Response surface methodology optimization of Congo Red dye adsorption onto MnFe-LDH adsorbent

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Abstract. This study was carried out to optimize the adsorption process toward Congo Red (CR) dye over Mn-Fe LDH material in aqueous media. The effects of three variables including initial concentration, pH and reaction time were investigated with respect to maximal CR removal efficiency by utilizing response surface methodology (RSM). Through the variance of ANOVA, the second-order polynomial model was established in accordance with experimental data with high $R^2$ values ($R^2=0.997$), large F-value and small p-value, indicating that the proposed model is statistically significant. The estimated optimal conditions were validated by confirmation experiments. It was revealed that CR adsorption efficiency reached 53.21% at following optimal conditions: $C_i = 48.09$ mg/L; pH = 5.62; reaction time = 107 min. These results show that Mn-Fe LDH is used as an effective adsorbent for the removal of organic pigments in aqueous solution.

1. Introduction
Organic dyes, due to advantages such as resistant color, high water solubility and inexpensiveness, have been widely used in various industries including weaving, leather processing, paper, printing, plastics, pharmaceuticals, tanning, and others [1,2]. However, the discharge of wastewater containing organic dyes adversely affects human health and the environment [3,4]. Therefore, before being discharged into the environment, these dyes should be treated to minimize potential hazards [5–7]. In this study, Congo Red (CR) dyes have been evaluated such as a representative dye because its strong adsorption capacity on solids and its use in characterizing adsorptive materials [8,9].

In recent years, methods of treating environmental pollution are attracting much attention and adsorption has been shown to be a potential physicochemical method for removing dyes due to its advantages such as high efficiency, no toxic byproducts, applicability to regulatory systems, economic feasibility and ease of operation [10–14]. In particular, layered double hidroxides (LDH), due to
advantages such as pore structure, large specific surface area and ion exchange capacity in the interlayer layer, has recently been proposed as a good candidate for manufacture of capable adsorbents [15–19].

In the previous studies, Mn-Fe LDH has been received much attention, which is a good candidate for the sensor, drug release [20]. The present study focuses on synthesizing Mn-Fe LDH materials and studying their adsorption capacity toward CR dye to expand the scope of applications. The conditions affecting adsorption performance including the initial concentration, pH value and reaction time were studied by surface response method (RSM).

2. Materials and method

2.1. Synthesis of Mn-Fe LDH
Mn-Fe LDH was prepared by urea hydrolysis. The chloride containing Mn\(^{2+}\), Fe\(^{3+}\) were mixed with urea solid (the molar ratios Mg\(^{2+}\): Fe\(^{3+}\): urea are 1:2:32), stirred for 15 min and then hydrothermally heated up to 100\(^\circ\)C for 24h. Afterwards, the powder was filtered, washed with distilled water and ethanol for three times and then subjected to drying in at 90\(^\circ\)C for 24h [20].

2.2. Experimental
Mn-Fe LDH (0.04 g) was added to 100 mL CR solution with an appropriate concentration (40 mg/L to 60 mg/L) and pH (2 to 12). HCl 0.1M and NaOH 0.1M were used to adjust the pH. After the reaction had finished, 1 mL of the mixture was withdrawn and subjected to centrifugation at 3000 rpm for 10 min to remove the adsorbent. The remaining dye content was determined spectrophotometrically at \(\lambda = 497 \text{ nm}\). The adsorption efficiency was calculated based on the dye concentration before and after the process as follows

\[
H(\%) = \left(1 - \frac{C_e}{C_o}\right) \times 100
\]

where \(C_o\) and \(C_e\) are, respectively, initial and equilibrium dye concentrations (mg/L).

2.3. Experimental design with RSM
The CCD matrix was designed to evaluate the compatibility of experimental data and the response was selected as the CR elimination efficiency, as shown in table 1. A total of twenty experiments were set up by the central composite design with five levels including the low (−1), high (+1) and rotatable (±\(\alpha\)).

Table 1. Independent variables and their encoded levels.

| No | Independent factors      | Unit | Code | Levels       |
|----|--------------------------|------|------|--------------|
|    |                          |      |      | −\(\alpha\) | −1 | 0 | +1 | +\(\alpha\) |
| 1  | pH of solution (pH)      | -    | A    | 4.31        | 5  | 6 | 7  | 7.68        |
| 2  | Concentration (\(C_o\))  | g/L  | B    | 33.18       | 40 | 50| 60 | 66.38       |
| 3  | Time                     | min  | C    | 86.36       | 100| 120|140 | 153.36      |

3. Results and discussion
Through RSM method, 20 experiments were conducted to estimate the removal efficiency of CR and shown in table 2. The results of table 2 show that the effect of removing color is dominated by independent variables (initial concentration, pH and reaction time) and that adsorption performance is greatly determined by changes in surveyed parameters [21–25]. To select an appropriate model with statistically significant variables, the p-value threshold of the regressors is selected as 0.01, thus resulting in the following quadratic equation:

\[
H(\%) = 50.34 - 3.87A - 6.24B - 2.20C + 0.7987AB - 2.31AC - 0.2227BC - 6.64A^2 - 3.4B^2 - 1.65C^2
\]
Table 2. Matrix of observed and predicted values for CR adsorption capacity.

| Run | pH (A) | C<sub>0</sub> (B) | Time (C) | Actual (%) | Predicted (%) | Run | pH (A) | C<sub>0</sub> (B) | Time (C) | Actual (%) | Predicted (%) |
|-----|--------|-----------------|---------|------------|--------------|-----|--------|-----------------|---------|------------|--------------|
| 1   | 5      | 40              | 100     | 49.51      | 49.21        | 11  | 6      | 33.18           | 120     | 51.1       | 51.19        |
| 2   | 7      | 40              | 100     | 44.7       | 44.5         | 12  | 6      | 66.38           | 120     | 30.83      | 30.21        |
| 3   | 5      | 60              | 100     | 35.93      | 35.58        | 13  | 6      | 50               | 86.36   | 48.95      | 49.37        |
| 4   | 7      | 60              | 100     | 33.61      | 34.07        | 14  | 6      | 50               | 153.63  | 42.92      | 41.97        |
| 5   | 5      | 40              | 140     | 49.96      | 49.88        | 15  | 6      | 50               | 120     | 50.99      | 50.34        |
| 6   | 7      | 40              | 140     | 35.19      | 35.92        | 16  | 6      | 50               | 120     | 50.49      | 50.34        |
| 7   | 5      | 60              | 140     | 34.79      | 35.36        | 17  | 6      | 50               | 120     | 50.25      | 50.34        |
| 8   | 7      | 60              | 140     | 23.92      | 24.6         | 18  | 6      | 50               | 120     | 50.03      | 50.34        |
| 9   | 4.31   | 50              | 120     | 37.78      | 38.06        | 19  | 6      | 50               | 120     | 50.35      | 50.34        |
| 10  | 7.68   | 50              | 120     | 25.87      | 25.06        | 20  | 5      | 6                | 120     | 49.87      | 50.34        |

Table 3 displayed the ANOVA results that are used to evaluate the suitability of quadratic model and regression co-efficients. In general, the proposed model is statistically significant (95%) confirmed by large F-value and small p-values. Moreover, the coefficient of variance (CV), which represents the standard error of the estimate, achieved very low intensity (1.63%) and a high accuracy (AP = 354.42), which is indicative of high reproducibility of the model [26,27]. In particular, the correlation coefficient ($R^2 = 0.997$) shows that a significant proportion (99.70%) of the total variation can be explained by experimental models. Furthermore, an apparent random pattern of residuals could be observed in figure 1(a) and data points corresponding to the experimental and predicted values were distributed linearly on a straight line. Based on the result of lack of fit ($p = 0.0561 > 0.05$), the proposed model is consistent with experimental data.

Table 3. ANOVA for the CR removal models

| Source | Sum of squares | Degree of freedom | Mean square | F-value | Prob. > F | Comment |
|--------|----------------|------------------|-------------|---------|-----------|---------|
| Model  | 1604.20        | 9                | 178.24      | 373.11  | < 0.0001<sup>a</sup> | SD = 0.6912 |
| A      | 204.26         | 1                | 204.26      | 427.57  | < 0.0001<sup>a</sup> | Mean = 42.35 |
| B      | 531.62         | 1                | 531.62      | 1112.81 | < 0.0001<sup>a</sup> | CV(%) = 1.63 |
| C      | 66.07          | 1                | 66.07       | 138.30  | < 0.0001<sup>a</sup> | Press = 31.92 |
| AB     | 5.10           | 1                | 5.10        | 10.68   | 0.0085<sup>a</sup> | $R^2 = 0.997$ |
| AC     | 42.84          | 1                | 42.84       | 89.68   | < 0.0001<sup>a</sup> | $R^2_{(adj)} = 0.994$ |
| BC     | 0.3969         | 1                | 0.3969      | 0.8308  | 0.3835<sup>a</sup> | AP = 354.42 |
| A<sup>2</sup> | 635.66    | 1                | 635.66      | 1330.59 | < 0.0001<sup>a</sup> |
| B<sup>2</sup> | 167.54   | 1                | 167.54      | 350.69  | < 0.0001<sup>a</sup> |
| C<sup>2</sup> | 39.41    | 1                | 39.41       | 82.50   | < 0.0001<sup>a</sup> |
| Lack of fit | 3.66    | 5                | 0.7317      | 4.75    | 0.0561    | Not significant |
Figure 1. Actual versus predicted plot (a,b) for regression model of the percentage of CR removal.

Figure 2. The response surfaces (a)–(f) for regression model of the percentage of CR removal.

The removal efficiency of CR depends on the three variables, as shown in figures 2(a)–(f). The interaction between concentration and pH is illustrated in figures 2(a,d). It can be seen that reducing the concentration and pH value increases the adsorption capacity CR, as reflected by corresponding contour lines figures 2(a,d). Figures 2(b,e) suggest that the interaction between reaction time and pH for CR percent depends significantly on pH value. In a low pH aqueous solution, improved color removal efficiency could be observed. This is evidenced by figure 2(e) showing that convergent regions tended to be out of the investigation regions. Therefore, optimal conditions are likely to lie outside the survey
area. Similarly, figures 2(c,f) show that the effect of concentration and reaction time on CR adsorption on Mn-Fe LDH. The optimal prediction results show that CR adsorption on Mn-Fe LDH depends significantly on the concentration and pH value. Attenuation of concentration and environmental pH leads to significant changes in adsorption performance [28–30]. In particular, the survey time reaches the optimal value in the survey conditions. The relationship between CR concentration and adsorption capacity could be explained by the lowered amount of adsorbed CR. In addition, increasing CR concentration also increased adsorption sites, leading to improved adsorption up to an equilibrium. On the other hand, changes in pH also are associated with the charge of adsorbent materials, leading to varying adsorption [25].

Solving the estimated equation with respect to maximal removal efficiency yielded following conditions: $C_i = 48.09$ mg/L; $pH = 5.62$; reaction time = 107 min. Actual experiment runs using those parameters resulted in the CR removal efficiency of 53.21%, approximately equal to the predicted value illustrated in the table 4. Those results demonstrate high compatibility of the proposed model with experimental data.

| Sample       | pH (-) | Concentration (mg/L) | Time (min) | Adsorption capacity (%) | Predicted | Tested | Error | Desirability |
|--------------|--------|----------------------|------------|-------------------------|-----------|--------|-------|--------------|
| Mn-Fe LDH    | 5.62   | 48.09                | 107        | 52.34                   | 53.21     | 0.87   | 1.0000|              |

### 4. Conclusion

Mn-Fe LDH material synthesized by hydrothermal method is used as an effective adsorbent to remove CR from aqueous solution. By adopting RSM optimization procedures, we found that optimal CR removal efficiency in this adsorption process was approximately 53.21%, corresponding to following optimal conditions: $C_i = 48.09$ mg/L; $pH = 5.62$; reaction time = 107 min. Further studies should contemplate the use of this promising adsorbent toward other dyes such as Methylene Blue or Rhodamine B to justify its applications in new wastewater treatment processes.

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