Synthesis of Metal−Organic Framework ZnOₓ-MOF@MnO₂ Composites for Selective Removal of Strontium Ions from Aqueous Solutions

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ABSTRACT: A Zn(II)-based metal−organic framework (MOF) compound and MnO₂ were used to prepare ZnOₓ-MOF@MnO₂ composites for selective Sr²⁺ removal in aqueous solutions. The ZnOₓ-MOF@MnO₂ composites were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis, and Brunauer−Emmett−Teller surface area analysis. The functional groups, morphologies, thermal stabilities, and specific surface areas of the composites were suitable for Sr²⁺ adsorption. A maximum adsorption capacity of 147.094 mg g⁻¹ was observed in batch adsorption experiments, and the sorption isotherms were fit well by the Freundlich model of multilayer adsorption. Adsorption reached equilibrium rapidly in kinetic experiments and followed the pseudo-second-order kinetic model. The adsorption capacity of the ZnOₓ-MOF@MnO₂ composite with the highest MnO₂ content was high over a wide pH range, and the composite was highly selective toward Sr²⁺ in solutions containing coexisting competing ions. Also, it has a good reusability for removing Sr²⁺.

INTRODUCTION

The strontium isotopes ⁹⁰Sr and ⁹⁰⁰Sr are fission products found in wastes from nuclear power plants and nuclear fuel reprocessing.¹ ⁹⁰Sr is a particularly hazardous radioactive contaminant because it emits high-energy 0.5460 MeV beta (β) particles and has a long half-life of 29 years.² Because it is chemically similar to calcium, ⁹⁰Sr in the human body can cause osteosarcoma and leukemia.³ Therefore, the removal of Sr²⁺ from aqueous media is essential to prevent harm to both the environment and human health. Numerous methods are available for removing Sr²⁺ from aqueous solutions, including chemical precipitation, solvent extraction, and adsorption.⁴,⁵ Among these techniques, adsorption is simple and well-suited to wastewater treatment.

The removal of Sr²⁺ using manganese(IV) oxide (MnO₂) has been reported by several researchers.⁶−⁸ MnO₂ particles have a large Sr²⁺ sorption capacity, and they are selective for Sr²⁺ in the presence of competing ions such as Na⁺, K⁺, Ca²⁺, and Mg²⁺.⁹ In the present paper, the adsorption of Sr²⁺ onto MnO₂ is highlighted. However, MnO₂ nanoparticles have drawbacks, such as a tendency to agglomerate because of van der Waals forces and other interactions. The nanoparticles are also difficult to separate from treated wastewater after adsorption.¹⁰ Nanoparticulate MnO₂ must therefore be immobilized onto a support to enhance its Sr²⁺ adsorption efficiency and reusability.¹¹ Potentially suitable solid supports for immobilized MnO₂ nanoparticles include carbon nano-tubes,¹² mesoporous silica,¹³ graphene oxide,¹⁴ and metal−organic frameworks (MOFs).¹⁵ Among these candidates, MOFs are particularly attractive because of their high removal efficiency.¹⁶,¹⁷ In particular, MOFs have been used as adsorbents for removal of alkaline-earth-metal ions in several studies.¹⁷−¹⁹ MOFs are porous materials composed of metal ions and organic ligands linked through coordinate bonds.¹⁰ MOFs have several unique advantages. Depending on their metal constituents and organic ligands, MOFs can exhibit various morphologies. MOFs also feature large specific surface areas, and their pore sizes can be controlled.¹⁰ Highly porous MOFs with a carefully designed pore space have been shown to capture metal ions and various pollutants.¹⁰ The Zn(II)-based ZnOₓ-MOF has not been widely studied for Sr²⁺ adsorption. The advantages of the ZnOₓ-MOF include a facile synthesis from inexpensive starting materials.¹⁶,¹⁷ ZnOₓ-MOF has a three-dimensional (3D) crystalline structure with cavities for metal ions.¹⁴,¹⁸

The aim of the present study was to synthesize ZnOₓ-MOF/MnO₂ (ZnOₓ-MOF@MnO₂) composites for the adsorption of...
Sr$^{2+}$ in aqueous media. A ZnO$_x$-MOF was impregnated with MnO$_2$ particles via alkali precipitation. To improve the Sr$^{2+}$ adsorption capacity of the ZnO$_x$-MOF, we prepared ZnO$_x$-MOF@MnO$_2$ composites with different MnO$_2$ contents. The ZnO$_x$-MOF@MnO$_2$ composites were then characterized using several analytical techniques. Finally, Sr$^{2+}$ adsorption by the composites was tested under various conditions. Several isotherm and kinetic models were applied to the experimental data to analyze the Sr$^{2+}$ adsorption behavior of the ZnO$_x$-MOF@MnO$_2$ composites.

RESULTS AND DISCUSSION

Characterization of ZnO$_x$-MOF@MnO$_2$ Composites.

The FT-IR spectra of the ZnO$_x$-MOF and the ZnO$_x$-MOF@MnO$_2$ composites are shown in Figure 1. The spectrum of the ZnO$_x$-MOF includes the various peaks reported by Kabir et al. Specifically, the ZnO$_x$-MOF spectrum shows a broad peak from 3350 to 3570 cm$^{-1}$, which is attributed to O–H groups participating in hydrogen bonding with cations. The broad peak from 1005 to 1120 cm$^{-1}$ is ascribed to O–H groups participating in hydrogen bonding with SO$_4^{2-}$ anions. C–O–C symmetric stretching vibrations are observed at 982, 1147, and 2988 cm$^{-1}$ in the spectrum of the ZnO$_x$-MOF. The peaks at 1055 and 1202 cm$^{-1}$ are attributed to a SO$_4^{2-}$ vibrational band. The peaks from 2800 to 2300 cm$^{-1}$ are attributed to C–H stretching vibrations in the ZnO$_x$-MOF. Some peaks disappeared after the addition of MnO$_2$, and the spectra of the ZnO$_x$-MOF@MnO$_2$ were nearly identical to each other irrespective of the MnO$_2$ concentration. The peak at 538 cm$^{-1}$ was attributed to Mn–O bonds in the MnO$_2$ structure. The O–H vibrations in the spectra of the ZnO$_x$-MOF@MnO$_2$ composites were the same as those observed from 3200 to 3600 cm$^{-1}$ in the ZnO$_x$-MOF spectrum. The vibrations of O–H groups interacting with adsorbed Mn$^{2+}$ were observed at 1166, 1172, and 1357 cm$^{-1}$, whereas hydrogen bonding was indicated by the band at 2081 cm$^{-1}$. In the spectra of both ZnO$_x$-MOF and ZnO$_x$-MOF@MnO$_2$ composites, sharp peaks ascribed to O–H vibrations were observed at 1727 cm$^{-1}$.

The powder X-ray diffraction (PXRD) patterns of the ZnO$_x$-MOF and the ZnO$_x$-MOF@MnO$_2$ composites are shown in Figure 2. In the ZnO$_x$-MOF, 3D hydrogen bonding appeared, indicating interaction between the dimethylammonium cations and sulfate anions. As indicated by the peaks in the pattern of ZnO$_x$-MOF, the ZnO$_x$-MOF composite was confirmed to be highly crystalline. The PXRD patterns of composites ZnO$_x$-MOF@MnO$_2$ (1), (2), and (3) showed broad, low-intensity peaks; however, a peak attributed to MnO$_2$ (rhombohedral) was observed at $22 \leq 20 \leq 25^\circ$. Obviously, the strong XRD intensity in ZnO$_x$-MOF significantly lowered the XRD peak through impregnated MnO$_2$ particles. Therefore, it is considered that some frameworks have the potential to be destroyed during the MnO$_2$ precipitation process.

The morphologies of the ZnO$_x$-MOF and the ZnO$_x$-MOF@MnO$_2$ composites were investigated via SEM (Figure 3). The micrographs of the ZnO$_x$-MOF show cubic structures and a rough surface. The specimen had a large surface area and pore size, and its morphology was similar to that of a reference sample of ZnO$_x$-MOF. The ZnO$_x$-MOF@MnO$_2$ composites exhibited the same spherical morphology irrespective of their MnO$_2$ content. The magnified image of the ZnO$_x$-MOF@MnO$_2$ composites in Figure 2 reveals nanowire-like structures that joined to form spherical shapes around the ZnO$_x$-MOF composite particles.

The contents of MnO$_2$ in the ZnO$_x$-MOF@MnO$_2$ (3) composites were confirmed by SEM-EDS (Figure 4). EDS analysis analyzes the content according to the sensitivity of each element. Elements such as O and N have low sensitivity, which reduces the accuracy. However, Zn and Mn have high sensitivity and reliable results. Therefore, ZnO$_x$-MOF has Zn and S contents of 5.10 and 5.08 at. %, respectively, and in addition, it was confirmed that the ZnO$_x$-MOF was well synthesized with high contents of C, N, and O. This may support the results of the FT-IR (Figure 1). In addition, ZnO$_x$-MOF@MnO$_2$ (3) was found to have 2.55 at. % K content using K$_2$SO$_4$ and the MnO$_2$ content of ZnO$_x$-MOF@MnO$_2$ (3) was about 28.4%. Accordingly, ZnO$_x$-MOF@MnO$_2$ (1), ZnO$_x$-MOF@MnO$_2$ (2), and ZnO$_x$-MOF@MnO$_2$ (3), which were synthesized from MnSO$_4$ and K$_2$SO$_4$ by ratio, were approximately 5.68, 11.36, and 28.4% in ZnO$_x$-MOF@MnO$_2$, respectively.

The thermal stabilities of the ZnO$_x$-MOF and the ZnO$_x$-MOF@MnO$_2$ composites were compared on the basis of their mass losses during thermal decomposition (Figure 5). The
The ZnO$_x$-MOF composite was stable to 210 °C, and its mass did not change. However, it lost mass rapidly at higher temperatures. The ZnO$_x$-MOF@MnO$_2$ components lost between 10 and 20% of their mass when heated to 1000 °C. Among the three composites, ZnO$_x$-MOF@MnO$_2$ (3), which had the highest MnO$_2$ content, was the most thermally stable.

The surface areas, pore sizes, and pore volumes of the samples were determined via Brunauer–Emmett–Teller (BET) analysis. The N$_2$ adsorption–desorption isotherms are shown in Figure 6, and Table 1 summarizes the physical properties of the ZnO$_x$-MOF and the ZnO$_x$-MOF@MnO$_2$ composites. The MOF structure of the ZnO$_x$-MOF exhibited a small surface area of 64.11 m$^2$ g$^{-1}$, which was not sufficient for Sr$^{2+}$ adsorption. The ZnO$_x$-MOF@MnO$_2$ composite, in which MnO$_2$ was combined with the ZnO$_x$-MOF, exhibited larger surface areas than the ZnO$_x$-MOF. The surface area of each of the ZnO$_x$-MOF@MnO$_2$ composites exceeded 100 m$^2$ g$^{-1}$, which indicates that the adsorbents had suitable physical properties. The pore sizes and volumes of the ZnO$_x$-MOF@MnO$_2$ composite were also larger than those of the ZnO$_x$-MOF, indicating that the composites had more active sites for adsorption.

Figure 3. SEM images of the ZnO$_x$-MOF and the ZnO$_x$-MOF@MnO$_2$ composites.

Figure 4. Results of SEM-EDS of the ZnO$_x$-MOF and the ZnO$_x$-MOF@MnO$_2$ (3) composites.

Figure 5. TGA curves of the ZnO$_x$-MOF and the ZnO$_x$-MOF@MnO$_2$ composites.
The Sr\textsuperscript{2+} adsorption isotherms of the MnO\textsubscript{2}, ZnO\textsubscript{2}-MOF, ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} (1), ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} (2), and ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} (3) are shown in Figure 7. The experimental data were subjected to regression analysis after fitting with the Langmuir, Freundlich, and Temkin isotherm models. The parameters of each isotherm model are listed for MnO\textsubscript{2}, ZnO\textsubscript{2}-MOF, and each of the composites in Table 2. Although MnO\textsubscript{2} and ZnO\textsubscript{2}-MOF themselves exhibited good Sr\textsuperscript{2+} adsorption, the ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} composites exhibited higher adsorption capacities. On the basis of the Langmuir model, ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} (3) exhibited a maximum adsorption capacity of 147.094 mg g\textsuperscript{-1}. This result confirms that the number of Sr\textsuperscript{2+} adsorption sites depended on the MnO\textsubscript{2} concentration. Thus, increasing the MnO\textsubscript{2} concentration resulted in a higher adsorption capacity. The Langmuir model afforded the best fit for the ZnO\textsubscript{2}-MOF adsorption isotherm data (r\textsuperscript{2} = 0.961), indicating monolayer adsorption of Sr\textsuperscript{2+} onto the ZnO\textsubscript{2}-MOF composite. By contrast, the best fits of the ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} composite isotherm data were obtained with the Freundlich model (r\textsuperscript{2} > 0.98), suggesting multilayer adsorption. Moreover, Sr\textsuperscript{2+} adsorption on MnO\textsubscript{2} particles was also most suitable for Freundlich. The Temkin isotherm was well-suited for Sr\textsuperscript{2+} adsorption onto the ZnO\textsubscript{2}-MOF; however, the Temkin r\textsuperscript{2} values of MnO\textsubscript{2} and ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} composites were low. The ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} (3) composite exhibited an adsorption capacity (q\textsubscript{e}) for Sr greater than that of previously reported adsorbents (Table 3). Among the previously reported adsorbents, MOF/KNiFC, MOF/Fe\textsubscript{3}O\textsubscript{4}/KNiFC, and Nd-BTC MOF are MOF-based adsorbents.

The adsorption is greatly dependent on the cation content of solution and binding sites of the adsorbent.\textsuperscript{47,48} To investigate the affinity of the adsorbent for the Sr\textsuperscript{2+} adsorption, distribution coefficient (K\textsubscript{d}) was calculated by

\[ K_d = \frac{C_o - C_e}{C_o} \times \frac{V}{m} \]  

Herein, C\textsubscript{o} and C\textsubscript{e} are the initial and effluent concentrations (mg L\textsuperscript{-1}) of Sr\textsuperscript{2+} in the solution, respectively. V is solution volume (mL), and m represents the mass of the adsorbent (g).

Table 4 shows the distribution coefficients of the ZnO\textsubscript{2}-MOF and the ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} composites in experimental ranges. The experiments were conducted in 10–400 ppm Sr\textsuperscript{2+}.

MnO\textsubscript{2} composites were also suitable for Sr\textsuperscript{2+} adsorption and were slightly larger than those of the ZnO\textsubscript{2}-MOF.

**Equilibrium Adsorption Isotherms.** The experimental adsorption isotherms were fitted using the Langmuir,\textsuperscript{35} Freundlich,\textsuperscript{36} and Temkin\textsuperscript{37} equilibrium isotherm models. The equations for the Langmuir, Freundlich, and Temkin models are expressed in eqs 1–3, respectively

\[ q_e = \frac{q_m b C_e}{1 + b C_e} \]  

\[ q_e = K_f C_e^{1/n} \]  

\[ q_e = \frac{RT}{B} \ln K_T C_e \]  

where q\textsubscript{m} is the maximum adsorption capacity of the adsorbent (mg g\textsuperscript{-1}). In eq 1, b is the Langmuir adsorption constant related to the free energy of adsorption (L mg\textsuperscript{-1}). K\textsubscript{f} [(mg g\textsuperscript{-1})(L mg\textsuperscript{-1})\textsuperscript{1/n}] and n in the Freundlich model are constants. K\textsubscript{T} (L g\textsuperscript{-1}) and B (L mg\textsuperscript{-1}) in eq 3 are isotherm constants, and R (8.314 J mol\textsuperscript{-1} K\textsuperscript{-1}) is the universal gas constant.

The error was evaluated by analyzing the correlation coefficient (r\textsuperscript{2}) and chi-squared (\chi\textsuperscript{2}) values.\textsuperscript{38} The \chi\textsuperscript{2} values were calculated using eq 4

\[ \chi^2 = \sum \frac{(q_{e,calc} - q_{e,exp})^2}{q_{e,exp}} \]  

where q\textsubscript{e,calc} and q\textsubscript{e,exp} are the calculated and experimental q\textsubscript{e} values, respectively.

**Table 1. Physical Properties of the ZnO\textsubscript{2}-MOF and the ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} Composites**

| Composite                  | BET surface area (m\textsuperscript{2} g\textsuperscript{-1}) | Pore size (Å) | Pore volume (cm\textsuperscript{3} g\textsuperscript{-1}) |
|----------------------------|---------------------------------------------------------------|---------------|----------------------------------------------------------|
| ZnO\textsubscript{2}-MOF     | 64.11                                                        | 33.92         | 0.085                                                    |
| ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} (1) | 162.73                                                        | 38.39         | 0.427                                                    |
| ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} (2) | 137.78                                                        | 37.34         | 0.124                                                    |
| ZnO\textsubscript{2}-MOF@MnO\textsubscript{2} (3) | 122.18                                                        | 37.26         | 0.091                                                    |
It is shown that the $K_d$ value increased as the MnO$_2$ concentration increased. ZnO$_x$-MOF showed the highest $K_d$ value at 100 ppm, and ZnO$_x$-MOF@MnO$_2$ composites all showed the highest $K_d$ value at 10 ppm. This means that, in the case of ZnO$_x$-MOF@MnO$_2$, ZnO$_x$-MOF@MnO$_2$ can be efficiently adsorbed even at a low concentration of Sr$^{2+}$. Normally, the adsorption process is not efficient at low concentrations because it is hardly adsorbed at low concentrations even if the $q_e$ value is very high at high concentrations. However, it was confirmed that the ZnO$_x$-MOF@MnO$_2$ synthesized in this study has a high partition coefficient in a wide range from low concentration to high concentration and is effective in various ranges.

**Adsorption Kinetics.** The adsorption behaviors of the composites depend on the duration of contact with the solution. The data was fit using the Lagergren pseudo-first-order$^{49}$ and pseudo-second-order$^{50}$ models.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t 
\]

and

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} 
\]

where $q_t$ and $q_e$ are the Sr$^{2+}$ concentrations at time $t$ and at equilibrium, respectively (mg g$^{-1}$), $k_1$ is the pseudo-first-order constant (min$^{-1}$), and $k_2$ is the pseudo-second-order constant (g mg$^{-1}$ min$^{-1}$).

Nonlinear fits of the experimental concentration vs contact time data obtained with the pseudo-first-order and pseudo-second-order models are shown in Figure 8. Sr$^{2+}$ adsorption kinetics on the ZnO$_x$-MOF@MnO$_2$ (3) composite at initial Sr$^{2+}$ concentrations of 50, 100, and 200 ppm.

**Table 2. Langmuir, Freundlich, and Temkin Isotherm Model Parameters**

| model          | parameter | MnO$_2$ | ZnO$_x$-MOF | ZnO$_x$-MOF@MnO$_2$ (1) | ZnO$_x$-MOF@MnO$_2$ (2) | ZnO$_x$-MOF@MnO$_2$ (3) |
|----------------|-----------|---------|-------------|-------------------------|-------------------------|-------------------------|
| Langmuir       | $q_m$ (mg g$^{-1}$) | 95.512  | 101.985     | 112.820                 | 135.049                 | 147.094                 |
|                | $b$ (L mg$^{-1}$)   | 0.002   | 0.006       | 0.008                   | 0.028                   | 0.048                   |
|                | $r^2$        | 0.994   | 0.961       | 0.954                   | 0.915                   | 0.937                   |
|                | $\chi$       | 1.380   | 43.162      | 53.985                  | 176.608                 | 183.616                 |
| Freundlich     | $K_f$ [(mg g$^{-1}$)(L mg$^{-1}$)$^{1/2}$] | 0.635   | 1.582       | 2.007                   | 3.202                   | 3.358                   |
|                | $n$         | 1.382   | 2.393       | 5.615                   | 21.760                  | 28.256                  |
|                | $r^2$        | 0.996   | 0.917       | 0.981                   | 0.982                   | 0.992                   |
|                | $\chi$       | 0.868   | 92.514      | 22.836                  | 36.764                  | 22.378                  |
| Temkin         | $K_T$ (L g$^{-1}$) | 0.110   | 0.087       | 0.812                   | 12.328                  | 14.661                  |
|                | $B$ (L mg$^{-1}$) | 9.861   | 24.483      | 14.436                  | 21.723                  | 21.844                  |
|                | $r^2$        | 0.859   | 0.945       | 0.790                   | 0.843                   | 0.877                   |
|                | $\chi$       | 34.129  | 61.367      | 246.412                 | 325.058                 | 357.946                 |

**Table 3. Comparison of Maximum Adsorption Capacities Reported in Various Studies**

| adsorbent                 | maximum adsorption capacity ($q_m$) | ref |
|---------------------------|-------------------------------------|-----|
| ZnO$_x$-MOF@MnO$_2$ (3)   | 147.094 mg g$^{-1}$ (1.689 mmol g$^{-1}$) | this study |
| MOF/KNiFe                | 110 mg g$^{-1}$                     | 39  |
| MOF/Fe$_3$O$_4$/KNiFe    | 90 mg g$^{-1}$                      | 39  |
| Nd-BTC MOF               | 58 mg g$^{-1}$                      | 40  |
| MnO$_2$-alginate beads   | 102.0 mg g$^{-1}$                   | 7   |
| bacterial cellulose membrane (BCM) | 44.86 mg g$^{-1}$                  | 41  |
| hydroxyapatite (HAP)     | 27 μmol g$^{-1}$                    | 42  |
| CTS-g-AMPS-PANI           | 88.89 mg g$^{-1}$                  | 43  |
| TNTs@DCH18C6             | 48.97 mg g$^{-1}$                   | 44  |
| alginate microspheres    | 110 mg g$^{-1}$                     | 45  |
| Fe$_3$O$_4$@titania fibers | 37.1 mg g$^{-1}$                  | 46  |

**Table 4. Distribution Coefficient ($K_d$) Values of the ZnO$_x$-MOF and the ZnO$_x$-MOF@MnO$_2$ Composites**

| parameter | concentration | ZnO$_x$-MOF | ZnO$_x$-MOF@MnO$_2$ (1) | ZnO$_x$-MOF@MnO$_2$ (2) | ZnO$_x$-MOF@MnO$_2$ (3) |
|-----------|---------------|-------------|-------------------------|-------------------------|-------------------------|
| $K_d$ (mL g$^{-1}$) | 10 ppm        | 206.89      | 9724.12                 | 136630.8                | 205006.6                |
|           | 20 ppm        | 292.99      | 3473.08                 | 173978.4                | 182673.5                |
|           | 50 ppm        | 428.37      | 936.95                  | 3911.89                 | 6344.85                 |
|           | 100 ppm       | 697.06      | 791.09                  | 1742.48                 | 3300.43                 |
|           | 200 ppm       | 472.26      | 472.76                  | 792.50                  | 1050.19                 |
|           | 300 ppm       | 345.58      | 419.58                  | 619.46                  | 786.61                  |
|           | 400 ppm       | 266.99      | 322.96                  | 461.91                  | 593.67                  |

**Figure 8.** Nonlinear Sr$^{2+}$ adsorption kinetics on the ZnO$_x$-MOF@MnO$_2$ (3) composite at initial Sr$^{2+}$ concentrations of 50, 100, and 200 ppm.
proceeded rapidly, and 50% of the maximum adsorption capacity at each concentration was attained within 5 min. The higher the concentration of Sr\(^{2+}\), the faster the equilibrium is achieved. The calculated pseudo-first-order and pseudo-second-order parameters are shown in Table 5. The kinetic behaviors of the composites were best fit with the pseudo-second-order model. The time required to reach equilibrium decreased with increasing Sr\(^{2+}\) concentration, and the corresponding \(q_e\) values were higher. The results indicate that the adsorption contact time in the isotherm experiments was sufficient.

**pH Effect of Sr\(^{2+}\) Adsorption.** The pH of a solution strongly influences Sr\(^{2+}\) adsorption.\(^{51}\) The effect of pH on Sr\(^{2+}\) adsorption by ZnO\(_x\)-MOF@MnO\(_2\) (3) was investigated in the pH range of 1 to 11 (Figure 9). At low pH (pH 1), the adsorption capacity \(q_e\) was low; \(Q_e\) values were higher in the range of pH 5 to 11, as determined on the basis of the point-of-zero charge (pHpzc). pHpzc is the point at which the net total charge on the particle is zero. A pHpzc value of 6.4 was obtained from the plot of initial pH vs the difference between the initial and final pH levels (Figure 10). The ZnO\(_x\)-MOF@MnO\(_2\) (3) composite was positively charged above pH 6.4. Adsorption of Sr\(^{2+}\) onto the composite was inhibited in acidic conditions because of interference by H\(^+\) ions.\(^{52}\)

**Sr\(^{2+}\) Selectivity.** Figure 11 shows the impact of competing cations on the Sr\(^{2+}\) adsorption capacity of ZnO\(_x\)-MOF@MnO\(_2\) (3). The concentrations of Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) ranged from 50 to 400 ppm in a 200 ppm Sr\(^{2+}\) solution. In a pure 200 ppm Sr\(^{2+}\) solution, the \(q_e\) of ZnO\(_x\)-MOF@MnO\(_2\) (3) for Sr\(^{2+}\) was 108.51 mg g\(^{-1}\). However, the concentrations of coexisting cations affected the adsorption capacity of the composite. The divalent Ca\(^{2+}\) and Mg\(^{2+}\) cations, in particular, reduced Sr\(^{2+}\) adsorption. Ca\(^{2+}\) interfered most with Sr\(^{2+}\) adsorption because Ca\(^{2+}\) has an ionic radius very similar to Sr\(^{2+}\).\(^{7}\) However, seawater contains a higher concentration of Na\(^+\), which does not substantially affect the removal of Sr\(^{2+}\).

**Reusability.** The results of three consecutive adsorption–desorption experiments are shown in Figure 12. When 0.1 N HNO\(_3\) solution, a desorption solution, was used, a desorption rate of 88.28% was obtained from the adsorbent adsorbed with Sr\(^{2+}\) once. The adsorption and desorption of the desorbed adsorbents were conducted two and three times, respectively. The adsorption rates decreased by 6.86 and 14.91%, respectively, and the desorption rates decreased by 86.29 and 78.01%. However, Sr\(^{2+}\) was sufficiently desorbed with 0.1 N HNO\(_3\), and the ZnO\(_x\)-MOF@MnO\(_2\) (3) adsorbent was judged to be reusable. Additionally, it is confirmed that 0.5 N HNO\(_3\) or more was required to complete desorption of Sr\(^{2+}\) and that no leaching of the adsorbent metal was observed.

### Table 5. Pseudo-first-order and Pseudo-second-order Kinetic Model Parameters for Sr\(^{2+}\) Adsorption at Initial Concentrations of 50, 100, and 200 ppm Using ZnO\(_x\)-MOF@MnO\(_2\) (3)

| [Sr\(^{2+}\)] (ppm) | \(q_e\) (mg g\(^{-1}\)) | \(k_1\) (min\(^{-1}\)) | \(r^2\) | \(\chi^2\) | \(q_e\) (mg g\(^{-1}\)) | \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) | \(r^2\) | \(\chi^2\) |
|----------------|----------------|----------------|--------|--------|----------------|----------------|--------|--------|
| 50            | 47.055         | 0.337          | 0.975  | 0.0024 | 48.808         | 0.015         | 0.994  | 0.0006 |
| 100           | 71.201         | 0.193          | 0.942  | 0.0034 | 76.121         | 0.004         | 0.981  | 0.0011 |
| 200           | 88.816         | 0.183          | 0.922  | 0.0028 | 94.956         | 0.003         | 0.968  | 0.0007 |

Figure 9. Effect of pH on Sr\(^{2+}\) adsorption by the ZnO\(_x\)-MOF@MnO\(_2\) (3) composite.

Figure 10. Point-of-zero charge (pHpzc) of the ZnO\(_x\)-MOF@MnO\(_2\) (3) composite.

Figure 11. Effect of competing cations on Sr\(^{2+}\) adsorption by the ZnO\(_x\)-MOF@MnO\(_2\) (3) composite.
A Zn(II)-based ZnO-MOF was successfully combined with MnO2 particles to afford ZnO-MOF@MnO2 composites for Sr2+ adsorption in aqueous solutions. The adsorption isotherms of the composites confirmed that the adsorption capacity increased with increasing MnO2 content. The ZnO-MOF@MnO2 (3) composite exhibited a maximum Sr2+ adsorption capacity of 147.094 mg g\(^{-1}\) on the basis of the Langmuir isotherm model. Its goodness of fit was highest with the Freundlich model of multilayer adsorption. Evaluation of the effects of pH, contact time, and coexisting ions confirmed that adsorbent sites were available within a wide pH range (5–11). Adsorption equilibrium was reached rapidly, and the selectivities of the composites for Sr2+ were high. Therefore, the ZnO-MOF@MnO2 composites can be used for the selective removal of Sr2+ in actual radioactive liquid waste.

**Materials and Methods**

**Materials.** Zinc sulfate heptahydrate (ZnSO\(_4\)·7H\(_2\)O, 99%, MW 287.56 g mol\(^{-1}\)), potassium sulfate (K\(_2\)SO\(_4\), 99%, MW 174.24 g mol\(^{-1}\)), sodium chloride (NaCl, 99%, MW 58.44 g mol\(^{-1}\)), anhydrous magnesium sulfate (MgSO\(_4\), 99%, MW 120.37 g mol\(^{-1}\)), and ethyl alcohol (C\(_2\)H\(_5\)OH, 94%) were purchased from Duksan Pure Chemicals (South Korea). N,N-Dimethylformamide (C\(_2\)H\(_5\)NO, 99.5%, MW 73.13 g mol\(^{-1}\)), oxalic acid dihydrate (H\(_2\)C\(_2\)O\(_4\)·2H\(_2\)O, 99.5–100.2%, MW 126.07 g mol\(^{-1}\)), 5 N sodium hydroxide standard solution, potassium permanganate (KMnO\(_4\), 99.3%, MW 158.03 g mol\(^{-1}\)), and manganese(II) sulfate pentahydrate (MnSO\(_4\)·5H\(_2\)O, 98%, MW 241.08 g mol\(^{-1}\)) were purchased from Daejeung Chemicals & Metals (South Korea). Calcium sulfate dihydrate (CaSO\(_4\)·2H\(_2\)O, 95%, MW 172.17 g mol\(^{-1}\)) was purchased from Oriental Chemical Industries (South Korea). Strontium nitrate (Sr(NO\(_3\))\(_2\), 99%, MW 211.63 g mol\(^{-1}\)) was purchased from Sigma-Aldrich (USA) and used to prepare simulated solutions. All solutions were prepared with deionized (D.I.) water.

**Synthesis of ZnO-MOF.** ZnO-MOF was synthesized using the method reported by Kabir et al.\(^{27}\) ZnSO\(_4\)·7H\(_2\)O (1 mmol) and H\(_2\)C\(_2\)O\(_4\)·2H\(_2\)O (2.50 mmol) were dissolved in 10 mL of N,N-dimethylformamide. The solution was stirred at 200 rpm for 30 min and then reacted in a Teflon-lined autoclave at 160 °C for 4 days. The obtained white product was washed several times with ethyl alcohol and dried for 24 h at 60 °C in a vacuum oven.

**Synthesis of ZnO-MOF@MnO2 Composites.** Dark-violet solutions were obtained by mixing KMnO4 and MnSO\(_4\)·5H\(_2\)O. The prepared ZnO-MOF powder (1 g) was added to each solution, and the solutions were stirred for 1 h. The solutions had initial pH values of 1–2, which were adjusted to between 8 and 9.5 using 5 N NaOH. The pH remained stable, and the color of the solutions changed from purple to brown. The brown ZnO-MOF@MnO2 powders were allowed to settle and then collected via filtration using 0.2 μm filters. The powders were washed several times with D.I. water to remove unreacted chemicals. The final products were dried in a 60 °C oven. The Sr2+ adsorption capacity was enhanced with increasing MnO2 content of the composites. ZnO-MOF@MnO2 (1), ZnO-MOF@MnO2 (2), and ZnO-MOF@MnO2 (3) were prepared using 0.02, 0.04, and 0.1 M KMnO4 along with 0.028, 0.056, and 0.14 M MnSO\(_4\)·5H\(_2\)O, respectively.

**Characterization of ZnO-MOF@MnO2 Composites.** FT-IR analysis was performed on a Frontier spectrometer (PerkinElmer, USA). The morphologies of the ZnO-MOF@MnO2 composites were analyzed using an SU8220 field-emission scanning electron microscope (FE-SEM, Hitachi, Japan). The thermal properties of the composites were characterized using a Q600 thermogravimetric analyzer (TA Instruments, Japan). The specific surface areas, pore volumes, and pore sizes of the ZnO-MOF@MnO2 composites were determined via BET analysis using Autosorb-iQ and Quadrasorb SI gas sorption analyzers (Quantachrome Instruments, USA).

**Adsorption Experiments.** All experiments were performed in duplicate in a batch system using 15 mL polyethylene conical tubes (SPL, South Korea). Simulant solutions with Sr2+ concentrations ranging from 10 to 400 mg L\(^{-1}\) were prepared for the adsorption experiments. Each of the synthesized composites (10 mg) was contacted with a Sr2+ solution (10 mL) at 250 rpm for 24 h at room temperature. For the kinetic experiments, the samples were suspended in 100, 200, and 300 mg L\(^{-1}\) Sr2+ solutions and contacted for various time intervals. Solutions containing 200 ppm Sr2+ were prepared over a range of pH values to evaluate the effect of pH on Sr2+ adsorption. The effect of coexisting ions (i.e., Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\)) on Sr2+ adsorption was evaluated using 200 ppm Sr2+ solutions. To investigate the reusability of adsorbent, three consecutive adsorption–desorption experiments were conducted using 0.1 N HNO3 as the desorption solution. The ZnO-MOF@MnO2 (3) adsorbent was used for the kinetics, pH, competitive adsorption, and reusability experiments. All of the samples were centrifuged at 3500 rpm for 10 min. The solids were removed via filtration using 0.20 μm nitrocellulose membrane filters (Whatman, USA). The Sr2+ concentrations in the filtered solutions were determined using an Optima 2100DV inductively coupled plasma optical emission spectrometer (PerkinElmer, USA).

The equilibrium adsorption capacity (\(q_e\) mg g\(^{-1}\)) was calculated using eq 8

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

where \(C_0\) and \(C_e\) are the initial and equilibrium Sr2+ concentrations, respectively, in mg L\(^{-1}\), \(V\) is the volume of
the Sr\(^{2+}\) simulant solution (mL), and \(W\) is the weight of the adsorbent (g).

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This research was supported by the Nuclear Energy Development Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Science and ICT (2018M2B2B1065631).

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