Effects of coexisting species on the selenate sorption using magnesium oxide

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ABSTRACT

Magnesium oxide (MgO) is commonly used in wastewater treatment because it can neutralize acidic water and sorb various pollutants. However, it has a low affinity with anions such as selenate (SeO_4^{2–}). In the present study, the effects of coexisting species on the SeO_4^{2–} sorption onto MgO were explored to find a way to enhance the SeO_4^{2–} sorption. Related characterizations including X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, thermogravimetric, and nuclear magnetic resonance were adopted to get a better understanding of the reaction process. It has been found that a much higher sorption amount of SeO_4^{2–} (0.33 mmol g^{-1}) can be achieved in the presence of Al^{3+} additive, mainly due to the formation of layered double hydroxide. However, silicate additive has a negative effect on the SeO_4^{2–} sorption (0.019 mmol g^{-1}). SiO_3^{2–} can react with MgO (or Mg(OH)_2) to form magnesium silicate hydrate, covering on the surface of MgO (or Mg(OH)_2) particles, then blocking the interaction between MgO (Mg(OH)_2) and SeO_4^{2–}. In the case of SO_4^{2–} additive, the sorption amount of SeO_4^{2–} (0.06 mmol g^{-1}) was maintained as that without additive (0.063 mmol g^{-1}). This might be because their corresponding salts (MgSO_4 and MgSeO_4) have similar solubilities. Then, less effect on the SeO_4^{2–} was caused by SO_4^{2–}. Based on this work, a novel stabilizer (MgO + Al species) can be proposed for the immobilization of SeO_4^{2–}.

Keywords: Magnesium oxide; Selenate; Sorption; Additives; Al species

1. Introduction

Selenium is an essential micronutrient for organisms but can be toxic if it is taken in excess [1]. The World Health Organization (WHO) has set a limit of 40 μg L^{-1} Se for drinking water [2]. Long-term uptake above the recommended limit of Se can result in serious health problems for human and animals [3,4]. However, Se pollution on soil and water have been gradually caused by anthropogenic activities such as mining, agriculture, coal combustion, insecticide production, and oil refining [5,6]. Therefore, Se removal/immobilization from surface water/soil needs proper treatments to achieve the purification process. Generally, Se has several chemical forms including selenide (Se^{2–}), elemental Se, selenite (SeO_3^{2–}), selenate (SeO_4^{2–}), and organic Se in the natural environment [7]. Among them, both SeO_3^{2–} and SeO_4^{2–} could bioaccumulate in organisms, and SeO_4^{2–} is found to be of high toxicity [8]. However, SeO_3^{2–} is more difficult to precipitate with other atoms, possessing much higher mobility compared to SeO_4^{2–} [9,10]. Thus, the immobilization of SeO_4^{2–} should be needed.

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Sorption has been extensively applied as an effective and economic technique compared to other methods involving coagulation, ion exchange, membrane filtration, etc. [11]. Magnesium oxide (MgO) as a nontoxic adsorbing material is commonly used in wastewater treatment to remove pollutants and adjust solution pH [12]. Cui et al. [11] prepared MgO nanosheet for the sorption of SeO$_4^{2-}$ and SeO$_3^{2-}$ and achieved the sorption capacities of 103.52 and 10.28 mg g$^{-1}$, respectively. This is consistent with the above state that SeO$_4^{2-}$ has higher mobility. Besides, Suzuki et al. and Tian et al. [9,13] also concluded that MgO cannot effectively immobilize SeO$_4^{2-}$. Thus, some strategies should be adopted to improve the sorption of SeO$_4^{2-}$ onto MgO. MgO can easily react with water to become Mg(OH)$_2$ and some other phase transformations can happen during the hydration of MgO in the presence of additives [9,14]. Layered double hydroxides (LDHs) as a kind of highly effective adsorbents for the removal of anions are the potential phases during the reaction in the presence of a trivalent element [14]. MgAl-LDH is commonly synthesized and used as adsorbents in substantial studies [15–17]. However, few studies focus on the enhancement of SeO$_4^{2-}$ removals by MgO in the presence of aluminum species from aqueous conditions. Therefore, the purpose of this study is (1) to explore the effect of coexisting species on the phase transformation during MgO hydration and the removal of SeO$_4^{2-}$ using MgO, (2) to make comparisons between these additives. Related characterizations including X-ray diffraction (XRD), Fourier-transform infrared (FTIR), scanning electron microscopy (SEM), thermogravimetric (TG), and nuclear magnetic resonance (NMR) were adopted in this study.

2. Environmental

2.1. Materials

A commercial magnesium oxide (MgO, light, >98%) was used in this study. Related characterizations are shown in Fig. 1. The XRD peaks of MgO matched well with these of the pure MgO phase (PDF#78-0430). The N$_2$ adsorption–desorption curves indicate that MgO has a large specific surface area of 48.7 m$^2$ g$^{-1}$ and a high pore volume of 0.52 cm$^3$ g$^{-1}$. SEM image suggests that the purchased MgO appeared to be partially exfoliated compared to the previous report [11]. Besides, the Se solution was prepared by dissolving sodium selenate (Na$_2$SeO$_4$, 97%). The aluminum nitrate nonahydrate (Al(NO$_3$)$_3$·9H$_2$O, 98%), sodium metasilicate nonahydrate (Na$_2$SiO$_3$·9H$_2$O, 98%), and sodium sulfate (Na$_2$SO$_4$, 99%) were used as additives.

2.2. Sorption experiments

The MgO was used as an adsorbent for the immobilization of SeO$_4^{2-}$ from solution (initial pH: 7). To explore...
the effect of coexisting species on the phase transformation and the removal of SeO$_4^{2-}$, the initial experimental condition was fixed. Thus, the sorption thermodynamics and dynamics were not conducted, as other studies did [18,19]. Specifically, 100 mg MgO was added into the solutions containing 1.266 mM (100 mg L$^{-1}$) with and without the same molar concentration of additives (Table 1). Then, these slurries were stirred at 400 rpm for 24 h under ambient conditions, and the mixtures were separated by membrane filtration. The solid residues were dried in a vacuum dryer, and the solutions were adjusted to acid condition for further analysis of elemental concentration.

### 2.3. Characterizations

The elemental concentrations in the supernatant were determined using an ICP-OES (Optima 8300, US). An X-ray diffraction equipment (D8 ADVANCE, Germany) was utilized to collect XRD patterns of solid residues using Cu Kα (40 kV, 30 mA) at a scanning step of 0.02°. SEM observations were conducted on a FEI Quanta™ 250 (US) with the acceleration voltages of 20 kV. Besides, the FTIR spectra of the samples diluted by KBr were recorded on a VERTEX 80v (BRUKER, Germany) spectrometer at a resolution of 4 cm$^{-1}$. Furthermore, thermogravimetric analysis was achieved on TGA8000 (US) with a heating rate of 10°C/min and an airflow of 100 mL min$^{-1}$. Both $^{27}$Al and $^{29}$Si MAS NMR measurements were conducted on a Bruker AVANCE III spectrometer.

### 3. Results and discussion

#### 3.1. Sorption results

Fig. 2 shows the sorption amount of SeO$_4^{2-}$ and pH values of solutions after sorption under different conditions. Without any additive, the sorption amount of 0.063 mmol g$^{-1}$ can be achieved using the MgO, which is consistent with the report [11]. A very high Se sorption amount (0.330 mmol g$^{-1}$) was obtained in the presence of Al species. However, it can be seen that silicate additive has a negative effect on the Se sorption onto MgO. For both Al and Si species, all of them have reacted with MgO during the reaction because of their non-detections in the supernatants, indicating the occurrence of other phase transformations besides MgO hydration. For sulfate additive, 1.21 mmol L$^{-1}$ of S was still left in the solution after the reaction. Under this situation, the sorption amount of Se was maintained as that without additive. This suggests that sulfate has less effect on the Se sorption onto MgO. Besides, it can be known that the MgO could get an equilibrium solution pH of 10.49 (Fig. 2b). The pH values for the solution containing SeO$_4^{2-}$ or Al species (E2 and E3) decreased mainly because their hydrolytic processes can consume a part of alkaline. In contrast, the silicate additive increased the solution pH after the reaction.

#### 3.2. Solid characterizations

The XRD patterns of solid residues (Fig. 3a) were collected to get a better understanding of phase transformations. The peaks for Mg(OH)$_2$ appeared in all cases. The most attractive point is that the 003 peak for LDH appeared, suggesting that LDH was formed in the presence of Al species. It should be noted that the crystallinity of newly formed LDHs is lower due to the low reaction temperature. The position of the 003 peak indicates that the main embedded anions in the interlayer of LDH should be CO$_3^{2-}$ [16]. The positive surface charge can still contribute a higher Se sorption amount. While, the crystallinities of Mg(OH)$_2$ seems to be much higher in the presence of silicate additive compared to other cases, mainly due to the higher

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO</th>
<th>SeO$_4^{2-}$</th>
<th>Al$^{3+}$</th>
<th>SiO$_2^{2-}$</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>o</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>E2</td>
<td>o</td>
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<td>–</td>
<td>–</td>
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<tr>
<td>E3</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>E4</td>
<td>o</td>
<td>o</td>
<td>–</td>
<td>o</td>
<td>–</td>
</tr>
<tr>
<td>E5</td>
<td>o</td>
<td>o</td>
<td>–</td>
<td>–</td>
<td>o</td>
</tr>
</tbody>
</table>

Note: o, Added; –, None.
solution pH. The high supersaturation of Mg$^{2+}$ could be achieved at high pH, contributing to the nucleation [20,21]. It has been proved that silicate can be reacted with MgO (or Mg(OH)$\text{$_2$}$) into magnesium silicate hydrate (M-S-H) [16], thereby affecting the Se sorption process. Therefore, the sorption amount of Se decreased in the presence of silicate compared to that without any additive. The FTIR spectra of solid residues are shown in Fig. 3b. According to the previous studies [22], the peaks at approximately 3,700 cm$^{-1}$ can be assigned to the stretching vibration of the OH group in Mg(OH)$\text{$_2$}$. Bending vibrations of OH groups can be found at 1,660 cm$^{-1}$ approximately. The absorbance at approximately 1,430 cm$^{-1}$ is attributed to the vibrations of carbonate. Obviously, the carbonate peak at the spectra of E3 seems to be different from other cases, indicating that different coordination environment of carbonates. This is consistent with the XRD description. On the other hand, selenate vibration can be found in the spectrum of E3, due to the high sorption amount.

SEM images of solid residues are shown in Fig. 4. Mg(OH)$\text{$_2$}$ plates appeared in the E1, E2, E3, and E5, and further aggregated into particles with various sizes. For E4, the crystallinity was much improved due to the higher pH, leading to a decrease in the particle size. This is consistent with the XRD result as well. In addition, TG results are shown Fig. 5. It can be seen that the dehydroxylation of Mg(OH)$\text{$_2$}$ occurred in all cases. For E3, besides the weight loss of Mg(OH)$\text{$_2$}$, there are another weight losses at temperatures of approximately 470°C–550°C and 720°C–810°C attributing to the dehydroxilation of LDH structure and Se elimination, respectively. Other additives have less effect on the dehydration process.

The $^{27}$Al spectrum of solid residue after reaction with Al additive is presented in Fig. 6a. Only an anisotropic peak at approximately 9 ppm can be observed in the $^{27}$Al NMR spectrum, mainly due to the Al six-coordination to oxygen atoms [23]. This suggests that all of the added Al salt has participated in the formation of LDH structure. As for MgO after reaction with silicate ion, the $^{28}$Si NMR spectrum and their corresponding deconvolutions are shown in Fig. 6b. According to the previous reports [16,24], two peaks at 85.5 and 97.2 ppm can be assigned to the characteristic peaks of Q$^0$ and Q$^1$ for magnesium silicate hydrate (M-S-H), respectively. However, these peaks centered at 59.1, 65.6, and 70.2 ppm are attributed to the Si coordination of Q$^0$ [25], indicating that a part of silicate ions is just weakly adsorbed on the surface of Mg(OH)$_2$ particles. Besides, the peaks at 77.0 and 81.5, 90.2, 101.1 ppm are caused by Q$^1$, Q$^2$, Q$^3$ for the silicate nucleation, respectively [25].

3.3. Mechanisms of the reaction

According to the above results, the higher sorption amount of Se can be achieved using MgO in the presence of Al species due to the formation of LDH structure. Mg-based LDHs can be regarded as the structure of the Mg(OH)$_2$ sheet where Al$^{3+}$ partially substituted for Mg$^{2+}$, and the regeneration of LDH structure should be mainly controlled by the hydration of MgO [16]. The MgO can react as Eq. (1) in the aqueous solution, with a Ksp of 1 × 10$^{-2}$. At alkaline conditions, Al$^{3+}$ can also react as shown in Eq. (2) [14]. The $^{27}$Al NMR result has also indicated that all of Al in solid residue after the reaction has six-coordination numbers. Thus, the possible reactions contributing to the formation of MgAl-LDH can be summarized in Fig. 7. The dissolved Al(OH)$_3$ can react with solid Mg(OH)$_2$ and dissolved Mg$^{2+}$ to form LDH structure, and the mechanism can be concluded as dissociation-deposition-diffusion as reported previously [14]. In addition, the reaction of SiO$_2$ with MgO (or Mg(OH)$_2$) can be in analogy with Al$^{3+}$, and the $^{28}$Si NMR result implies that M-S-H has been generated after the reaction. This newly formed phase can cover the surface of MgO, blocking the
hydration process [16]. Due to the large specific surface area of MgO used in this study, the hydration process was not seriously affected as other reports showed [16]. However, these silicate species (Q\textsuperscript{0}, Q\textsuperscript{1}, and Q\textsuperscript{2}) are still covered on the surface of Mg(OH)\textsubscript{2} particles. However, both M-S-H and silicates have fewer affinities with SeO\textsubscript{4}\textsuperscript{2–} compared to MgO (or Mg(OH)\textsubscript{2}), thereby reducing the sorption sites for SeO\textsubscript{4}\textsuperscript{2–}. Thus, the sorption amount of Se decreased in the presence of SiO\textsubscript{3}\textsuperscript{2–}. As for SO\textsubscript{4}\textsuperscript{2–}, it has similar properties with SeO\textsubscript{4}\textsuperscript{2–}, and both of them have low affinities with MgO (or Mg(OH)\textsubscript{2}) in the solution. Only approximately 0.05 mmol g\textsuperscript{–1} of SO\textsubscript{4}\textsuperscript{2–} was sorbed onto Mg(OH)\textsubscript{2}. Thus, the Se sorption amount in the presence of SO\textsubscript{4}\textsuperscript{2–} was maintained with that without additive. Based on the above discussion, MgO has low affinity with SeO\textsubscript{4}\textsuperscript{2–}. In order to enhance the sorption ability, a novel stabilizer (MgO + Al species) can be proposed. In this study, aluminum nitrate was selected as the Al source. Other Al sources such as aluminum oxide, aluminum chloride can also be selected.

\[
\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \quad (1)
\]

\[
2\text{Al(OH)}_3 \rightleftharpoons 2\text{Al(OH)}_2^+ + 2\text{OH}^- \rightleftharpoons 2\text{Al(OH)}_2^{2+} + 4\text{OH}^- \rightleftharpoons 2\text{Al}^{3+} + 6\text{OH}^- \quad (2)
\]

4. Conclusions

MgO was adopted to sorb SeO\textsubscript{4}\textsuperscript{2–}, and the effects of coexisting species on the sorption process were explored in the present study. In the absence of additive, the sorption amount of

Fig. 4. SEM images of solid residues.
Fig. 5. TG results of (a) E1, (b) E2, (c) E3, (d) E4 and (e) E5.

Fig. 6. (a) $^{27}$Al NMR spectrum of solid residue after reaction with Al species and (b) $^{29}$Si NMR spectrum of solid residue after reaction with Si additive.

Fig. 7. Reaction process of MgO in the presence of additives.
0.063 mmol g\(^{-1}\) Se can be achieved by using MgO. The additive of Al\(^{3+}\) has a positive effect on the sorption performance, and 0.33 mmol g\(^{-1}\) Se can be obtained. This was mainly because Mg-Al-LDH was formed during the reaction. However, the position of the 003 peak indicates that the interlayer anions should be mainly CO\(_3^{2-}\). Thus, surface sorption onto LDH could be the main SeO\(_4^{2-}\) immobilization mechanism. In the presence of SiO\(_2\), the magnesium silicate hydrate (M-S-H) can be formed on the surface of Mg(OH)\(_2\), blocking the interaction between Mg(OH)\(_2\), and SeO\(_4^{2-}\). Therefore, the sorption amount of Se decreased in the case of SiO\(_2\) additive. As for SO\(_4^{2-}\), it has less effect on the SeO\(_4^{2-}\) sorption onto MgO (or Mg(OH)\(_2\)), mainly because the interaction between SO\(_4^{2-}\) and Mg(OH)\(_2\) are similar with the case of SeO\(_4^{2-}\). In this study, a novel stabilizer (MgO + Al species) can be proposed. Besides the Al species used in this work, Other Al sources such as aluminum oxide, aluminum chloride can also be selected.

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### References


