p-values were lower than 0.05 [6]. Meanwhile, the parameter with the highest F-value caused the most significant effect to the MB removal efficiency. Hence, as shown in table 2, MB concentration was identified as the major parameter, followed by MMWCNTs dosage and temperature. Figure 1(a)-(c) illustrate the individual effect of single parameter to MB removal efficiency. From figure 1(a), MB removal efficiency increased with higher temperature at the fixed concentration of MB and MMWCNTs. This can be justified as

| Table 1: Coded variable levels for independent variables using CCD |
|---------------------------------------------------------------|
| Variables | Codes | Unit | -α | -1 | 0 | +1 | +α |
| Temperature | A | °C | 25 | 30 | 38 | 45 | 50 |
| MB concentration | B | ppm | 10 | 18 | 30 | 42 | 50 |
| MMWCNTs dosage | C | g/20mL | 0.01 | 0.02 | 0.03 | 0.04 | 0.05 |

$\alpha$ = axial design point
higher temperature can increase collision frequency between MMWCNTs and MB molecules, activate the adsorbent surface and allowing MB ions to penetrate through sample pores more easily by increasing the dye mobility [8, 9]. However, as shown in figure 1(a), the increment of MB removal efficiency was around 5% upon the increasing of temperature from 30 °C to 45 °C. This observation was supported by the fact that the temperature was the least significant parameter as it possessed the lowest F-value. Figure 1(b) showed that MB removal efficiency reduced with higher MB concentration. MB concentration played an important role as the driving force to overcome the mass transfer resistance between solid phases and aqueous phases [8, 10]. In general, the availability of adsorption sites at a fixed adsorbent dosage were more than enough at low MB concentration due to low amount of MB molecules. However, the increase of MB concentration led to fully occupied of the adsorption sites of MMWCNTs when the dosage of MMWCNTs was fixed. Therefore, the adsorption of MB molecules onto the MMWCNTs was prohibited. As shown in figure 1(b), there was a significant reduction of 20% in MB removal efficiency upon the increment of MB concentration (from 18 ppm to 42 ppm). This was in agreement that MB concentration was the most significant parameter as it had the highest F-value. On the other hand, figure 1(c) showed an increment of 18% in MB removal efficiency upon the increasing in MMWCNTs dosage (from 0.018 g/20 mL to 0.042 g/20 mL). This was because the increase in MMWCNTs dosage may increase the availability of adsorption sites, thus promoting the adsorption of MB molecules by MMWNCTs [9, 11].

| Table 2: Analysis of variance (ANOVA) results of the updated response model. |
|-----------------------------------|-----------------|----------------|-----------------|-----------------|-----------------|
| Source | Sum of Squares | df | Mean Square | F-value | p-value |
|--------|----------------|----|-------------|---------|---------|
| Model  | 3338.35 | 7  | 476.91      | 128.12  | < 0.0001| significant |
| A-Temperature | 107.98 | 1  | 107.98      | 29.01   | 0.0002 | significant |
| B-MB concentration | 1424.07 | 1  | 1424.07 | 382.56  | < 0.0001| significant |
| C-MMWCNTs dosage | 1011.20 | 1  | 1011.20 | 271.65  | < 0.0001| significant |
| AB     | 74.59 | 1  | 74.59       | 20.04   | 0.0009 | significant |
| BC     | 468.94 | 1  | 468.94      | 125.97  | < 0.0001| significant |
| B²     | 152.86 | 1  | 152.86      | 41.06   | < 0.0001| significant |
| C²     | 133.80 | 1  | 133.80      | 35.94   | < 0.0001| significant |
| Residual | 40.95 | 11  | 3.72       |         |         |             |
| Pure Error | 0.2639 | 5  | 0.0528  |         |         |             |
| Cor Total | 3379.29 | 18 | R²       | 0.9879  |         |             |
| Std. Dev. | 1.93   |       | Adjusted R² | 0.9802 |         |             |
| Mean    | 89.36  |       | Predicted R² | 0.9289 |         |             |
| C.V. %  | 2.16   |       | Adequate Precision | 39.4182 |         |             |
Figure 1. Individual effect of single parameter to MB removal efficiency; (a) temperature, (b) MB concentration and (c) MMWCNTs dosage.

3.3 Interaction between parameters
Figure 2 illustrated the three-dimensional response surface model plots for parameter interaction. Figure 2(a) showed that the parameter interaction between MB concentration and MMWCNTs dosage at fixed temperature (30°C). Both MMWCNTs dosage and MB concentration were significant to each other as any changes in MMWCNTs dosage or MB concentration could affect the MB removal efficiency significantly at a fixed temperature. The highest MB removal efficiency (100%) could be achieved even at the temperature of 30°C but only with relatively high MMWCNTs dosage and low MB concentration as illustrated in figure 2(a). On the other hand, figure 2(b) showed that the parameter interaction between temperature and MB concentration at fixed MMWCNTs dosage. It was found that the MB removal efficiency barely increased at any MB concentration except MB concentration of 42 ppm when adsorption temperature increased from 30 °C to 45 °C. This can be explained that the adsorption of MB by MMWNCTs achieved saturation even at temperature of 30 °C. However, when the MB concentration was fixed at the highest of 42 ppm, slight increase in the MB removal efficiency can still be observed when the adsorption temperature increased from 30 °C to 45 °C. High temperature increased collision frequency between MMWCNTs and MB molecules, activate the adsorbent surface and allow MB ions to penetrate through sample pores more easily by increasing the dye mobility.
However, further increase of adsorption temperature in this study caused only a mere increase in the MB removal efficiency. This was because at a fixed adsorbent dosage, MMWCNTs became the limiting factor for the adsorption process. Again, as shown by the ANOVA results, temperature was the least significant parameter as compared to MMWCNTs dosage and MB concentration. Furthermore, this behavior also shows that the interaction between temperature and MB concentration is less significant as compared to the interaction between MB concentration and MMWCNTs dosage.

Figure 2. Three-dimensional response surface model plots for MB removal efficiency; (a) Effect of MB concentration and MMWCNTs dosage at temperature of 30°C and (b) Effect of temperature and MB concentration at MMWCNTs dosage of 0.018g/20mL.

3.4 Process Optimization
A numerical method mode was chosen in obtaining the optimum condition for MB removal efficiency using MMWCNTs. All constraints were set to be in range in order to obtain the maximum MB removal efficiency. The goals were set to be in the range of lower and upper limits for all the three factors (A, B and C) in order to get a maximum MB removal efficiency of 99 % and a predicted optimum condition was proposed as in figure 3. The optimum condition for MB removal efficiency was found at adsorption temperature of 38 °C, MB concentration of 23 ppm and MMWCNTs dosage of 0.033 g/20 mL. The desirability value for this optimum condition was 1.000 which is evidence for the application of this model [6]. In order to validate the predicted value, experiments had been repeated in triplicate at the predicted optimum conditions and returned with MB removal efficiency of 99.19 %, 99.21 % and 99.24 %, respectively. These results showed an average value of 99.21 %, in which only 0.21 % of error was found as compared to that of the predicted value (99%). As such, it could be concluded that the regression model developed as shown in equation (3) is valid and of high accuracy in predicting the MB removal efficiency using MMWCNTs.
4. Conclusion
RSM coupled with CCD was employed to optimize the MB removal efficiency using MMWCNTs with adsorption temperature, MB concentration and MMWCNTs dosage as coded variables. High accurate empirical quadratic response model was developed as equation (3) with a coefficient of determination ($R^2$) value of 98.79%. All of these coded factors were found to have a significant effect toward the MB removal efficiency response with the sequence of significance as MB concentration, followed by MMWCNTs dosage and lastly, temperature. The optimized conditions of MB removal efficiency using MMWCNTs were obtained at adsorption temperature of 38°C, MB concentration of 23 ppm and MMWCNTs dosage of 0.033 g/20mL. Response validation tests showed that the predicted optimized conditions were highly accurate, as only 0.21% of error was observed when compared to the actual experimental data. In conclusion, the significances of the interaction between the tested parameters and the MB removal efficiency were successfully elucidated. The optimized condition for the maximum MB removal efficiency was also predicted using the highly accurate and reliable developed model in this study.

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