



Effect of the specific surface area of MgO on the treatment of boron and fluorine

Tomohito Kameda¹ · Yusuke Yamamoto¹ · Shogo Kumagai¹ · Toshiaki Yoshioka¹

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Abstract

To realize improved wastewater treatment processes, the study investigated the processing of boron and fluorine and the processing of real landfill leachate using MgO with different specific surface areas. By optimizing the MgO absorbent, the time required for boron and fluorine processing can be reduced dramatically and uniform wastewater quality standards can be achieved. The rate constants for boron and fluorine removal increased with both temperature and specific surface area. In the processing of actual wastewater, which contained many coexisting ions, MgO was successfully applied to the removal of boron.

Keywords MgO · Specific surface area · Wastewater treatment · Boron · Fluorine

Introduction

As high boron concentrations are certainly toxic to humans (Ferreira et al. 2006; Ay et al. 2007), effective methods for boron removal from wastewater are required. Some studies have examined the treatment of borate in wastewater using MgO. The optimum conditions for boron removal have been examined (García-Soto and Camacho 2006), and the modelization and mechanism of this process have been also investigated (García-Soto and Camacho 2009). The adsorption of boron by MgO has been also studied (Kipçak and Özdemir 2012; Sasaki et al. 2013; Sasaki and Moriyama 2014). There is also keen demand for a single-step treatment for F⁻ in wastewater. Various studies have examined MgO for the treatment of F⁻ in wastewater (Li et al. 2014; Jin et al. 2016; Lee et al. 2017). Despite these efforts, the desorption of boron and F⁻ and the recycling of these MgO materials after they have been used for the removal of these two species were not considered. In the previous study (Kameda et al.

2018a, b), MgO was found to adsorb boron and F⁻ from solutions. Even after boron and F⁻ were desorbed from MgO using NaOH solution, the regenerated MgO could adsorb boron and F⁻ again from the solution. Therefore, it is possible to recycle MgO for boron and F⁻ adsorption. The previous studies (Kameda et al. 2018a, b) clarified the feasibility of treating boron and F⁻ with MgO. To improve the processing time, this study conducted kinetic analyses of boron and F⁻ removal using MgO with various specific surface areas. In addition, we investigated the processing of actual wastewater.

Experimental

Specific surface area effects

Table 1 shows the specific surface areas and particle diameters of the various MgO sample used. The MgO material is expressed as MgO₅, MgO₃₀, MgO₁₀₀, and MgO₁₅₀.

H₃BO₃ and NaF solutions were prepared by dissolving H₃BO₃ and NaF in deionized water. MgO was added to 500 mL of 100 mg L⁻¹ H₃BO₃ and NaF solutions without initial pH control, and the resultant suspension was stirred at 300 rpm at 10, 30, or 60 °C for 100 h. Samples of the suspension were withdrawn at different time intervals and filtered immediately, and the filtrates were analyzed for residual boron and F⁻. MgO was added to H₃BO₃ and NaF solutions

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✉ Tomohito Kameda
tomohito.kameda@tohoku.ac.jp

¹ Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

Table 1 Specific surface area and particle diameter of the various MgO used

	Specific surface area (m ² /g)	Particle diameter (μm)
MgO ₅	4.8	29 ± 25
MgO ₃₀	45	< 75
MgO ₁₀₀	80	< 75
MgO ₁₅₀	149	< 75

at Mg/B and Mg/F molar ratios of 50 and 10, respectively. The residual concentrations of boron and F⁻ in the filtrate were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and ion chromatography (IC) using a Dionex DX-120 chromatograph equipped with a Dionex AS12A column (eluent: 2.7 mM Na₂CO₃ and 0.3 mM NaHCO₃; flow rate: 1.3 mL min⁻¹). The pH after adsorption was also measured.

Actual wastewater processing

Table 2 shows the concentrations of ions contained in the landfill leachate. Landfill leachate (20 mL) was added to a 50 mL Erlenmeyer flask, and 1.0 g of MgO₅ or MgO₁₅₀ was added to the flask. The flask was then placed in a shaking apparatus set to 30 °C and shaken at 150 rpm for 48 h (MgO₅) or 8 h (MgO₁₅₀). Subsequently, the suspension was filtered through a 0.45 μm membrane filter. After adjusting the filtrate volume to 100 mL and diluting appropriately, boron and the various other ions present in the solution were quantified using ICP-AES and IC.

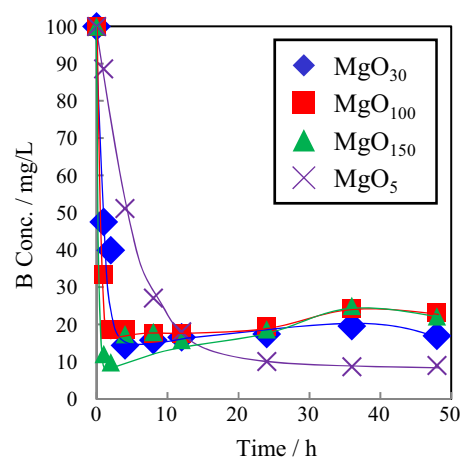
Results and discussion

Specific surface area effects

Figure 1 and S1 show the effects of the specific surface area and the changes in pH over time during boron removal using MgO. As the specific surface area increased, the rate of decrease of the boron concentration increased. It was possible to reduce the time required for processing dramatically

Table 2 Concentration of ions contained in the landfill leachate

		Initial concentration [mg/L]	
Li	1.0	Cl	23,999
B	328.3	SO ₄	774
Na	9501	Br	503
Mg	221.4		
Ca	3027		
Sr	25.0		

**Fig. 1** Effect of specific surface area on the boron removal using MgO (Amount of MgO: Mg/B = 50, 30 °C)

compared with MgO₅. The pH rose rapidly to approximately pH 11 immediately following the start of the experiment and remained almost constant thereafter. At this pH, boron exists as B(OH)₄⁻, and it is thought that electrostatic attraction acts between the positively charged MgO surface and B(OH)₄⁻, causing boron to be adsorbed onto the surface of MgO. Figure 2 shows the changes in boron concentration over time at 10, 30, and 60 °C for each MgO sample. The boron concentration decreased as the temperature increased. No significant difference in boron concentration was observed at equilibrium at any temperature. Moreover, the removal rate increased together with the specific surface area at each temperature. Using the data from the beginning of the reactions in Fig. 2, $-\ln(1-x)$ was plotted against time, as shown in Fig. S2. Because a strong linear relationship was observed between time and $-\ln(1-x)$, the boron removal reaction during the early stage of the reaction can be said to follow a pseudo-first-order reaction. Table 3 shows the reaction rate constants for boron removal at each temperature for each MgO sample. The rate constant for boron removal increases with increases in both temperature and the specific surface area of MgO. The Arrhenius plot of these rate constants exhibited good linearity. Table 4 shows the apparent activation energy and the frequency factor of this reaction obtained from the slope and intercept of the straight line. As the activation energy was greater than 40 kJ mol⁻¹, this process is suggested to be under chemical reaction control. In addition, it is thought that a larger specific surface area results in a greater number of adsorption sites, and therefore, the frequency factor increases. In the processing of actual wastewater containing boron, MgO₁₅₀, which had the highest reaction rate constant, was used.

Figure 3 and S3 show the effects of the specific surface area and the changes in pH over time when removing fluorine using MgO. As the specific surface area increased, the

Fig. 2 Changes in boron concentration over time at 10, 30, and 60 °C for **a** MgO₅, **b** MgO₃₀, **c** MgO₁₀₀, and **d** MgO₁₅₀ (Amount of MgO: Mg/B = 50)

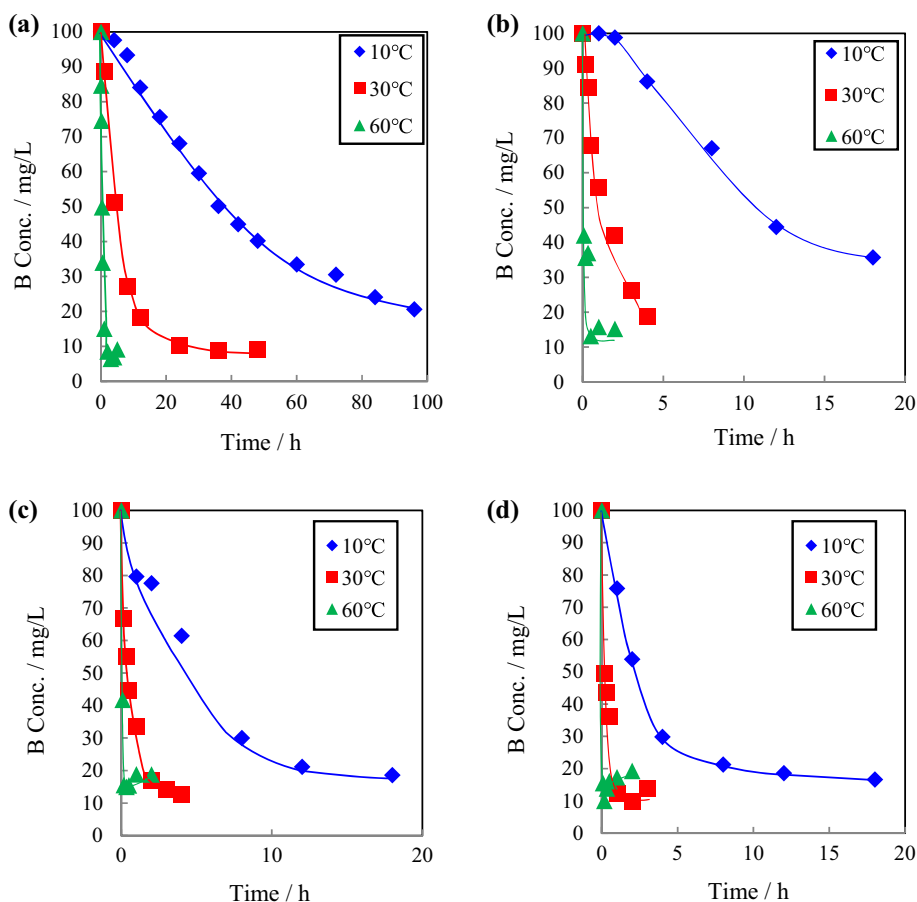


Table 3 Reaction rate constant for boron removal at each temperature for each MgO

	Specific surface area (m ² /g)	<i>k</i> [h ⁻¹]		
		10 °C	30 °C	60 °C
MgO ₅	4.8	2.0 × 10 ⁻²	1.5 × 10 ⁻¹	1.9
MgO ₃₀	45	6.3 × 10 ⁻²	4.1 × 10 ⁻¹	3.6
MgO ₁₀₀	80	1.3 × 10 ⁻¹	1.0	1.1 × 10
MgO ₁₅₀	149	3.1 × 10 ⁻¹	2.0	1.4 × 10

Table 4 Apparent activation energy and the frequency factor of this reaction

	Specific surface area (m ² /g)	A [-]	Ea [kJ/mol]
MgO ₅	4.8	3.75 × 10 ¹¹	72.0
MgO ₃₀	45	3.20 × 10 ¹⁰	63.3
MgO ₁₀₀	80	9.22 × 10 ¹¹	69.5
MgO ₁₅₀	149	5.17 × 10 ⁸	59.5

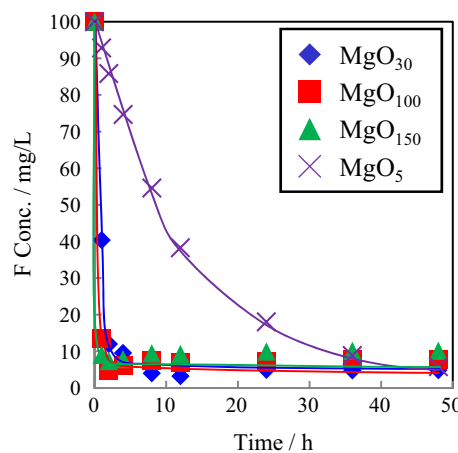


Fig. 3 Effect of specific surface area on the fluoride removal using MgO (Amount of MgO: Mg/F = 10, 30 °C)

rate of decrease of the fluoride concentration increased, and it was possible to greatly reduce the time required for processing compared with MgO₅. The pH rose sharply to pH 11–12 immediately following the start of the experiment and remained almost constant thereafter. Under these conditions, fluoride exists as F⁻, and it is thought that electrostatic

Fig. 4 Changes in fluorine concentration over time at 10, 30, and 60 °C for **a** MgO₅, **b** MgO₃₀, **c** MgO₁₀₀, and **d** MgO₁₅₀ (Amount of MgO: Mg/F = 10)

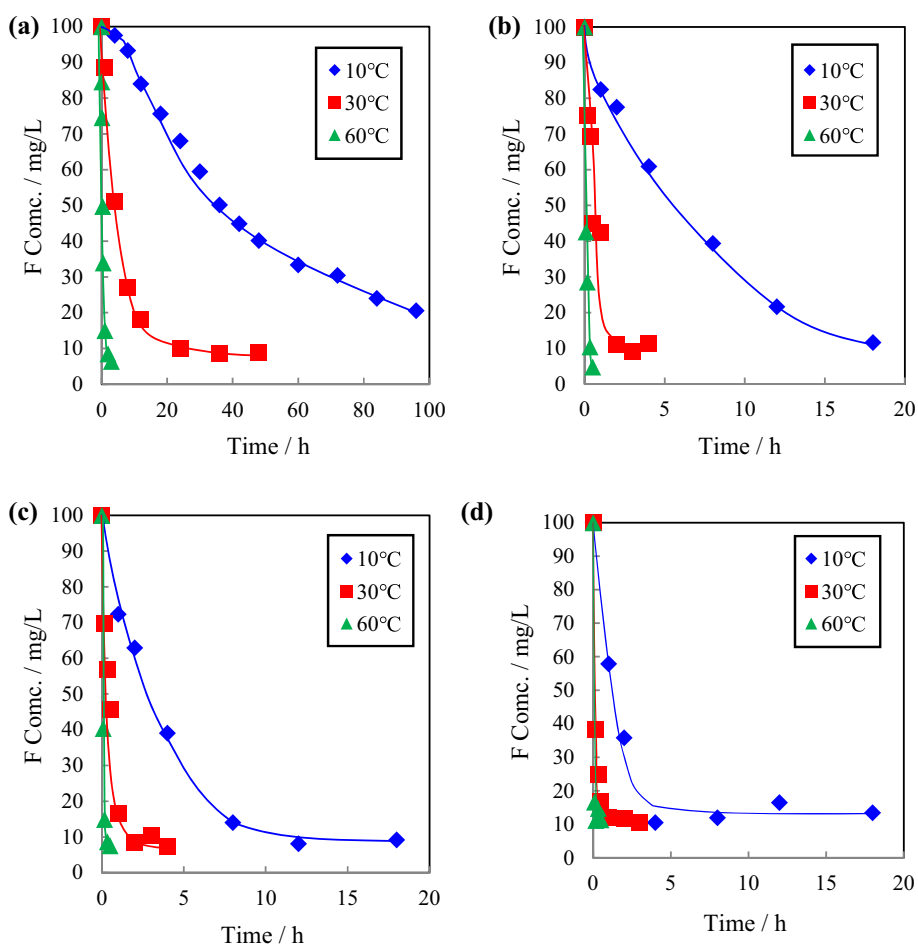


Table 5 Reaction rate constant for fluorine removal at each temperature for each MgO

	Specific surface area (m ² /g)	<i>k</i> [h ⁻¹]		
		10 °C	30 °C	60 °C
MgO ₅	4.8	8.1 × 10 ⁻³	7.1 × 10 ⁻²	7.8 × 10 ⁻¹
MgO ₃₀	45	1.2 × 10 ⁻¹	1.0	5.9
MgO ₁₀₀	80	2.4 × 10 ⁻¹	1.8	1.1 × 10
MgO ₁₅₀	149	5.6 × 10 ⁻¹	4.2	2.2 × 10

Table 6 Apparent activation energy and the frequency factor of this reaction

	Specific surface area (m ² /g)	A [-]	Ea [kJ/mol]
MgO ₅	4.8	1.3 × 10 ¹⁰	71.4
MgO ₃₀	45	2.2 × 10 ¹⁰	61.0
MgO ₁₀₀	80	3.3 × 10 ¹⁰	60.1
MgO ₁₅₀	149	1.9 × 10 ¹⁰	56.7

attraction between the positively charged MgO surface and F⁻ causes fluorine to be adsorbed on the MgO surface. Figure 4 shows the change in fluorine concentration over time at 10, 30, and 60 °C for each MgO sample. The Fluorine concentration decreased with increasing temperature, and no significant difference in concentration was observed in the equilibrium fluorine concentration at any temperature. Moreover, the removal rate increased with the specific surface area at each temperature. Figure S4 shows the results of plotting -ln(1 - x) against time using the results from the start of the reaction shown in Fig. 4. As a strong linear relationship was observed between time and -ln(1 - x),

the initial stage of the fluorine removal reaction can be said to follow a pseudo-first-order reaction. Table 5 shows the apparent reaction rate constants of fluorine removal using each MgO sample at each temperature. It was found that the rate constant increases not only with increasing temperature but also with increases in the specific surface area of MgO. The Arrhenius plot of the obtained rate constants exhibited good linearity. Table 6 shows the frequency factor and apparent activation energy obtained from the slope and intercept of the straight line. The activation energy was greater than 40 kJ mol⁻¹, suggesting that this process was under chemical reaction control. A larger specific surface

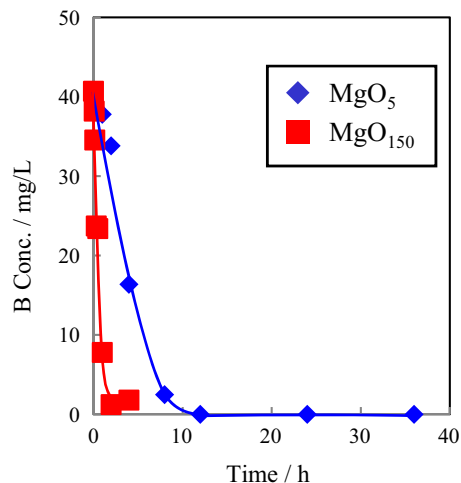


Fig. 5 Changes in boron concentration following treatment of landfill leachate using MgO (Amount of MgO: 1.0 g, 30 °C)

area provided a greater number of adsorption sites, resulting in an increase of the frequency factor.

Actual wastewater processing

Figure 5 and S5 show the changes in the boron concentration and pH following treatment of landfill leachate using MgO. The boron concentration decreased over time and became constant after 2 h. With MgO₁₅₀, the residual concentration of boron was 7.8 mg L⁻¹ after 1 h and a uniform wastewater quality standard was achieved. Because the boron concentration became constant after 2 h, the effects of the input volume were active for 2 h. As the pH during the reaction was lower than the point of zero charge (PZC) of MgO, the MgO surface is thought to be positively charged, allowing boron to be removed as an anion (e.g., B(OH)₄⁻); however, other anions could not be removed. Figure S6 show the change in the concentration of each ion over time. Although the Mg²⁺ ion concentration was observed to increase because of the elution of Mg²⁺ from MgO, there was a tendency for it to be consumed in the generation of Mg(OH)₂. Moreover, a reduction in the Ca²⁺ concentration was observed, probably because Ca²⁺ was precipitated as a hydroxide. In addition to boron, Cl⁻, Br⁻, and SO₄²⁻ were present as anionic species. As shown in Figure S6(c) and (d) for the changes in the Cl⁻ and SO₄²⁻ ion concentrations over time, the concentrations of anions other than boron increased for the first hour and then remained constant thereafter, irrespective of duration. Because the increase in anion concentration during the initial stage of the reaction does not depend on MgO, it is thought that some of the precipitate present in the raw water was eluted. Thus, when using MgO, only the target, boron, was removed from the solution containing coexisting anions.

Conclusion

We investigated the effect of MgO with different specific surface areas on the processing of boron and fluorine and the processing of real landfill leachate. As the rate constants for boron and fluorine removal increased with increases in both the specific surface area of MgO and the temperature, it was possible to reduce the processing time for boron and fluorine treatment. Moreover, increasing the specific surface area of MgO allowed uniform wastewater quality standards to be achieved. The application of MgO to the processing of actual wastewater allowed the removal of boron, even under conditions where many coexisting ions were present.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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References

- Ay AN, Zümreoglu-Karan B, Temel A (2007) Boron removal by hydrotalcite-like, carbonate-free Mg–Al–NO₃-LDH and a rationale on the mechanism. *Microporous Mesoporous Mater* 98:1–5
- García-Soto MDD, Camacho EM (2006) Boron removal by means of adsorption with magnesium oxide. *Sep Purif Technol* 48:36–44
- de la Fuente G-S, Camacho EM (2009) Boron removal by means of adsorption processes with magnesium oxide — Modelization and mechanism. *Desalination* 249:626–634
- Ferreira OP, de Moraes SG, Durán N, Cornejo L, Alves OL (2006) Evaluation of boron removal from water by hydrotalcite-like compounds. *Chemosphere* 62:80–88
- Jin Z, Jia Y, Zhang K-S, Kong L-T, Sun B, Shen W, Meng F-L, Liu J-H (2016) Effective removal of fluoride by porous MgO nanoparticles and its adsorption mechanism. *J Alloys Compd* 675:292–300

- Lee SG, Ha J-W, Sohn E-H, Park IJ, Lee S-B (2017) Synthesis of pillar and microsphere-like magnesium oxide particles and their fluoride adsorption performance in aqueous solutions. *Korean J Chem Eng* 34:2738–2747
- Li L-X, Xu D, Li X-Q, Liu W-C, Jia Y (2014) Excellent fluoride removal properties of porous hollow MgO microspheres. *New J Chem* 38:5445–5452
- Kameda T, Yamamoto Y, Kumagai S, Yoshioka T (2018a) Mechanism and kinetics of aqueous boron removal using MgO. *J Water Process Eng* 26:237–241
- Kameda T, Yamamoto Y, Kumagai S, Yoshioka T (2018b) Analysis of F^- removal from aqueous solutions using MgO. *J Water Process Eng* 25:54–57
- Kipçak İ, Özdemir M (2012) Removal of boron from aqueous solution using calcined magnesite tailing. *Chem Eng J* 189–190:68–74
- Sasaki K, Qiu X, Moriyama S, Tokoro C, Ideta K, Miyawaki J (2013) Characteristic sorption of $H_3BO_3/B(OH)_4^-$ on magnesium oxide. *Mater Trans* 54:1809–1817
- Sasaki K, Moriyama S (2014) Effect of calcination temperature for magnesite on interaction of MgO-rich phases with boric acid. *Ceram Int* 40:1651–1660

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