Removal of boron from gas field wastewater by Zn/Mg/Al-layered double hydroxides

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Abstract. The presence of boron in gas field wastewater poses a serious risk to human and ecosystem health. Zn/Mg/Al-layered double hydroxides (LDHs) were synthesized by the co-precipitation method and used for boron removal from gas field wastewater. The adsorption conditions were optimized by response surface methodology (RSM) based on the Box–Behnken (BBD) method. The highest removal efficiency achieved was approximately 68% when the Zn/Mg/Al LDHs adsorbent was prepared with a Zn/Mg/Al molar ratio of 2.6:0.4:1 and calcination temperature of 773 K. The maximum removal efficiency was obtained under a temperature, time, dosage and pH of 10 °C, 4.8 h, 15 g L⁻¹ and 5.0, respectively. The results of boron adsorption were fitted to a Langmuir isotherm, achieving an \( R^2 = 0.9633 \), and the adsorption process followed second-order kinetics.

1. Introduction

Natural gas is a relatively clean energy resource, and has therefore been widely exploited in recent decades. However, wastewater produced by gas fields poses a hazard to human and ecological health due to high contents of certain soluble salts, suspended particles, organic compounds and boron. Boron in particular is extremely toxic and must therefore be removed from wastewater [1]. The World Health Organization (WHO) established a boron health-based guideline of 2.4 mg L⁻¹ for drinking water in 2011 [2]. However, the guideline for European countries is 1.0 mg L⁻¹ according to the Drinking Water Directive of the European Union [3]. The recommended boron concentration for irrigation is 0.75 mg L⁻¹ [4]. Thus, methods for removal of boron from wastewater are of significance.

Existing methods for boron removal include reverse osmosis [5], electrocoagulation [6] and adsorption [7]. The adsorption method is widely used due to its low-cost and high-efficiency [8,9]. Various different adsorption media have been investigated, including red mud [10], calcined alunite [11], magnesia [12] and activated alumina [13]. However, these adsorbents do have some shortcomings, such as high dosage required, low adsorption capacity and high cost, thereby limiting their wide application.

Layer double hydroxides (LDHs) are a group of adsorbents containing many divalent cations that are useful for the uptake of various boron species. The cations can be replaced by trivalent cations, resulting in a net positive charge, after which they can be replaced with anions in the layer structure [14,15]. Due to the variability in layer cations and interlayer anions, the use of LDHs for boron adsorption is promising [16]. Kentjono et al. [17] treated optoelectronic wastewater containing high concentrations of boron and iodine with high efficiency with the use of Mg-Al(NO₃) LDH. Ay et al. [18] achieved 95% boron remove efficiency from synthetic wastewater with the use of Mg-Al-(NO₃) LDHs. However, few studies have applied LDHs for the removal of boron from gas field wastewater.
Thus, the present study aimed to investigate the removal of boron from gas field wastewater using LDHs. Conditions and operating parameters for preparing Zn/Mg/Al LDHs were optimized by response surface methodology (RSM). Kinetic parameters were also determined for the adsorption of boron by the LDHs.

2. Materials and methods

2.1. Preparation of Zn/Mg/Al LDHs
LDHs were synthesized by the co-precipitation method. The molar ratios of Zn/Mg/Al were 2.6:0.4:1. An aqueous solution was prepared (100 mL) containing 0.0572 M, 0.0088 M and 0.022 M of Zn(NO₃)₂·6H₂O, Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O, respectively. To this solution, 0.2 M and 0.06 M of NaOH and Na₂CO₃, respectively, was added slowly (3 mL min⁻¹) under mechanical stirring and a temperature of 65 °C. Once the addition of the nitrate was completed, a thick slurry was obtained, which was heated for 12 h at 75 °C for ageing. The solid products were separated by filtration and washed several times with deionized water until a pH of 7. Finally, the solids were dried at 60 °C for 24 h and then crushed to pass through a 100-mesh sieve mesh. LDHs were then obtained after calcination at 500 °C for 6 h. All chemicals used were of analytical grade and were not further purified. All solutions were prepared with deionized water.

2.2. Characterization of Zn/Mg/Al LDHs
The Brunauer–Emmett–Teller (BET) surface areas of LDHs were determined by the N₂ adsorption-desorption method at 77 K using a surface area analyzer (ASAP 2460, Micromeritics, USA). The BET-specific surface area (S_{BET}), microporous volume (V_{mic}) and mesoporous volume (V_{meso}) of the LDHs were calculated by the BET, t-plot and BJH methods, respectively. X-ray powder diffraction (XRD) patterns were obtained with a Dandong DX-2700 XRD diffractometer using Cu Ka (k = 1.5406 Å) radiation at 30 mA and 40 kV and a scanning rate of 1 °C min⁻¹. Thermogravimetric (TG) and Differential Thermal Analyzer (DTA) curves were obtained with a NETZSCE STA490PC/PG differential thermal analyzer from 25 °C to 800 °C at a heating rate of 15 °C min⁻¹ under nitrogen gas.

2.3. Adsorption isotherms
Adsorption isotherms were determined by the batch equilibration technique. Zn/Mg/Al LDHs (75 mg) placed into centrifuge tubes, to which 25 mL of boron solution (pH~9) was added, for final concentrations ranging between 10 mg L⁻¹ to 100 mg L⁻¹. The mixture was stirred for 6 h at room temperature, filtered, and the filtrate was collected for determination of boron. Boron concentration was determined by the curcumin spectrophotometric method at 540 nm, and boron adsorbed at equilibrium, \( q_e \) (mg g⁻¹), was calculated using the following formula:

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

where \( V \) is the volume of solution (L), \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of boron, respectively (mg L⁻¹) and \( W \) is the weight of Zn/Mg/Al LDHs (g).

The Langmuir (equation 3) and Freundlich (equation 4) equations are the models most frequently employed to represent adsorption. In the present study, two models were used to describe the relationship between the adsorbed boron and its equilibrium concentration in solution:

\[
q_e = \frac{q_L K_L C_e}{1 + K_L C_e}
\]

\[
q_e = K_F C_e^{1/n}
\]
An equilibrium parameter ($R_L$), as the essential characteristics of this isotherm [19], was adopted to determine whether the boron adsorption process of calcined Zn/Mg/Al LDHs was favorable or unfavorable for the Langmuir-type adsorption process, which can be expressed as follows:

$$RL = \frac{1}{1 + KLC_0} \quad (4)$$

where $q_L$ is the Langmuir maximum uptake of boron per unit mass of Zn/Mg/Al LDHs, (mg g$^{-1}$), $K_L$ is the Langmuir constant (L mg$^{-1}$), $K_F$ and $n$ are Freundlich constants, $C_0$ is the highest initial solute concentration and $R_L$ indicates reversibility of the isotherm ($R_L = 0$, $0 < R_L < 1$, $R_L = 1$ and $R_L > 1$ represent reversible, favorable, linear and unfavorable, respectively). This program provided the parameters of each equation and the degree of fitting between experimental and calculated data in terms of the correlation coefficient $R^2$.

2.4. Adsorption dynamics

Adsorption dynamics were determined by adding 100 mg of Zn/Mg/Al LDHs into centrifuge tubes, to which 25 mL of solution was added containing 100 mg L$^{-1}$ of boron (pH~9). The solutions were stirred for 6 h at different temperatures ranging from 10 °C to 80 °C. The adsorbed boron at time t, $q_t$ (mg g$^{-1}$), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (5)$$

where $C_t$ (mg L$^{-1}$) is the concentration of boron at time t (min). Pseudo first- and second-order models were used to analyze the kinetic data. These models can be expressed as:

Pseudo first-order

$$\ln(q_e - q_t) = \ln(q_e) - K_1t \quad (6)$$

Pseudo second-order

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where $q_e$ and $q_t$ (mg g$^{-1}$) represent the uptake of boron at equilibrium and at time t (min), respectively, $K_1$ (min$^{-1}$) is the adsorption rate constant of the first-order equation and $K_2$ (g mg$^{-1}$ min$^{-1}$) is the adsorption rate constant of the second-order equation.

2.5. Response surface designs

Gas field wastewater was obtained from the gas field from Sichuan Basin, LTD. The wastewater had a gasoline-like odor and a yellowish color. The wastewater was preserved under 4 °C until use in the experiment. Adsorbent (75 mg) was added to gas field wastewater (25 mL) with a boron concentration of 65.43 mg L$^{-1}$. The mixture was stirred for 2 h and then filtered, following which the filtrate was collected for determination of boron concentration.

The Zn/Mg/Al LDH boron adsorption process was optimized following the RSM based on Box–Behnken with four factors. The four factors (Table 1) were coded at two levels between −1 and +1, corresponding to the minimum and maximum value of each variable, respectively: 1) temperature (A); 2) adsorption time (B); 3) adsorbent dosage (C) and 4) pH (D).

| Run | Code variable | Natural variable |
|-----|---------------|------------------|
|     | X1 X2 X3 X4   | Temperature (°C) (X1) | Time (h) (X2) | Dosage (mg L$^{-1}$) (X3) | pH (X4) | Removal boron (%) of |
| 1   | 1 0 0 1       | 60               | 3.5         | 9                          | 10.0    | 18.51             |
| 2   | 0 1 0 −1      | 35               | 6.0         | 9                          | 5.0     | 35.21             |
| 3   | 0 −1 0 −1     | 35               | 1.0         | 9                          | 5.0     | 6.81              |
| 4   | 1 0 1 0       | 60               | 3.5         | 15                         | 7.5     | 35.54             |
| 5   | 0 1 1 0       | 35               | 6.0         | 15                         | 7.5     | 41.69             |
| 6   | −1 0 0 −1     | 10               | 3.5         | 9                          | 5.0     | 47.62             |

Table 1. Experimental design and results of adsorption experiment.
3. Results and discussion

3.1. Preparation of Zn/Mg/Al LDHs

The relationship between the molar ratios of Zn and Mg in LDHs and the removal of boron was investigated under a calcined temperature of 600 °C. The molar ratio ranges of Zn, Mg and Al investigated were 2.2–2.8, 0.2–0.8 and 1.0, respectively (Figure 1). Under a Zn molar ratio of 2.6, the boron removal efficiency increased with increasing molar ratio of Mg from 0.2 to 0.4, beyond which it decreased. The maximum boron removal efficiency was achieved with molar ratio for Zn and Mg of 2.6 and 0.4, respectively. Thus, the LDHs with a Zn/Mg/Al molar ratio of 2.6:0.4:1 were selected for further research.

![Figure 1. The effect of the molar ratios of Mg (a) and Zn (b) in Zn/Mg/Al LDHs on the removal of boron from gas field wastewater.](image)
The Zn/Mg/Al LDHs were calcined at different temperatures ranging from 200 °C to 800 °C for 6 h, under room temperature (25 °C), and their boron removal efficiencies were investigated (Figure 2). The boron removal efficiencies increased with increasing calcination temperature from 200 °C to 500 °C due to the transformation of LDHs into aluminum and magnesium oxides by the loss of interlayer anions [20]. However, calcination temperature > 500 °C resulted in the complete decomposition of the interlayer carbonate of LDHs, and consequent decreased boron adsorption capacity. The maximum removal efficiency of boron was obtained at a calcination temperature of approximately 500 °C.

![Figure 2. The effect of calcination temperature on the removal of boron from gas field wastewater.](image)

3.2. Characterization of Zn/Mg/Al LDHs

3.2.1 Textural properties. The N₂ adsorption-desorption isotherm of the Zn/Mg/Al LDHs is presented in figure 3, and is of was type VI with a clear capillary condensation step evident at a relative pressure (P/P₀) of 0.8–1.0. The quantity of boron adsorbed increased sharply when the relative pressure reached 0.8, indicating that the structure of Zn/Mg/Al LDHs might be porous with abundant macropores. The values of S_{BET}, V_{mic} and V_{meso} were 66.85 m² g⁻¹, 0.0006 cm³ g⁻¹ and 0.2297 cm³ g⁻¹, respectively. The low surface area and few micropores of the Zn/Mg/Al LDHs indicate that the physical adsorption capacity of LDHs does not account for its main boron removal effect.
3.2.2 X-ray powder diffraction (XRD) patterns. Figure 4 shows the XRD patterns of Zn/Mg/Al LDHs before and after calcination at 500 °C, were it is evident that the XRD patterns of the two samples were significantly different. This indicates that the metal crystal in Zn/Mg/Al LDHs changed greatly after calcination. Before calcination, several significant characteristic peaks of Mg₄Al₂(OH)₁₂CO₃ꞏH₂O were observed at 2θ = 11.68°, 23.53°, 34.88°, 39.47°, 46.99°, 56.52°, 62.12°, 63.83° and 69.96° (JCPDs 51–1525) [21,22], and the characteristic peaks of Zn₆Al₂O₉ were also detected at 2θ = 32.17°, 34.60°, 36.50°, 47.57°, 56.78° and 62.73° (JCPDs 51–0037). After calcination, the peaks of Mg₄Al₂(OH)₁₂CO₃ꞏH₂O disappeared, indicating the presence of a possible Mg₄Al₂(OH)₁₂CO₃ꞏH₂O decomposition reaction during the calcination process, with the decomposition products possibly being of poor crystal form, and therefore not detected by XRD analysis [23]. On the other hand, the characteristic peaks of Zn₆Al₂O₉ on the Zn/Mg/Al LDHs remained detectable after calcination.

3.2.3 Thermogravimetry-differential thermal analysis (TG-DTA). The TG-DTA analysis of the Zn/Mg/Al hydrotalcite was conducted under an N₂ atmosphere (Figure 5). Four weight-loss periods were evident for the sample: 1) at around 95 °C with a weight loss of 1.75%, which can be attributed to the evaporation of free water in the LDHs; 2) at around 230 °C with a weight loss of 13.92%, which may be derived from the removal of adsorbed H₂O on the LDHs [22]; 3) at around 424 °C with a weight loss of 10.28%, possibly due to decomposition of CO₃²⁻ and OH⁻ in the interlayer spaces of the LDH flakes; 4) > 425 °C with a weight loss of 4.43%, possibly due to the decomposition of large quantities of OH⁻ in the LDH flakes and the removal of residual OH⁻ and CO₃²⁻ [24]. The results for the first three periods correspond well with those of previous studies [23,25].
Figure 4. X-ray powder diffraction (XRD) patterns of Zn/Mg/Al LDHs before (a) and after (b) calcination at 500 °C.

Figure 5. Thermogravimetry-differential thermal analysis (TG-DTA) of Zn/Mg/Al LDHs.

3.3. Adsorption optimization by RSM

3.3.1 Regression model and statistical analysis. The Box–Behnken (BBD) method was adopted to evaluate interactions between four independent variables during the Zn/Mg/Al LDH boron adsorption process: 1) reaction temperature (A); 2) adsorption time (B); 3) adsorbent dosage (C) and; 4) pH (D). The results are show in Table 1. The Zn/Mg/Al LDH boron removal efficiencies ranged from 1.19% to 62.17%, indicating that the investigated variables greatly affected LDH boron adsorption capacity. Multiple regression models and quadratic polynomials were used to investigate interactions between the response values and the four investigated variables. The best fit model was as follows:

\[
RE = 34.72 - 10.02A + 11.550B + 12.14C - 2.65D - 1.97AB - 2.66AC - 0.82AD + 0.70BC - 0.85BD - 2.84CD + 0.88A^2 - 14.32B^2 + 0.71C^2 - 1.34D^2
\]
Analysis of variance (ANOVA) of the regression model and related terms was conducted (Table 2). The F-value, p-value, $R^2$ and lack of fit were used to evaluate the model against the experimental data. An F-value of 27.79 indicated that the model was significant. A p-value $< 0.05$ implied a significant corresponding model term. It was clear that variables A–C have large effects on the boron removal capacities of Zn/Mg/Al LDHs due to their high F-values. Furthermore, the lack of fit for the F-value was 0.53, which was significant relative to pure error.

Table 2. Analysis of variance (ANOVA) of the regression model and the related model terms.

| Source     | Sum of Squares | df | Mean Square | F Value | p-Value Prob > F |
|------------|----------------|----|-------------|---------|-----------------|
| Model      | 6,206.53       | 14 | 443.32      | 27.79   | $< 0.0001$      |
| A-Temperature | 1,204.6     | 1  | 1,204.6     | 75.5    | $< 0.0001$      |
| B-Time     | 1,600.14       | 1  | 1,600.14    | 100.29  | $< 0.0001$      |
| C-Dosage   | 1,768.56       | 1  | 1,768.56    | 110.85  | $< 0.0001$      |
| D-pH       | 84.16          | 1  | 84.16       | 5.28    | 0.0376          |
| AB         | 15.48          | 1  | 15.48       | 0.97    | 0.3413          |
| AC         | 28.2           | 1  | 28.2        | 1.77    | 0.205           |
| AD         | 2.72           | 1  | 2.72        | 1.70E–01| 0.6858          |
| BC         | 1.93           | 1  | 1.93        | 0.12    | 0.733           |
| BD         | 2.89           | 1  | 2.89        | 0.18    | 0.6769          |
| CD         | 24.7           | 1  | 24.7        | 1.55    | 0.2338          |
| $A^2$      | 5              | 1  | 5           | 0.31    | 0.5845          |
| $B^2$      | 1,329.61       | 1  | 1,329.61    | 83.33   | $< 0.0001$      |
| $C^2$      | 3.24           | 1  | 3.24        | 0.2     | 0.6592          |
| $D^2$      | 11.71          | 1  | 11.71       | 0.73    | 0.4061          |
| Residual   | 223.37         | 14 | 15.96       |         |                 |
| Lack of Fit| 127.06         | 10 | 12.71       | 0.53    | 0.812 not significant |
| Pure Error | 96.31          | 4  | 24.08       |         |                 |
| C or Total | 6,429.9        | 28 |             |         |                 |
| Std. Dev.  | 3.99           |    | $R^2$       |         | 0.9653          |
| Mean       | 28.89          |    | Adj. $R^2$  |         | 0.9305          |
| CV (%)     | 13.83          |    | Pred. $R^2$ |         | 0.8628          |
| PRESS      | 882.36         |    | Adeq. Precision |      | 21.931          |

The model obtained a high $R^2$ of 0.9653, i.e., 96.53% of observed variations in adsorption capacity were explained by the independent variables (A–D). The adjusted $R^2$ (Adj. $R^2$) value of 0.9305 for boron removal efficiency was also in good agreement with the $R^2$.

3.3.2 Effect of process variables. Three-dimensional (3D) response surface plots were constructed from the developed models to analyze the individual and interactive effects of the process variables on the adsorption process (Figure 6). The results can also be used identify the optimal value of each factor to achieve the maximum boron removal efficiency.

The Zn/Mg/Al LDH boron removal efficiencies under different temperatures and adsorption times are shown in Figure 6a. The boron removal efficiency increased considerably with longer adsorption time up until 5 h, following which the efficiency decreased. On the other hand, the boron removal rate
decreased slightly with increased temperature. These results indicate that boron adsorption is a spontaneous and exothermic process, as also concluded by a previous study [17].

Figure 6b shows the effect of reaction temperature and dosage on the boron removal rate, where it is evident that the removal rate increased linearly with increasing LDH dosage and decreased with increasing reaction temperature, but with dosage having a more significant effect, as indicated by the higher slope in figure 6b.

Figure 6e shows the interaction between pH and time on the boron removal rate, showing that the rate increased with increasing adsorption time, whereas the effect of pH was not significant. This could be attributed to the high buffering capacity of the LDHs, which is in a good agreement with the study by Jiang et al. [26].

Figure 6 shows that the interaction between any pair of independent variables did not have a significant effect on the response value, which is supported by equation 8. The coefficients containing one factor in equation 8 represent their effect on the response value, whereas coefficients containing two factors represent interaction between the two factors. The effects of coefficients containing two variables on the response variable were far smaller than the effects of those containing one factor, indicating larger impacts of independent factors on boron removal compared to the effects of interactions between any pair of variables.

The derivatives of the RSM model were calculated, with the maximum removal rate estimated to be 68% under a temperature of 10 °C, time of 4.82 h, dosage of 15 g L\(^{-1}\) and pH of 5.0. The development of a satisfactory RSM model accounting for the range of independent variables can be used for the optimization of the boron adsorption process.

### 3.4. Adsorption isotherms

Figure 7a shows Langmuir plots for the removal of boron by Zn/Mg/Al LDHs, showing a linear plot for \(C_r/q_e\) versus \(C_r\), which indicates that the adsorption of boron followed a Langmuir isotherm. The slope and intercept were used to calculate values of \(q_L\) and \(K_L\), respectively (Table 3). \(R_L\) was 0.0027 L mg\(^{-1}\) under a temperature of 303 K, indicating the favorability of boron adsorption using Zn/Mg/Al LDHs as the adsorbent. The values of \(K_F\) and \(n\) were calculated from the intercept and slope of the Freundlich plot (Figure 7b), respectively. The value of \(1/n\) was 0.651, further supporting the argument for the use of calcined Zn/Mg/Al LDHs as a boron adsorbent. The Langmuir isotherm represented the experimental data very well, with a higher \(R^2\) value than that of the Freundlich isotherm. This indicates that the adsorption of boron by the Zn/Mg/Al LDHs falls into the category of monolayer adsorption.

| Temperature (K) | Langmuir isotherm | Freundlich isotherm |
|----------------|-------------------|---------------------|
|                | \(q_L\) (mg g\(^{-1}\)) | \(K_L\) (L mg\(^{-1}\)) | \(R_L\) | \(K_F\) (mg g\(^{-1}\) (L mg\(^{-1}\))\(^{1/n}\)) | \(n^{-1}\) | \(R^2\) |
| 303            | 12.5786           | 3.5572              | 0.0027 | 0.5895           | 0.651    | 0.9386 |
Figure 6. The response surface and interaction of temperature, dosage, pH and time on the removal of boron from gas field wastewater.
3.5. Adsorption dynamics

Kinetic data from the boron adsorption experiment derived by equation 5 were correlated to two kinetic models, the pseudo first- and second-order equations (equation 6 and equation 7, respectively). Table 4 shows the calculated constants of the two kinetic equations along with $R^2$ values. Figure 8 shows the plots of pseudo first-order and pseudo second-order kinetic for boron adsorption. The linear plot of $\ln(q_e - q_t)$ versus $t$ for the pseudo first-order equation had a relatively low $R^2$ value (0.9811), indicating a difference between the experimental adsorption capacity and calculated values and demonstrating a poor pseudo first-order fit to the experimental data. As shown in figure 8b, the $R^2$ value was higher for the linear plot of $t/q_t$ versus $t$ when applying the pseudo second-order equation, suggesting that the pseudo second-order kinetic model better represents the experimental Zn/Mg/Al LDH boron adsorption kinetics and that the adsorption process is controlled by a chemical adsorption mechanism that involves electron sharing or transfer rather than intraparticle diffusion [27].

Table 4 Kinetic parameters for boron adsorption by Zn/Mg/Al LDHs.

| $C_0$ (mg L$^{-1}$) | $q_{e,exp}$ (mg L$^{-1}$) | $k_1$ (1/min$^{-1}$) | $q_{e,cal}$ (mg L$^{-1}$) | $R^2$ | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $q_{e,calc}$ (mg L$^{-1}$) | $R^2$ |
|------------------|------------------|------------------|------------------|------|------------------|------------------|------|
| 100              | 7.92             | 0.2994           | 6.2647           | 0.9811 | 0.061           | 8.834           | 0.9973 |
4. Conclusions
The present study showed that the highest boron removal efficiency from gas field wastewater was obtained under Zn/Mg/Al LDH adsorbent with a molar ratio of Zn/Mg/Al of 2.6:0.4:1 and a calcination temperature of 500 °C. The maximum boron removal rate based on the RSM model was estimated as 68% under a temperature of 10 °C, time of 4.82 h, dosage of 15 g L−1 and pH of 5. The Langmuir isotherm explained the experimental data very well, thereby indicating that the adsorption of boron by Zn/Mg/Al LDHs fell within the category of monolayer adsorption. The adsorption of boron followed second-order kinetics. These results demonstrate that calcined Zn/Mg/Al LDH is a promising adsorbent for the removal of boron from gas field wastewater.

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