

Suppressive effects of magnesium oxide materials on cadmium uptake and accumulation into rice grains I: Characteristics of magnesium oxide materials for cadmium sorption

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Abstract

The objective of this study is to assess the applicability of a commercial magnesium oxide (MgO) and a composite material containing MgO and natural minerals ('MgO-SH-A') as the soil amendments for suppression of cadmium (Cd) uptake and accumulation into rice grains. Firstly, the mineralogical and physicochemical properties, soil neutralizing capacities and Cd sorption characteristics of these materials were investigated. Both materials were strongly alkaline and possessed large surface areas. The X-ray diffraction pattern of MgO-SH-A indicated the presence of MgO and a magnesium-silicate mineral (antigorite) as the main components. MgO-SH-A showed a milder soil neutralizing capacity as compared to commercial MgO. The sorptions of Cd on commercial MgO and MgO-SH-A both fitted Langmuir isotherm. The maximum Cd sorption capacity of commercial MgO (46.8 mmol g⁻¹ DW) was higher than that of MgO-SH-A (5.87 mmol g⁻¹ DW), although the latter material showed higher affinity to Cd as compared to the former one. The dominant reaction involved in the Cd sorptions was suggested to be precipitation of Cd(OH)₂ on the material surface. About 40% of Cd sorbed on MgO-SH-A was resistant to desorption by 0.1 M HCl, implying that this portion was strongly retained on the material surface.

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1. Introduction

The worldwide guideline of cadmium (Cd) contents in food-stuff has been discussed in Codex Alimentarius Commission (CAC) of FAO/WHO for 35 years. In 2006, the maximum level of Cd for polished rice (0.4 mg kg⁻¹), which had been proposed

by Japanese government, was adopted as the guideline [1]. On the other hand, the current domestic guidelines for brown rice and polished rice in Japan, which were established in 1970, are 1.0 and 0.9 mg kg⁻¹, respectively [2]. The establishment of the international guideline may have strong influences on rice production in Japan.

In Japan, remedial practices based on civil engineering, agronomical and chemical methods have been implemented in Cd-polluted areas by a single approach or in combination. Majority of the practices is based on civil engineering methods, including replacement of polluted soil with uncontaminated soil and dressing of uncontaminated soil on polluted soil [3]. The mechanism of Cd uptake by rice plants has been also analyzed,

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and it has been widely recognized that continuous flooding in paddy fields for 2–3 weeks before and after heading of rice plants could effectively suppress translocation of Cd into rice grain [4]. In addition, rice cultivation experiments with application of soil amendments, such as phosphate fertilizers and lime, have been conducted, and the effectiveness of these materials has been confirmed [5–7]. Applications of alkaline materials increase soil pH and the net negative charge of the surface of soil particles, which is favorable for sorption of Cd²⁺ onto the soil particle and subsequent reduction of its availability for plant uptake [8,9]. Calcium carbonate and phosphate materials applied into soil are also suggested to form hardly soluble compounds with Cd and reduce its phytoavailability [10,11].

However, the methods mentioned above have several problems in practical use. For civil engineering methods, thickness of covering soil is sometimes uneven and contamination of the covering soil by underlying polluted soil in the area with thin covering soil could occur under certain rice cultivation and tillage practices. Effectiveness of applications of soil amendments for suppression of Cd accumulation into rice grain is also inconsistent [12].

Various materials have been tested for their capability to reduce Cd uptake by plants in contaminated sites. They include apatites [13], clay minerals, e.g., zeolite, iron and manganese oxides, organic matter, e.g., farmyard manure and compost, [13,14] and industrial by-products, e.g., bauxite residue, slag and gravel sludge [15–18], and they are considered to reduce solubility and bioavailability of Cd in soil through precipitation, sorption and occlusion. Applications of several materials among them successfully reduced plant uptake of Cd in soil. However, some of them, especially industrial by-products containing high levels of heavy metals (for example, see [17,19]), can cause undesirable accumulation of those metals in soils.

In the present study, we focused on the materials containing magnesium oxide (MgO) as the amendments for Cd-contaminated paddy soils to suppress uptake and accumulation of Cd into rice grains. García et al. [20] studied the effectiveness of low-grade MgO as a stabilizer agent of soils heavily polluted by the flue-dust of pyrite roasting and confirmed significant reduction of heavy metal solubility in the amended soils due to increase in soil pH.

In this paper, we report on the mineralogical and physicochemical properties, soil neutralizing capacities and Cd sorption characteristics of a commercial MgO and a composite material derived from MgO and natural minerals, named 'MgO-SH-A'. In the second paper [21], we state the effectiveness of these materials in suppression of Cd accumulation into rice grains based on the results obtained from a rice cultivation experiment in an actual Cd-contaminated paddy field.

2. Materials and methods

2.1. Magnesium oxide materials and chemicals used

The commercial magnesium oxide used was manufactured by Nihon Kaisui Kakou, Co. Ltd. for industrial use. MgO-SH-A was produced by Ams Engineering, Co. Ltd. and made up from

light-burned magnetite and/or brucite and dolomitic quicklime. This amendment had been originally developed as a cementing agent for such hazardous materials containing toxic inorganic and organic substances as heavily polluted soils and fly ash.

All reagents used in this study were of special grade (Wako, Osaka, Japan), except for HCl and HNO₃ used for preparation of the stock solution and acidification of the samples, which were for analysis of poisonous metal (Wako). Distilled and deionized water was also used for preparation of stock solutions.

2.2. Mineralogical and physicochemical properties of magnesium oxide materials

The X-ray diffraction (XRD) analysis of MgO-SH-A was carried out by an X-ray diffractometer (MX-Labo, MAC Science, Yokohama, Japan) equipped with Ni-filtered Cu K_α radiation ($\lambda = 0.154056$ nm) operating at 40.0 kV, 30.0 mA, scanning (2θ) between 3.010° and 65.000° at a rate of 2.000° min⁻¹.

The elemental analyses of commercial MgO and MgO-SH-A were performed by a wavelength-dispersive X-ray fluorescence analyzer (XRF) (Axios, PANalytical, Almelo, Netherlands) equipped with a Rh target tube operating at 2.4 kW (ranging from 60 kV–40 mA to 30 kV–80 mA) and a scintillation counter. The dispersive crystals used were LiF220, LiF200, Ge111, TlAp 100 coated, PX1 and PX4A. The detectable elements ranged from boron (B) to uranium (U). A non-standard quantification software, UniQuant5, was used for determination of elements.

The pH values (material:water = 1:2.5) of commercial MgO and MgO-SH-A were determined by a pH meter (TES-1380, Custom, Tokyo, Japan) equipped with a glass electrode (PT-200, Custom), and their surface areas were determined by glycerol adsorption method [22].

2.3. Soil neutralizing capacities of magnesium oxide materials

The soil sample used was collected from the plough layer (0–15 cm depth) of one of the paddy fields in the Hommachi Farm, Field Science Center for Education and Research of Tokyo University of Agriculture and Technology located in Fuchu City, Tokyo. This soil is classified into Aquic Fluvents [23] and the soil texture was silt loam. The collected sample was air-dried, sieved through a 2-mm nylon screen and stocked. The pH(H₂O) and surface area of the soil sample are shown in Table 2.

Five grams of the soil sample was placed into a 30 mL polyethylene vial and commercial MgO or MgO-SH-A was added at rates ranging from 0 to 6 wt%. Distilled-deionized water (12.5 mL) was added, and the sample was lightly shaken and then left at rest at 25 °C for 24 h. The sample was further shaken with a reciprocal shaker (SR-II, Taitec, Saitama, Japan) at 25 °C for 5 h and aerated for 2 min to let the generated CO₂ gas out from the sample suspension. The pH of the sample suspension was measured immediately after aeration by a pH meter (M-7, Horiba, Kyoto, Japan) equipped with a glass electrode (#6066-10C, Horiba) [24].

2.4. Sorption of cadmium on magnesium oxide materials

One hundred milligram of commercial MgO or MgO–SH–A was weighed into a 50 mL centrifuge tube, and then 25 mL of Cd solution, the Cd concentration ranging from 0.1 to 50 mmol L⁻¹, was added to the tube. Sodium nitrate (0.01 mol L⁻¹) was dissolved in the Cd solution as an electrolyte. The tube was shaken with a reciprocal shaker (SR-II, Taitec) at 25 °C for 24 h to make the equilibrium. The supernatant after centrifugation (11,700 × g) was filtered through a membrane filter (mixed cellulose ester with a 0.45 μm pore size, Advantec, Tokyo, Japan). The pH of the equilibrium solution was measured by a pH meter (M-13, Horiba) equipped with a glass electrode (#6366-10D, Horiba), and the equilibrium solution was then acidified with 0.2 mL of concentrated HNO₃. The residues of the samples with which 0.1, 1 and 37.3 mmol L⁻¹ of Cd had been reacted were rinsed with 25 mL of 95% (v/v) ethanol twice, air-dried and stocked for the desorption experiment described in the next section. The Cd concentrations in the initial and equilibrium solution were determined using an atomic absorption spectrophotometer (AAS) (Z-5010, Hitachi, Tokyo, Japan) with air–acetylene flame at 228.8 nm. The amount of Cd sorbed (Cd_{Sorb}) on the materials was calculated by the following equation:

$$\text{Cd}_{\text{Sorb}} = \frac{([\text{Cd}_{\text{Init}}] - [\text{Cd}_{\text{Equi}}])v}{m} \quad (1)$$

where [Cd_{Init}] represents the initial concentration of Cd in the solution added, [Cd_{Equi}] the Cd concentration in the equilibrium solution, *v* the volume of the Cd solution added (=25 mL) and *m* is the amount of the material. The amount of Cd precipitated as hydroxide (Cd(OH)₂) was also estimated from the equilibrium pH assuming the solubility product (*K*_{sp}) of Cd(OH)₂ to be 2.8 × 10⁻¹⁴ mol³ L⁻³ at 25 °C [25].

A sample of Cd-sorbed MgO–SH–A was also prepared to investigate the form of Cd on the material surface by XRD. Two grams of MgO–SH–A was weighed into a 250 mL centrifuge tube, 125 mL of 50.7 mmol L⁻¹ Cd solution was added to the tube and then shaken with a reciprocal shaker (SR-II, Taitec) at 25 °C for 24 h. The supernatant after centrifugation (13,400 × g) was filtered through a membrane filter (mixed cellulose ester with a 0.45 μm pore size, Advantec) and Cd concentration in the supernatant was determined by an AAS (Z-5010, Hitachi) to calculate the amount of Cd sorbed on the material. The residue (Cd-sorbed sample) was rinsed with 25 mL of 95% (v/v) ethanol twice and air-dried for XRD analysis. The X-ray diffractometer used and its operating condition were the same as those described in Section 2.2.

2.5. Desorption of cadmium sorbed on magnesium oxide materials by 0.1 M HCl

The Cd-sorbed material prepared in the sorption experiment (see the previous section) was weighed into another 50 mL centrifuge tube and 25 mL of 0.1 M HCl was added to the tube. The sample was shaken with a reciprocal shaker (SR-II, Taitec) at 25 °C for 1 h. After shaking, the sample was centrifuged

(11,700 × g) and the supernatant was filtered through a membrane filter (mixed cellulose ester with a 0.45 μm pore size, Advantec). The pH of the supernatant (eluate) was measured by a pH meter (M-13, Horiba) equipped with a glass electrode (#6366-10D, Horiba), and the Cd concentration in the eluate was determined using an AAS (Z-5010, Hitachi).

3. Results and discussion

3.1. Mineralogical and physicochemical properties of magnesium oxide materials

The X-ray diffraction pattern of MgO–SH–A is shown in Fig. 1(a). Remarkable diffraction peaks derived from MgO and antigorite (Mg₃Si₂O₅(OH)₄) were observed. In addition, the peak of MgCO₃ as accessory minerals was also identified. The MgCO₃ was considered to be derived from hydration of MgO and the subsequent absorption of CO₂.

The elemental compositions of commercial MgO and MgO–SH–A are summarized in Table 1. The most abundant element present in MgO–SH–A was Mg (61.41% as MgO), which was although smaller than that in commercial MgO (90.17%). Silica (SiO₂) was the second dominant element in MgO–SH–A (21.11%), implying that silicate minerals were also dominant constituents of this material. This consideration was supported by the results of the XRD analysis (Fig. 1(a)) showing remarkable peaks of a magnesium-silicate mineral.

The pH(H₂O) values and surface area of commercial MgO and MgO–SH–A are shown in Table 2. The high pH values of the two materials were suggested to be provided by the hydration of MgO to generate Mg(OH)₂. Large surface areas of commercial MgO and MgO–SH–A, 776.5 and 165.0 m² g⁻¹,

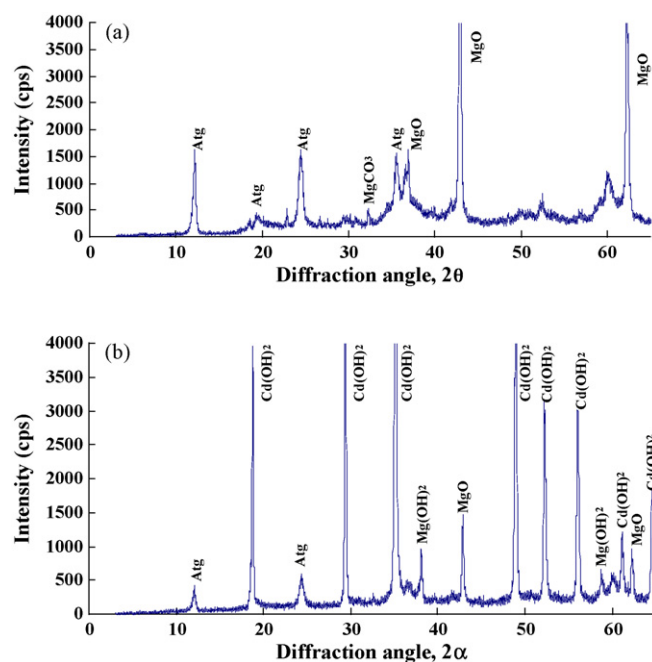


Fig. 1. The X-ray diffraction patterns of MgO–SH–A: (a) original material and (b) Cd-sorbed material (the amount of Cd sorbed = 3.2 mmol g⁻¹ DW). Atg: antigorite.

Table 1
Elemental composition of the magnesium oxide materials

	MgO ^a (wt%)	MgO–SH–A (wt%)
Na ₂ O	0.38	0.207
MgO	90.17	61.41
Al ₂ O ₃	0.203	0.894
SiO ₂	0.589	21.11
P ₂ O ₅	0.0267	0.913
SO ₃	0.753	0.0318
Cl	0.199	0.0032
K ₂ O	0.0059	0.0162
CaO	1.58	3.81
TiO ₂	0.0133	0.0483
V ₂ O ₅	0.0008	0.005
Cr ₂ O ₃	0.0019	0.163
MnO	0.0272	0.107
Fe ₂ O ₃	0.28	4.42
Others	5.75	6.62
Total	99.98	99.76

^a Commercial MgO.

Table 2
The pH(H₂O) and surface area of the magnesium oxide materials and the soil sample used

Material	pH(H ₂ O) ^a	Surface area (m ² g ⁻¹)
MgO	11.2	776.5
MgO–SH–A	10.7	165.0
Soil	6.2	99.9

MgO: commercial MgO.

^a Material:water = 1:2.5.

respectively, as well as high pH would be appropriate for sorption of Cd.

3.2. Soil neutralizing capacities of magnesium oxide materials

Fig. 2 shows the neutralizing capacities of commercial MgO and MgO–SH–A for the paddy soil used. The degree of increase in soil pH due to addition of commercial MgO was higher than that of MgO–SH–A at 0–1 wt% of the addition rate, suggesting that MgO–SH–A would be more suitable as a soil amendment because the soil pH should be maintained below 7.0 in order to

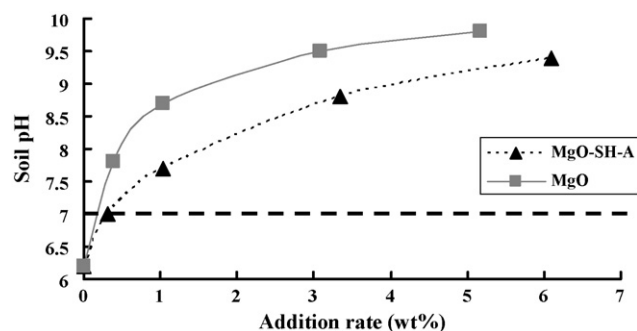


Fig. 2. The soil neutralizing capacities of commercial MgO ('MgO' in legend) and MgO–SH–A for a paddy soil (Aquic Fluvents).

avoid precipitation of other essential nutrient elements for crops in soil. From Fig. 2, the addition rates of commercial MgO and MgO–SH–A required to adjust the soil pH to 7.0 were estimated to be 0.15 and 0.30 wt% of the soil, respectively. These values were applicable to 2250 and 4500 kg ha⁻¹ for the field level, respectively, assuming that the bulk density and the depth of the soil with which the materials were to be mixed were 1.0 Mg m⁻³ and 15 cm, respectively.

3.3. Sorption of cadmium on magnesium oxide materials

The Cd sorption isotherms for the MgO materials are illustrated in Fig. 3. These isotherms well fitted Langmuir sorption isotherm:

$$\frac{q_e}{q_{\max}} = \frac{bc_e}{1 + bc_e} \quad (2)$$

where q_e is the amount of Cd sorbed on the material at equilibrium state (Cd_{Sorb} in Eq. (1)), q_{\max} the maximum sorption capacity, b the ratio of the sorption rate constant to the desorption rate constant, referred to as the 'affinity constant', and c_e is the Cd concentration in solution phase at equilibrium state. The values of q_{\max} and b for the two MgO materials, as well as the regression coefficients, are summarized in Table 3. The maximum Cd sorption capacities of commercial MgO and MgO–SH–A were estimated to be 46.8 and 5.87 mmol g⁻¹ DW (DW: dry weight), respectively. The higher Cd sorption capacity of the commercial MgO was deduced from the larger surface area and the higher pH compared to those of

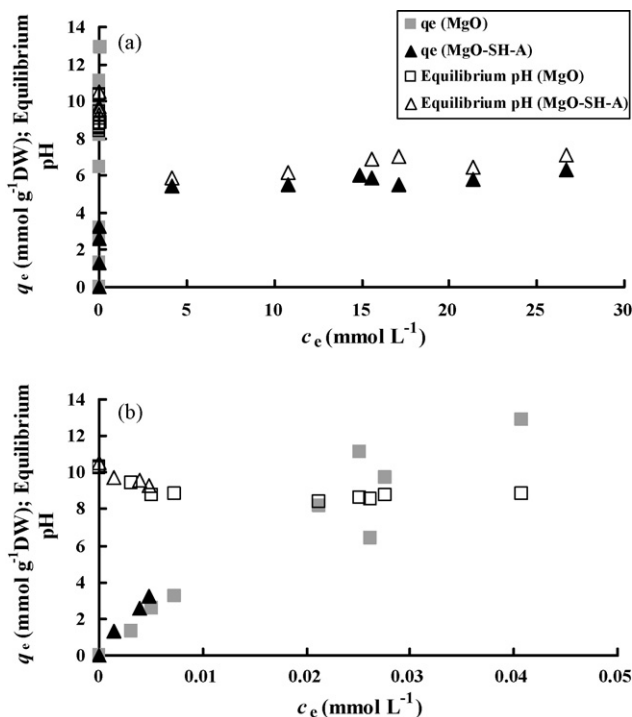


Fig. 3. The Cd sorption isotherms for commercial MgO ('MgO' in legend) and MgO–SH–A, together with the corresponding equilibrium pH: (a) $c_e = 0\text{--}30$ mmol L⁻¹ and (b) $c_e = 0\text{--}0.05$ mmol L⁻¹.

Table 3
Langmuir parameters for Cd sorption on the magnesium oxide materials

	q_{\max} (mmol g ⁻¹ DW)	b (L mmol ⁻¹)	R
MgO	46.8	9.78	0.989**
MgO–SH–A	5.87	206	0.997**

q_{\max} : maximum sorption capacity; b : the ratio of the sorption rate constant to the desorption rate constant; MgO: commercial MgO.

** Significant at $p < 0.01$.

MgO–SH–A (Table 2). On the other hand, MgO–SH–A showed higher b value than the commercial MgO, which implied that the former material had higher affinity to Cd than the latter one.

In case of commercial MgO, the precipitation of Cd(OH)₂ was estimated to comprise 86.7–100% of the total amount of Cd sorbed at every concentration of Cd in the added solution, suggesting that the dominant mechanism involved in Cd sorption on this material would be precipitation of Cd(OH)₂ of which OH⁻ ion was supplied from dissociation of Mg(OH)₂ formed on the surface of MgO particles. In case of MgO–SH–A, the precipitation of Cd(OH)₂ was calculated to occupy almost 100% of the total amount of Cd sorbed when the solution containing 0.1–13 mmol L⁻¹ of Cd was added, although it was not estimated to be formed when the higher concentration of Cd was added. The XRD pattern of the Cd-sorbed MgO–SH–A (Fig. 1(b)), whose Cd sorption amount was calculated to be 3.2 mmol g⁻¹ DW, showed remarkable peaks of Cd(OH)₂ and reduction of MgO peaks as compared to the original one (Fig. 1(a)). These results implied that the dominant reaction involved in Cd sorption on MgO–SH–A would be precipitation of Cd(OH)₂ on the surface of the material particles, which would be the same with the case of commercial MgO. The pH of the region near the surface of the material is considered to be higher than that of the bulk solution because the dissociation rate of Mg(OH)₂ formed on the surface of MgO particles is low. High pH (OH⁻ concentration) in the region near the material surface is favorable for Cd²⁺ to precipitate on the material surface as hydroxide even if the pH of the bulk solution is lower than that at which Cd(OH)₂ starts to precipitate calculated from K_{sp} of Cd(OH)₂.

The XRD analysis of the Cd-sorbed MgO–SH–A revealed no formation of CdCO₃ on the material surface (Fig. 1(b)). However, Rötting et al. [26] observed the presence of otavite (CdCO₃) as a major Cd phase on the Cd-treated caustic magnesia, although they also identified several peaks of Cd(OH)₂ in the XRD pattern of the material. This discrepancy may be partly explained by the fact that the Cd concentration in the Cd solution used in the experiment by Rötting et al. [26] (1.5 mmol L⁻¹) was much lower than that in the Cd solution used for preparation of the Cd-sorbed MgO–SH–A for XRD analysis in this study (50 mmol L⁻¹). Theoretically, the pH of the solution at which Cd(OH)₂ starts to precipitate will increase as Cd concentration in the solution decreases. In addition, the Cd solution used in the experiment by Rötting et al. [26] contained a high concentration of sulfate (5.67 mmol L⁻¹), which was found to strongly affect the speciation of Cd in the system.

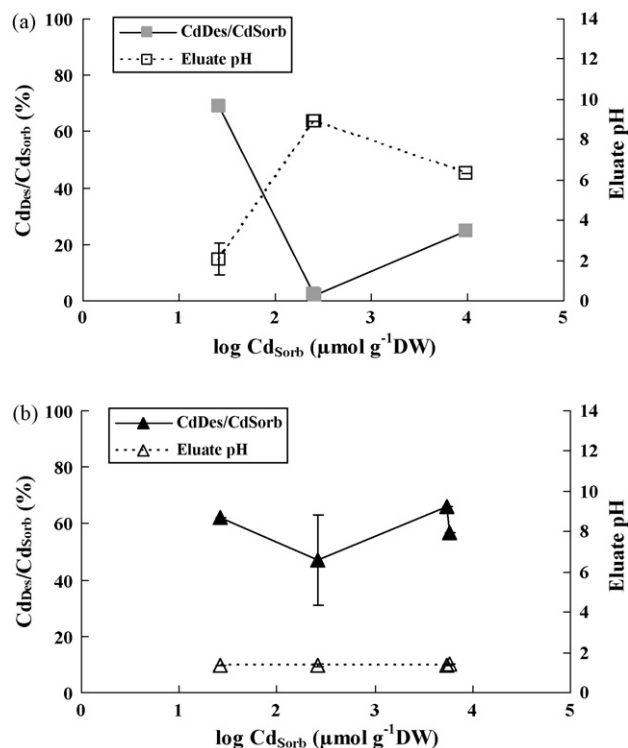


Fig. 4. The desorption of Cd sorbed on commercial MgO (a) and MgO–SH–A (b) by 0.1 M HCl, together with the corresponding eluate pH. Cd_{Sorb}: the initial amount of Cd sorbed on the material; Cd_{Des}: the amount of Cd desorbed by 0.1 M HCl. Error bar represents standard deviation ($n = 2$).

3.4. Desorption of cadmium sorbed on magnesium oxide materials by 0.1 M HCl

The percentage of the amount of Cd desorbed from Cd-sorbed magnesium oxide materials by 0.1 M HCl (Cd_{Des}) to the total amount of Cd sorbed (Cd_{Sorb}), together with the pH of the eluate, and the relationship between eluate pH and Cd_{Des}/Cd_{Sorb} are shown in Figs. 4 and 5, respectively. The Cd_{Des}/Cd_{Sorb} value and the eluate pH for commercial MgO varied with the initial amount of Cd sorbed (Fig. 4(a)), and there was a significant negative correlation between eluate pH and Cd_{Des}/Cd_{Sorb} regardless

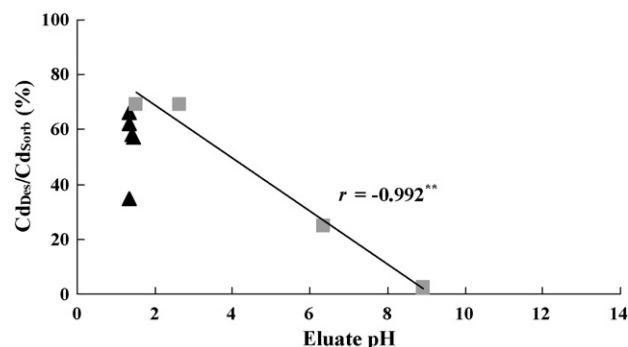


Fig. 5. The relationship between pH of eluate and Cd_{Des}/Cd_{Sorb} (%) of the MgO materials. (■) commercial MgO and (▲) MgO–SH–A. Cd_{Sorb}: the initial amount of Cd sorbed on the material; Cd_{Des}: the amount of Cd desorbed by 0.1 M HCl. ** Significant at $p < 0.01$.

of the initial amount of Cd sorbed (Fig. 5). On the other hand, the Cd_{Des}/Cd_{Sorb} and the pH of the eluate for MgO–SH–A were $56.7 \pm 11.1\%$ and 1.37 ± 0.04 (Fig. 4(b)), respectively, irrespective of the initial amount of Cd sorbed. This result indicates that about 40% of the sorbed Cd on this material would be retained on the material even in strongly acid condition. Furthermore, the Cd_{Des}/Cd_{Sorb} of MgO–SH–A appeared to be smaller than that of the commercial MgO when compared at the same pH of the eluate (Fig. 5).

The release of OH^- ion due to dissociation of $Mg(OH)_2$ formed on the particle surface of MgO–SH–A is suggested to be suppressed by the co-existing minerals (e.g. antigorite) as compared to that from single MgO, which could also partly be explained by the experimental result that MgO–SH–A exhibited a lower pH and a milder soil neutralizing capacity as compared to commercial MgO (Fig. 2). This implies that in the suspension of MgO–SH–A, precipitation of $Cd(OH)_2$ is more likely to occur in the region near the material surface than in the bulk solution and the precipitated $Cd(OH)_2$ is more strongly retained on the surface as compared to the case of MgO alone.

4. Conclusions

The mineralogical and physicochemical properties, soil neutralizing capacity and Cd sorption characteristics of two MgO materials, commercial MgO and MgO–SH–A, which were expected to be utilized as the soil amendments to suppress Cd uptake by rice plants, were studied.

1. The MgO materials possessed high pH and large surface area, which were appropriate for sorption of Cd.
2. MgO–SH–A contained MgO and antigorite as the main components.
3. MgO–SH–A had a milder soil neutralizing capacity as compared to that of the commercial MgO, which would be appropriate to avoid precipitation of the essential nutrient elements for crops in the soil caused by a rapid increase in soil pH due to application.
4. The sorptions of Cd on commercial MgO and MgO–SH–A fitted Langmuir isotherm, and the maximum Cd sorption capacities were estimated to be 46.8 and 5.87 $mmol\ g^{-1}\ DW$, respectively. The majority of Cd sorbed on the surface of these materials was suggested to be in the form of $Cd(OH)_2$ precipitate.
5. A portion (about 40%) of sorbed Cd on MgO–SH–A was not desorbed by 0.1 M HCl solution, implying that this fraction was strongly retained on the material surface.

In conclusion, both commercial MgO and MgO–SH–A have potentials as the soil amendments for suppression of Cd uptake and accumulation into rice grains. Especially, MgO–SH–A has a sufficient capacity to sorb and retain Cd usually existing in the soil solution of contaminated paddy soils, and a milder neutralizing capacity as compared to the commercial MgO.

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References

- [1] CAC, Codex General Standard for Contaminants and Toxins in Foods, CODEX STAN 193-1995, Rev.2-2006, http://www.codexalimentarius.net/download/standards/17/CXS_193e.pdf.
- [2] T. Asami, Toxic Metal Pollution in Soils of Japan, Agune Gijutsu Center, Tokyo, Japan, 2001, p. 402 (in Japanese).
- [3] Japanese Agency of Environment, Handbook of Countermeasures for Soil Pollution, Kougai-Kenkyu Center, Tokyo, Japan, 1992 (in Japanese).
- [4] Ministry of Agriculture, Forestry and Fishery (MAFF) and National Institute for Agro-Environmental Sciences (NIAES), The Technical Manual for Suppression of Cadmium Uptake by Rice Plants, <http://www.maff.go.jp/cd/PDF/D3.pdf> (in Japanese).
- [5] MAFF, The Results of the Survey on Measures to Combat Soil Pollution in 1971 and 1972 (in Japanese).
- [6] MAFF, The Results of the Survey on Measures to Combat Soil Pollution in 1972 and 1973 (in Japanese).
- [7] E. Hasegawa, H. Shima, M. Saito, E. Tatsuno, Effect of autoclaved lightweight concrete on suppression of cadmium uptake by rice plants in clayey paddy field, Bull. Miyagi Prefect. Agric. Res. Cent. 61 (1995) 13–32 (in Japanese with an English summary).
- [8] N.S. Bolan, D.C. Adriano, P.A. Mani, A. Duraisamy, Immobilization and phytoavailability of cadmium in variable charge soils. II. Effect of lime addition, Plant Soil 251 (2003) 187–198.
- [9] X.L. Zhao, M. Saigusa, Effect of porous hydrated calcium silicate on sorption and desorption of cadmium by soils, Soil Sci. Plant Nutr. 50 (2004) 315–319.
- [10] NIAES, The Technologies for Suppression of Cadmium Uptake by Rice Plants, <http://www.niaes.affrc.go.jp/magazine/mgzn030.html#030005> (in Japanese).
- [11] B.J. Alloway, Cadmium, in: B.J. Alloway (Ed.), Heavy Metals in Soils, second ed., Blackie Academic and Professional, London, 1995, pp. 122–151.
- [12] Japanese Agency of Environment, Soil Pollution, Hakua-shobo, Tokyo, 1973 (in Japanese).
- [13] C. Keller, M. Marchetti, L. Rossi, N. Lugon-Moulin, Reduction of cadmium availability to tobacco (*Nicotiana tabacum*) plants using soil amendments in low cadmium-contaminated agricultural soils: a pot experiment, Plant Soil 276 (2005) 69–84.
- [14] Z.S. Chen, G.J. Lee, J.C. Liu, The effects of chemical remediation treatments on the extractability and speciation of cadmium and lead in contaminated soils, Chemosphere 41 (2000) 235–242.
- [15] R. Krebs, S.K. Gupta, G. Furrer, R. Schulen, Gravel sludge as an immobilizing agent in soils contaminated by heavy metals: a field study, Water Air Soil Poll. 115 (1999) 465–479.
- [16] H.M. Chen, C.R. Zheng, C. Tu, Z.G. Shen, Chemical methods and phytoremediation of soil contaminated with heavy metals, Chemosphere 41 (2000) 229–234.
- [17] E. Lombi, F.J. Zhao, G. Zhang, B. Sun, W. Fitz, H. Zhang, S.P. McGrath, In situ fixation of metals in soil using bauxite residue: chemical assessment, Environ. Pollut. 118 (2002) 435–443.
- [18] E. Lombi, F.J. Zhao, G. Wieshammer, G. Zhang, S.P. McGrath, In situ fixation of metals in soils using bauxite residue: biological effects, Environ. Pollut. 118 (2002) 445–452.
- [19] W. Friesl, O. Horak, W.W. Wenzel, Immobilization of heavy metals in soils by the application of bauxite residue: pot experiments under field conditions, J. Plant Nutr. Soil Sc. 167 (2004) 54–59.
- [20] M.A. García, J.M. Chimenos, A.I. Fernández, L. Miralles, M. Segarra, F. Espiell, Low-grade MgO used to stabilize heavy metals in highly contaminated soils, Chemosphere 56 (2004) 481–491.

- [21] T. Kikuchi, M. Okazaki, S.D. Kimura, T. Motobayashi, J. Baasansuren, T. Hattori, T. Abe, Suppressive effects of magnesium oxide materials on cadmium uptake and accumulation into rice grains. II: Suppression of cadmium uptake and accumulation into rice grains due to application of magnesium oxide materials, *J. Hazard. Mater.* 154 (2008) 294–299.
- [22] S. Diamond, E.B. Kinter, Surface areas of clay minerals as derived from measurements of glycerol retention, in: *Proceedings of the 5th National Conference on Clays, Clays and Clay Minerals*, 1958, pp. 334–346.
- [23] Soil Survey Staff, *Keys to Soil Taxonomy*, SMSS Technical Monograph No. 19, Virginia Polytechnic Institute and State University, Virginia, 1990.
- [24] A. Chiba, H. Shinke, Estimation of lime requirement of soil with calcium carbonate and aeration method, *J. Sci. Soil Manure Jpn.* 48 (1977) 237–242 (in Japanese).
- [25] Hokkaido Branch and Tohoku Branch of Japanese Society of Analytical Chemistry, *Fundamentals of Chemical Reactions in Analytical Chemistry*, Baifu-Kan, Tokyo, Japan, 1994 (in Japanese).
- [26] T.S. Rötting, J. Cama, C. Ayora, J.L. Cortina, J. de Pabro, Use of caustic magnesia to remove cadmium, nickel, and cobalt from water in passive treatment systems: column experiments, *Environ. Sci. Technol.* 40 (2006) 6438–6443.