Catalytic oxidation of dye waste water by biomass charcoal loaded multiple rare earth composite material

Suriga^1 and Liping CHEN^2,3

^1^College of Chemistry and Environment Science, postgraduate, Inner Mongolia Normal University, Hohhot 010022, China
^2^College of Chemistry and Environment Science, Inner Mongolia Normal University, Hohhot 010022, China

E-mail: clp@imnu.edu.cn

Abstract. The main purpose of this study is to investigate the individual effect as well as the interactions of different influencing factors like catalyst dosage, aeration rate, temperature and pH on the removal of methylene blue (MB) using biomass charcoal loaded multiple rare earth composite material. Design-Expert 7.0 was used to design testing program and establish response surface model. The result showed that among the factors, catalyst dosage played the most important role, then pH value, aeration rate and temperature in turn. By the optimization of process parameters, the optimum experimental conditions were catalyst dosage of 2.50 g, aeration rate of 2.5 L min^{-1}, temperature of 21 °C and pH value of 12, under these optimum conditions, maximum predicted and observed decolorization rate were 100.00% and 99.61%, the observed value was well match with the predicted value.

1. Introduction
With growing urbanization and industrialization, the problem of the dye waste water has been of increasing concern in many parts of the world. China discharge 1.6 hundred million m³ of dye waste water every year [1]. They damage the environment and contain many chemicals that are toxic, mutagenic, hazardous and cancerogenic [2,3]. They also block light penetration, destroy the water quality of the receiving streams, and deliver hazardous and toxic materials to organisms in the food chain [4]. Therefore, dye waste water needs to be treated for the sake of the protection of human beings health and environmental safety. For the practical purpose of water treatment, it was necessary to investigate an efficient, practical method for application in industrial degradation. Dyes were very stable and difficult to be biodegraded because of the synthetic origin and complex aromatic molecular structures, chemical coagulation and biodegradation lead to secondary pollution [5,6]. Recently, the treatment of waste water through catalytic oxidation techniques has proven to be simple, cheap, efficient and nontoxic [7].

Biomass charcoal is a solid waste produced in the agriculture production process. In China, the biomass charcoal has discharged increasing numbers with the increase of sunflower planting, its output is 11.8 billion ton every year in china. Biomass charcoal is a kind of low cost and easily available catalyst and often used in wastewater treatment due to its large surface area, porosity, high adsorption capacity and good stability [8].

In order to study the optimal parameters for catalytic oxidation of MB, we used response surface methodology to design testing program and establish response surface model. RSM is a useful method...
which studying the effect of individual factors as well as their interaction by a limited number of experiments. So, the optimum conditions for desirable responses could be obtained.

In our previous study, biomass charcoal loaded multiple rare earth composite material has been prepared for the removal of MB and investigated the influences of catalyst dosage, aeration rate, temperature and pH on the catalytic oxidation process through single factor test, then obtained the optimal conditions by using RSM and then briefly discussed the experimental result. The results provides a theoretical basis for preparation of the biomass charcoal composite material and catalytic oxidation study.

2. Experimental

2.1. Materials and chemicals

Sunflower straw was taken from the Hetao region of Inner Mongolia; Mixed rare earth was obtained from Baotou of Inner Mongolia. The rare earth oxides and their contents in mixed rare earth used in this study are given in table 1. It was evident from the table that the mixed rare earth were rich in CeO$_2$ of 52% and La$_2$O$_3$ of 28%. That is, CeO$_2$ played a bigger role in mixed rare earth for catalytic oxidation of MB. The other chemicals were methylene blue, phosphoric acid (15 mol∙L$^{-1}$), HCl (0.1 mol∙L$^{-1}$), NaOH (0.1 mol∙L$^{-1}$), sodium silicate, distilled water.

| Oxides       | Contant / (wt %) |
|--------------|------------------|
| La$_2$O$_3$  | 28               |
| CeO$_2$      | 52               |
| Pr$_6$O$_{11}$ | 5                |
| Nd$_2$O$_3$  | 15               |

2.2. Preparation of Biomass Charcoal

Select the sunflower straw before preparation and sheared to desired size fragment (1-2 cm), then fully washed with distilled water several times and oven dry. The samples were immersed in phosphate solution for 12 h with an impregnation rate of m (sunflower straw): m (phosphate) = l: 1.8, then placed the mixture into the oven and activation for 24 h at 150°C, remove the mixture and rinsed with distilled water until the pH was neutral, oven dry at 105°C, Then, the catalyst was ground and sieved to a particle size of 120 meshes for further studies.

2.3. Preparation of Multiple Rare Earth/Biomass Charcoal Composite Material

Activated carbon, mixed rare earth oxide powder and sodium silicate were mixed with the quality ratio of 40:1:1, appropriate amount of water added into the mixture and transferred into the sludge, heating to 70-80°C and washing with distilled water until the pH value neutral, drying, grinding 1-2 hours, 120 mesh sieve, then get the composite materials.

2.4. Catalytic oxidation experiment

30 mL MB solution (500 mg∙L$^{-1}$) was added into the beaker, adjusted the pH by the NaOH solution(0.1 mol∙L$^{-1}$) and HCl solution(0.1 mol∙L$^{-1}$),then 0.1 g composite material was added into above solution to form a mixed system with surging for 3 h on a ED-85A thermalstat oscillator, 1 mL filtrate was separated from the solution and measuring the concentration of MB by 722N visible spectrophotometer at 665 nm. The decolorization rate was calculated by the following equation (1):

$$\eta = (1 - \frac{c}{c_0})\times 100\%$$  

Where $\eta$ (%) represented the decolorization rate of MB, $c_0$ (mg∙L$^{-1}$) represented the initial concentration of MB, c (mg∙L$^{-1}$) represented the concentration of MB after reaction.
2.5. Box–Behnken experimental design

According to single-factor experiment, a four factor, three level Box–Behnken experimental design was established. The experimental levels of independent variables considered in this study were presented in Table 2. The levels of independent factors of the Box–Behkenk experimental design were chosen based on the single factor experiment, the experimental result was analyzed by response surface methodology.

3. Results and discussions

3.1. Box–Behnken experimental result and ANOVA analysis

The relationship between decolorization rate and four influencing factors (catalyst dosage, aeration rate, temperature and pH) and the interaction between variables were analyzed based on the box–behkenkenk experimental design. The results were tabulated in Table 3. Final equation in terms of coded factors was evaluated and given in Eq. (2).

\[
\eta = 97.47 + 3.83x_1 - 0.44x_2 + 0.000x_3 + 2.83x_4 + 1.69x_1x_2 + 5.00 \times 10^{-3}x_1x_3 - 4.58x_1x_4 + 5.00 \times 10^{-3}x_2x_3 - 0.44x_2x_4 + 0.023x_3x_4 - 2.09x_1^2 - 1.60x_2^2 + 3.86x_3^2 - 0.56x_4^2
\]  

(2)

The significance of the model was studied by analysis of variance (ANOVA). The ANOVA for response surface quadratic model for MB removal was listed in Table 4. F-value indicated the significant level of the model and homologous variables, F-value > 3 indicates that the model or homologous variables are significant. In this Model, F-value of 3.16 implies the model is significant.

The homologous variables or interaction effect would be more significant if the p-value < 0.05, values greater than 0.1000 indicate the model terms are not significant, p-value of 0.0197 in this model implies the model is significant.

In this case, \(x_1, x_4, x_1x_4\) and \(x_3^2\) are significant model terms. The significant level of the four factors is \(x_1 > x_4 > x_2 > x_3\). "Adeq Precision" measures the signal to noise ratio, a ratio greater than 4 is desirable. In this model, ratio of 7.918 indicates an adequate signal. This model can be used to navigate the design space.

| Table 2. Independent variables and their coded levels. |
|------------------------------------------------------|
| Variables   | Symble | Range and level |
|-------------|--------|-----------------|
| Catalyst dosage (g) | \(x_1\) | 0.20 0.25 0.30 |
| Aeration rate (L·min⁻¹) | \(x_2\) | 0.31 1.41 2.50 |
| Temperature (°C) | \(x_3\) | 20 25 30 |
| pH          | \(x_4\) | 8 10 12 |
### 3.2. Response surface analysis and optimization by RSM

The R² and adjusted R² values were found to be 0.7594 and 0.5189, which indicates that there was a good agreement between the actual and the predicted values[9], as shown in Figure 1. This suggests that the obtained regression model is adequate to explain most of the variability for MB removal under a given experimental condition.

Three dimensional response surface was estimated the interactive effect of two variables on decolorization rate of MB. Figure 2 showed the effect of catalyst dosage and pH on efficiency of composite material for decolorization of MB when the temperature and aeration rate were coded factor (0.000). The interaction between catalyst dosage and pH has significant influence on MB removal with an P value<0.05. The capacity of composite material for the removal of MB can be determined by the catalyst dosage at any given pH, the decolorization rate gradually increased with the increase of the catalyst dosage at any given pH, the decolorization rate gradually increased with the increase of the catalyst dosage and pH, and then reached a stable level. During the initial reaction stage, with the increase of catalyst dosage, surface area and dispersion of catalyst has increased, so the reaction becomes faster, to a certain dosage, reaction basically completed and decolorization rate had no obvious change. With the increase of dissolved oxygen concentration, a series of free radical reactions occurring on the surface of the catalyst [10]:\[ \text{O}_2 + \text{RH} \rightarrow \text{R} + \text{HO}_2^-; \text{H}_2\text{O} + \text{HO}^- + \text{O}^\cdot \rightarrow \text{HO}_2^- + \text{O}^\cdot \] (RH represents the organic matter), HO- and HO2- are free radicals with strong oxidizing properties.

#### Table 3. Box-Behken experimental design and experimental data.

| Run | Coded variables x₁ | Coded variables x₂ | Coded variables x₃ | Coded variables x₄ | η % |
|-----|---------------------|---------------------|---------------------|---------------------|-----|
| 1   | -1                  | 0                   | 0                   | 1                   | 99.83 |
| 2   | -1                  | 0                   | 1                   | 0                   | 99.93 |
| 3   | 0                   | 0                   | 0                   | 0                   | 97.47 |
| 4   | 0                   | -1                  | 0                   | 1                   | 99.81 |
| 5   | 0                   | 0                   | 0                   | 0                   | 97.47 |
| 6   | -1                  | 0                   | 0                   | -1                  | 81.07 |
| 7   | 0                   | 0                   | 1                   | -1                  | 99.95 |
| 8   | 0                   | 0                   | 0                   | 0                   | 97.47 |
| 9   | 1                   | -1                  | 0                   | 0                   | 99.84 |
| 10  | 0                   | -1                  | 1                   | 0                   | 99.91 |
| 11  | 1                   | 0                   | 1                   | 0                   | 99.95 |
| 12  | 0                   | 1                   | 0                   | -1                  | 93.09 |
| 13  | -1                  | 0                   | -1                  | 0                   | 99.95 |
| 14  | 0                   | 0                   | 0                   | 0                   | 97.47 |
| 15  | -1                  | 1                   | 0                   | 0                   | 82.52 |

#### Table 4. ANOVA for response surface quadratic model analysis of variance.

| Source | Sum of square | DF | Mean square | F-value | P value |
|--------|---------------|----|-------------|---------|---------|
| Model  | 547.64        | 14 | 39.12       | 3.16    | 0.0197  |
| x₁     | 175.95        | 1  | 175.95      | 14.20   | 0.0021  |
| x₂     | 2.33          | 1  | 2.33        | 0.19    | 0.6710  |
| x₃     | 0.000         | 1  | 0.000       | 0.000   | 1.0000  |
| x₄     | 95.99         | 1  | 95.99       | 7.75    | 0.0147  |
| x₁x₂   | 11.36         | 1  | 11.36       | 0.92    | 0.3546  |
| x₁x₃   | 2.500E-005    | 1  | 2.500E-005  | 2.018E-006 | 0.9989 |
| x₁x₄   | 83.91         | 1  | 83.91       | 6.77    | 0.0209  |
| x₂x₃   | 1.000E-004    | 1  | 1.000E-004  | 8.071E-006 | 0.9978 |
| x₂x₄   | 0.77          | 1  | 0.77        | 0.062   | 0.8073  |
| x₃x₄   | 2.025E-003    | 1  | 2.025E-003  | 1.634E-004 | 0.9900 |
| x₁²    | 28.40         | 1  | 28.40       | 2.29    | 0.1523  |
| x₂²    | 16.61         | 1  | 16.61       | 1.34    | 0.2664  |
| x₃²    | 96.83         | 1  | 96.83       | 7.81    | 0.0143  |
| x₄²    | 2.06          | 1  | 2.06        | 0.17    | 0.6895  |
| Residual | 173.47        | 14 | 12.39       |         |         |
| Lack of fit | 173.47       | 10 | 17.35       |         |         |
property, attack the -C=N-, -C=S- and other heterocyclic structures of MB, so that the MB conversion to two methyl aniline and further oxidized to two methyl amine, then be degraded into CO₂, H₂O and other small molecular substances eventually [11,12], at alkaline condition, the intermediate organic acids were further reacted with alkali, so the MB was degraded [13].

![Image](image1)

**Figure 1.** Plot of the actual response versus predicted response for decolorization rate.

![Image](image2)

**Figure 2.** The three-dimensional response plot.

The model predicted a maximum decolorization rate of 100.00%, the optimum conditions were found to be as follows: catalyst dosage 2.50 g, aeration rate 2.5 L·min⁻¹, temperature 21 °C and pH value 12.

To confirm that the model is satisfactory in predicting the maximum decolorization rate of MB, an experiment was performed under the optimum conditions, the experimental result was 99.61%, which is in good agreement with the predicted value. It indicated that the response surface methodology could be an reliable and effective methods to optimizing the catalytic oxidation process of MB onto the biomass charcoal loaded multiple rare earth composite material.
4. Conclusion
The present investigation was carried to study the removal of MB using biomass charcoal loaded multiple rare earth composite material and to conduct process optimization using RSM for finding the optimum values of parameters affecting the process to achieve maximum removal efficiency. The significant level of the four factors is $x_1 > x_2 > x_3$, the interaction between catalyst dosage and pH was found to be a significant factor. The optimum conditions were found to be as follows: catalyst dosage 2.50 g, aeration rate 2.5 L·min$^{-1}$, temperature 21 $^\circ$C and pH value 12, under these optimum conditions, the maximum decolorization rate of MB was 99.61%. The observed values were consistent with the theoretical values, leading support to the conclusion. The optimized result showed that the biomass charcoal loaded multiple rare earth composite material was supposed to be an environmentally friendly, economically and efficiency catalyst for the treatment of MB.

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