Selective Sorption of Co$^{2+}$ over Ni$^{2+}$ Using Biogenic Manganese Oxides

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Preferential sorption of Co$^{2+}$ ions over Ni$^{2+}$ ions was achieved using biogenic Mn oxides produced by the Mn-oxidizing fungus Paraconiothyrium sp. WL-2 strain with a maximum selectivity coefficient ($K_{11}$) of 18. The selective sorption was based on different sorption mechanism for Co$^{2+}$ and Ni$^{2+}$ and unique properties of biogenic Mn oxides. The octahedral Co$^{2+}$ ions occupy vacancies of central metal sites and edge sites in the octahedral Mn oxide unit structures of biogenic Mn oxides, where they are immobilized by oxidation to CoOOH by Mn(III). In contrast, Ni$^{2+}$ ions are sorbed primarily on layer edges at circumneutral pHs without oxidation. Selective sorption of Co$^{2+}$ over Ni$^{2+}$ on the biogenic Mn oxides results from more vacant sites, higher Mn(III) contents, and larger specific surface areas compared to synthetic Mn oxides.

Sorption experiments using both materials were conducted as follows: 0.020 g of freeze-dried biogenic Mn oxide or 0.015 g of freeze-dried synthetic Mn oxide powder was suspended in 0.150 dm$^3$ of 0.01–1.7 mmol-dm$^{-3}$ Co(NO$_3$)$_2$·6H$_2$O or 0.03–2.11 mmol-dm$^{-3}$ NiCl$_2$·6H$_2$O in 0.500 dm$^3$ in Erlenmeyer flasks capped with rubber stoppers. Under these conditions the solid Mn concentration corresponds to 1 mmol-dm$^{-3}$ Mn for both the biogenic and synthetic Mn oxides. KNO$_3$ was added in each sample to provide a constant ionic strength of 100 mmol-dm$^{-3}$. The initial pH of the Co$^{2+}$ and Ni$^{2+}$ solutions, buffered using PIPES (piperazine-N, N’-bis(2-ethane sulfonic acid)), was 6.5. Each experiment was conducted in duplicate. The flasks were installed on a reciprocating shaker at 25°C and 100 rpm for 300 h. At intervals, the supernatants were sampled and filtered by a 0.2-μm membrane filter for determination of the Co$^{2+}$, Ni$^{2+}$ and Mn$^{2+}$ concentrations in the solution using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500c). The detection limits by ICP-MS are 0.06 μg-dm$^{-3}$ for Mn, and 0.01 μg-dm$^{-3}$ for Co and Ni.

Sorption experiments of Co$^{2+}$ and Ni$^{2+}$ ions in a binary system using biogenic and synthetic Mn oxides were also conducted. For these experiments the initial concentration of Co$^{2+}$ ions was fixed at 0.3 mmol-dm$^{-3}$ while the initial concentrations of Ni$^{2+}$ were varied from 0.1 to 1.0 mmol-dm$^{-3}$. The ratio of sorbent mass to solution volume was the same as in a single-solute experiment. Each experiment was conducted in duplicate. The solid residues were filtered using a 0.45-μm membrane filter, and then lyophilized overnight.

To investigate the chemical states of Mn, Co and Ni in the precipitates, XPS-spectra for the biogenic and synthetic Mn oxides after Co-Ni sorption were collected using a PHI 5800 ESCA. After evacuating to less than 5.0 × 10$^{-7}$ Pa for more
than 30 min, the sample was transferred into the analysis chamber at less than 2.0 × 10⁻⁵ Pa, and then irradiated with monochromatic Al Kα X-rays using a neutralizer. The pass energy was 93.90 eV, the step energy was 0.800 eV and the step was 20 ms. The binding energy, Eₐ, was calibrated with Eₐ [C 1s] = 284.8 eV. Data were analyzed with CASAXPS software (Ver. 2.1.1). Backgrounds were drawn using the Shirley method.¹⁶)

**3. Results and Discussion**

Molar ratios of Mn(II), Mn(III) and Mn(IV), and average oxidation states (AOS) of biogenic and synthetic Mn oxides are summarized in Table 1. The proportions of constituents in the two solids are quite different. The Mn(II) species are Mn(III) in biogenic Mn oxides ten times greater in biogenic Mn oxides than synthetic Mn oxides. The dominant Mn species are Mn(III) in biogenic Mn oxides. The proportions of constituents in both materials (Figs. 1(a), 2(a), 3(a), 4(a)). It took less than 50 h to attain equilibrium with the biogenic Mn oxide even in case of Co²⁺ ions with time (b) (n = 2). Symbols: ×: initial [Co²⁺] = 0 mmol·dm⁻³, ●: 0.0539 mmol·dm⁻³, ○: 0.197 mmol·dm⁻³, ▲: 0.314 mmol·dm⁻³, △: 0.670 mmol·dm⁻³, ■: 0.957 mmol·dm⁻³, □: 1.74 mmol·dm⁻³. The error bar indicates 1σ.

![Figure 1](image)

Figure 1 shows the time courses of Co²⁺ and Mn²⁺ ions during sorption of Co²⁺ ions on biogenic Mn oxides at 25°C. The Co²⁺ ions were well sorbed on the biogenic Mn oxides in Fig. 1(a). About 200 h were required to achieve equilibrium when the initial Co²⁺ concentration was 1.74 mmol·dm⁻³. In experiments with higher initial concentrations of Co²⁺, data scatter was probably caused by the small amount of sorbent (0.020 g) relative to solute. Initial release of Mn²⁺ was caused by ion-exchange with Co²⁺ ions, indicating that the selectivity of ion-exchange is in the order of Co²⁺ > Mn²⁺, followed by gradual re-sorption of Mn²⁺ in Fig. 1(b). The maximum release of Mn was from 0.10 to 0.12 mmol·dm⁻³ in the presence of 0.197–1.74 mmol·dm⁻³ Co²⁺ ions. The mass of biogenic Mn oxides used here includes Mn(II) corresponding to around 0.12 mmol·dm⁻³ of Cu-exchangeable Mn(II), based on around 5 mass% Mn(II) contents as previously reported.⁷ The re-sorption rate Mn²⁺ was faster with lower initial Co²⁺ concentrations. In the absence of Co²⁺ Mn release was still observed (about 0.04 mmol·dm⁻³), but the re-sorption was much slower than when Co²⁺ was present. It has been reported that Co²⁺ ions are oxidized by biogenic and synthetic Mn oxides to form CoOOH and that Mn(III) species are more effective oxidants of Co²⁺ than Mn(IV) species in the biogenic Mn oxides.⁷ These observations indicate that released Mn(II) ions are immobilized by co-precipitation with CoOOH.⁷

In contrast, Co²⁺ ions were less sorbed on the synthetic Mn oxides and no release of Mn ions was observed (Fig. 2). The results are consistent with the lack of Cu-exchangeable Mn(II) and Mn(III) in the synthetic Mn oxides.⁷ Nickel ions were much less sorbed than Co²⁺ ions on the biogenic and synthetic Mn oxides as shown in Figs. 3(a) and 4(a). These results are consistent with previous reports by Tani et al.⁸ Very little sorbed Ni²⁺ was detectable by ICP-MS with the synthetic Mn oxides (Fig. 4(a)). The required times to reach equilibrium were shorter than in case of Co²⁺ in both materials (Figs. 1(a), 2(a), 3(a), 4(a)). It took less than 50 h to attain equilibrium with the biogenic Mn oxide even when the initial Ni²⁺ concentration was 2.3 mmol·dm⁻³ (Fig. 3(a)). Fewer Mn²⁺ ions were released (Fig. 3(b) and Fig. 1(b)) and the response was slower, depending on the loading of Ni²⁺ ions (Fig. 3(b)). The selectivity for ion-exchange is in the order of Co²⁺ > Mn²⁺ > Ni²⁺ (Figs. 1(b), 3(b)).

Sorption data for Co²⁺ and Ni²⁺ on the biogenic and synthetic Mn oxides system were well described by the linearized Freundlich isotherm as shown in Fig. 5.

\[
\log Q = \log F + n \log C_e
\]

(1)

in which \( Q \) is the sorbed quantity of the solute per unit mass of sorbent as Mn-kg (mmol kg⁻¹·Mn), \( C_e \) is the equilibrium concentration of solute (mmol dm⁻³), and \( F \) (dm³ kg⁻¹) and \( n \) (dimensionless) are constants. In preliminary experiments, it was confirmed that cellular tissues were not responsible for sorption of Co²⁺ and Ni²⁺ on the biogenic Mn oxides. The \( Q \) values were normalized for mass of Mn(III, IV) excluding Mn(II) in Mn oxides in Fig. 5. It can be seen that \( Q \) values for Co²⁺ and Ni²⁺ sorption to biogenic Mn oxide were in an order of magnitude greater than those to the synthetic Mn oxide. The difference is primarily caused by the large

| Table 1 Molar ratios of Mn(II), Mn(III) and Mn(IV) and average oxidation states (AOS) of Mn in the biogenic and synthetic Mn oxides. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| biogenic        | synthetic       |
| Mn(II)          | Mn(III)         | Mn(IV)          | AOS             |
| 0.11            | 0.694           | 0.196           | 3.09            |
| 0.014           | 0.296           | 0.690           | 3.68            |

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Shirley method.¹⁶)
specific surface area of the biogenic oxides. In addition, the $Q$ values were in an order of magnitude greater for $\text{Co}^{2+}$ than for $\text{Ni}^{2+}$ in both Mn oxides. This indicates there is specific sorption of $\text{Co}^{2+}$ rather than physical sorption.

The sorption data of $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ ions on the biogenic and synthetic Mn oxides in Figs. 1, 2, 3 and 4 were also fit with the linearized Langmuir equation, as shown in Fig. 6.

$$C_e Q^{-1} = 1/(Q_{\text{max}} L) + C_e/Q_{\text{max}}, \quad (2)$$

in which $Q_{\text{max}}$ is sorption capacity of the solid and $L$ is the Langmuir constant corresponding to the affinity of com-
pounds to the solid. As can be seen from the correlation coefficients, larger scatter was observed for the biogenic Mn oxides compared to the synthetic ones, and sorption of Ni\(^{2+}\) was better described by the linearized Langmuir equation than was sorption of Co\(^{2+}\). These results suggest that there is poorer uniformity in sorption sites on biogenic Mn oxides than on synthetic ones, and that Ni\(^{2+}\) ions are more preferably sorbed on the limited and uniform sites than are Co\(^{2+}\) ions.

![Fig. 5 Sorption isotherms of Co\(^{2+}\) and Ni\(^{2+}\) on biogenic and synthetic Mn oxides fitted with the linearized Freundlich model. Symbols: • & •: Co\(^{2+}\); ▲ & △: Ni\(^{2+}\). Solid and open symbols indicate biogenic and synthetic Mn oxides.](image)

![Fig. 6 Sorption isotherm of Co\(^{2+}\) and Ni\(^{2+}\) on biogenic and synthetic Mn oxides fitted with the linearized Langmuir model. Symbols are the same as in Fig. 5.](image)

Time courses of Co\(^{2+}\), Ni\(^{2+}\), and Mn\(^{2+}\) concentrations during sorption of Co\(^{2+}\) and Ni\(^{2+}\) on the biogenic Mn oxide. Symbols: ×: initial [Co\(^{2+}\)] and [Ni\(^{2+}\)] are 0.31 mmol dm\(^{-3}\) and 0 mmol dm\(^{-3}\); •: initial [Co\(^{2+}\)] and [Ni\(^{2+}\)] are 0.31 mmol dm\(^{-3}\) and 0.10 mmol dm\(^{-3}\); ▲: initial [Co\(^{2+}\)] and [Ni\(^{2+}\)] are 0.35 mmol dm\(^{-3}\) and 0.35 mmol dm\(^{-3}\); △: initial [Co\(^{2+}\)] and [Ni\(^{2+}\)] are 0.34 mmol dm\(^{-3}\) and 1.00 mmol dm\(^{-3}\). The error bar indicates 1σ.

Time courses of Co\(^{2+}\), Ni\(^{2+}\), and Mn\(^{2+}\) for competitive sorption in the presence of 0.3 mmol dm\(^{-3}\) Co\(^{2+}\) and 0.1–1.0 mmol dm\(^{-3}\) Ni\(^{2+}\) onto the biogenic Mn oxides are shown in Fig. 7. The Mn\(^{2+}\) ions (0.10–0.12 mmol dm\(^{-3}\)) were released within 24 h primarily due to ion-exchange with Co\(^{2+}\) ions in biogenic Mn oxides (Fig. 8(a), (c)), in a manner similar to the data shown in Fig. 1. After that Mn\(^{2+}\) ions were immobilized by co-precipitation with CoOOH. While nickel ions were less sorbed, they inhibited sorption of Co\(^{2+}\) ions (Fig. 7(a), (b)). This trend was observed also in synthetic Mn oxides in Fig. 8(a), (b).

Significantly greater selective sorption of Co\(^{2+}\) over Ni\(^{2+}\) was observed on the biogenic Mn oxides. The selectivity coefficient (\(α_t\)) of component 1 in the presence of component 2 is expressed in the following equations, where \(X\) and \(C\) indicate the mole fractions in sorbed and aqueous phases, respectively.

\[
α_t = (X_1/C_1)/(X_2/C_2) \tag{3}
\]

The selectivity coefficients of Co\(^{2+}\) (\(α_{Co}\)) and Ni\(^{2+}\) (\(α_{Ni}\))
Based on the results in Figs. 7 and 8 are summarized in Table 2. It can be seen that biogenic Mn oxides showed greater \( /C11 \) values than synthetic ones, and that the greatest \( /C11 \) value was obtained with the greatest co-existing Ni \( 2^+ \) concentration. Release of Mn \( 2^+ \) ions was almost independent of coexisting Ni \( 2^+ \), and primarily dependent on loaded mass of Co \( 2^+ \) ions (Fig. 1(b), Fig. 7(c)). This is reasonable considering that selectivity of ion exchange with Mn \( 2^+ \) in the biogenic Mn oxide is greater for Co \( 2^+ \) over Ni \( 2^+ \). However, as shown in Fig. 8, the selective sorption as above was not clearly seen with the synthetic Mn oxides. The high selectivity is one of the unique characteristics of the biogenic Mn oxides.

XP-spectra of the Mn 3s, Co 2p, and Ni 2p regions for the biogenic Mn oxide and the synthetic Mn oxide after Co-Ni sorption in a binary system were collected. Based on the analysis of Mn 3s spectra for both Mn oxides, the splitting of Mn 3s and the satellite was 4.7 eV for both (Fig. 9), suggesting that the surfaces of the Mn oxides consist of mostly Mn(IV). Figure 10 shows there are two distinct peaks at \( E_B[Co 2p_3/2] = 780.8 \) eV and \( E_B[Co 2p_1/2] = 795.9 \) eV without satellite peaks of Co 2p, that is, Co(III) is the dominant species on both surfaces. Redox reactions between Co \( 2^+ \) and Mn(III, IV) on the solid surfaces generated Mn(II) and/or Mn(III). However, in the Ni 2p spectra for

![Time courses of Co and Ni concentrations during sorption of Co and Ni on the synthetic Mn oxide. Symbols: ×: initial \([Co^{2+}]/mM = 0.31\) and \([Ni^{2+}]/mM = 0.1\); ○: initial \([Co^{2+}]/mM = 0.35\) and \([Ni^{2+}]/mM = 0.35\); □: initial \([Co^{2+}]/mM = 0.34\) and \([Ni^{2+}]/mM = 1.0\). The error bar indicates 1σ.](image1)

![XP-spectra of the Mn 3s region for (a) the biogenic Mn oxide and (b) the synthetic Mn oxide after Co-Ni sorption.](image2)

![XP-spectra of the Co 2p-Mn 2s region for (a) the biogenic Mn oxide and (b) the synthetic Mn oxide after Co-Ni sorption.](image3)

**Table 2** Selectivity coefficients of Co \( 2^+ \) and Ni \( 2^+ \) ions in the binary system.

<table>
<thead>
<tr>
<th></th>
<th>Biogenic</th>
<th>Synthetic</th>
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<tbody>
<tr>
<td>initial ([Co^{2+}]/mM)</td>
<td>0.31</td>
<td>0.35</td>
</tr>
<tr>
<td>initial ([Ni^{2+}]/mM)</td>
<td>0.1</td>
<td>0.35</td>
</tr>
<tr>
<td>(\alpha_{Co})</td>
<td>7.92</td>
<td>7.47</td>
</tr>
<tr>
<td>(\alpha_{Ni})</td>
<td>0.126</td>
<td>0.134</td>
</tr>
</tbody>
</table>

Based on the results in Figs. 7 and 8 are summarized in Table 2. It can be seen that biogenic Mn oxides showed greater \(\alpha_{Co}\) values than synthetic ones, and that the greatest \(\alpha_{Co}\) value was obtained with the greatest co-existing Ni \( 2^+ \) concentration.

Release of Mn \( 2^+ \) ions was almost independent of coexisting Ni \( 2^+ \), and primarily dependent on loaded mass of Co \( 2^+ \) ions (Fig. 1(b), Fig. 7(c)). This is reasonable considering that selectivity of ion exchange with Mn \( 2^+ \) in the biogenic Mn oxide is greater for Co \( 2^+ \) over Ni \( 2^+ \). However, as shown in Fig. 8, the selective sorption as above was not clearly seen with the synthetic Mn oxides. The high selectivity is one of the unique characteristics of the biogenic Mn oxides.

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both materials there are satellite peaks around 861.5 eV and 879.5 eV as well as $E_{\text{g}}[\text{Ni } 2p_{3/2}] = 856.0$ eV and $E_{\text{g}}[\text{Ni } 2p_{1/2}] = 873.8$ eV (Fig. 11), indicating Ni(II) is the dominant species. Nickel ions are simply sorbed on Mn oxides without any redox reactions.

Manceau et al.,8 using analysis of XANES spectra, reported Ni$^{2+}$ ions have a strong preference for isomorphic substitution for Mn in the manganiferous layer at circumneutral pH. Released Mn$^{2+}$ ions are more competitive with Ni$^{2+}$ ions to occupy the same sites on the biogenic Mn oxides, compared with Co$^{2+}$ ions (Figs. 1(b), 3(b)).

The selective sorption of Co$^{2+}$ over Ni$^{2+}$ is based on the different sorption mechanisms of Co$^{2+}$ and Ni$^{2+}$. Ion exchange with labile Mn$^{2+}$ ions were observed for both Co$^{2+}$ and Ni$^{2+}$ (Fig. 12(1), (2)), with the preference in the order of Co$^{2+} >$ Mn$^{2+} >$ Ni$^{2+}$. The Co$^{2+}$ ions are taken up in vacant sites (Fig. 12(3)) and edge sites (Fig. 12(4), (5)) of the biogenic Mn oxides. Nickel ions do not compete with Co$^{2+}$ for edge sites. In addition, the Co$^{2+}$ ions taken up would be preferentially oxidized by the nearest Mn(III) and/or Mn(IV) and immobilized as Co(III) compounds such as CoOOH with the release of Mn$^{2+}$ ions. Therefore, in the biogenic Mn oxides, competitive sorption of Mn$^{2+}$ and Ni$^{2+}$ ions occurred at the vacant sites. It has been speculated based on XANES and other structural analysis techniques21) that there are many more vacant sites and edge sites in biogenic Mn oxides than in synthetic Mn oxides. In addition, biogenic Mn oxides are usually poorly crystalline with non-uniform morphologies but highly uniform pore sizes of around 4 nm.7) The unique properties of biogenic Mn oxides suggest a potential to separate Co from Ni in leachates of natural resources.

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