FULL PAPER

Removal of strontium from aqueous solutions using scallop shell powder

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It is important to efficiently remove radioactive substances contained in polluted waters before they are discharged from nuclear power plants. In particular, there is an urgent need for the development of technology that can adsorb radioactive Sr^{2+} , but there are currently no inexpensive Sr^{2+} adsorbents with low environmental burden. We found that scallop shell powder adsorbs Sr^{2+} in aqueous solutions at various initial concentrations. In this study, to obtain fundamental knowledge of the mechanism of Sr^{2+} removal using waste scallop shell, we analyzed the removability of Sr^{2+} . Scallop shell showed the same capacity to remove Sr^{2+} at a high initial concentration ($\geq 0.50 \text{ g/dm}^3$) as the reagent CaCO_3 , but a clear difference in removability appeared at a low initial concentration (0.010 g/dm^3), where scallop shell proved to be superior. In addition, scallop shell powder had slit-shaped pores and a specific surface area of $4.3 \text{ m}^2/\text{g}$. Measurement of the adsorption isotherm in the low concentration aqueous solution showed that Sr^{2+} removal occurred by chemisorption; the adsorbed Sr is present on the surface of the scallop shell powder particles.

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Key-words : Scallop shell, Adsorption, Strontium, Calcium carbonate, Radioactive elements, Water treatment

[Received August 17, 2018; Accepted November 20, 2018]

1. Introduction

Processing of the ~ 1 million tons of contaminated water currently accumulated around the Fukushima Daiichi Nuclear Power Plant has stagnated.¹⁾ The efficient removal of radioactive substances such as Cs^+ and Sr^{2+} are necessary for processing to proceed. Residual Sr^{2+} is particularly dangerous to the human body due to its propensity to replace Ca^{2+} in bones. Studies have attempted Sr^{2+} removal from aqueous solutions by Sr^{2+} adsorption using antimony oxide,²⁾ tantalum-doped tungsten oxide,³⁾ and layered potassium titanate.⁴⁾ However, since these adsorbent materials use rare metals, they involve high manu-

facturing costs and are not suitable for the treatment of large amounts of contaminated water; thus, these methods have not been put to practical use. Hence, in order to treat contaminated water, there is still an urgent need to develop an inexpensive adsorbent with low environmental burden.

One potential adsorbent is recycled scallop shell, which has been utilized previously as a removal agent for harmful substances; for example, as an aldehyde remover,⁵⁻⁷⁾ volatile organic compounds adsorbent,^{5,6,8)} desulfurization material,^{9,10)} and dephosphorization material.¹¹⁾ It is expected that waste scallop shells, which are currently discarded, can be utilized as raw materials for inexpensive and environmentally friendly agents that remove harmful substances. From this perspective, aim to apply scallop shells for the treatment of contaminated water generated from nuclear power plants. While scallop shell powder

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removes Sr^{2+} from aqueous solutions, we are yet to elucidate the mechanism by which the powder removes Sr^{2+} . In this report, we attempt to elucidate basic knowledge as to mechanism the of Sr^{2+} removal by scallop shell powder.

2. Experimental procedures

2.1 Preparation of scallop shell powder

The meat of the scallops was removed from the shells, which were then cleaned to remove any dirt or stains, then air dried at room temperature. The shells (60 g) were crushed for 3 h with a stamp mill (NITTO KAGAKU, ANS-143) and a further 3 h with an automatic mortar (NITTO KAGAKU, AMM-140D). We then analyzed the Sr^{2+} removability of the obtained powder. The reagent CaCO_3 was used for comparison (Kishida Chemical, Special Grade).

2.2 Evaluation of Sr^{2+} removability

$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ hydrate (Kishida Chemical, Special Grade) was dissolved in ion exchanged water to prepare a SrCl_2 aqueous solution of a known concentration. The SrCl_2 aqueous solution was stirred, and 3.0 g of scallop shell powder or reagent CaCO_3 powder were added, such that the powder concentration was 60 g/dm^3 . After a certain period of time, the aqueous solution was sampled using a syringe with a filter (Advantec, pore size $0.20 \mu\text{m}$), and then suitably diluted. Measurements were taken with an atomic absorption spectrometer (AAS; Thermo, iCE 3300) to determine the Sr^{2+} concentration. The removability of Sr^{2+} was evaluated by comparing the initial Sr^{2+} concentration of the aqueous solution to that of the sampled aqueous solution. The Sr^{2+} removability of each powder was expressed by the Sr^{2+} residual rate, calculated by $(\text{Sr}^{2+} \text{ concentration in sample aqueous solution}) / (\text{Sr}^{2+} \text{ initial concentration}) \times 100 = \text{Sr}^{2+} \text{ residual rate}$. Where the Sr^{2+} initial concentration is the concentration of Sr^{2+} in aqueous solution prior to adding the powder.

2.3 Method of evaluating the analysis of scallop shell powder

Individual identification was performed using X-ray diffractometry (XRD; Rigaku, RINT-2000), and X-ray photoelectron spectroscopy (XPS; PerkinElmer, PHI 5000 VersaProbe). The XRD patterns were obtained at room temperature using $\text{Cu K}\alpha$ radiation (40 kV and 40 mA). Data were collected in the range of $20^\circ \leq 2\theta \leq 50^\circ$ in steps of 0.01° . The XPS data were obtained by using characteristic $\text{Al K}\alpha$ X-ray radiation (1486.6 eV).

The morphology and elemental composition of the solids were analyzed before and after suspension using scanning electron microscopy (SEM; JEOL, JSM-6360A), and time of flight secondary ion mass spectrometry (TOF-SIMS; ULVAC-PHI, PHI TRIFT V nanoTOF). In TOF-SIMS, the liquid metal ion source consisted of an Au projectile (Au_3^+), and the range of analysis was $100 \times 100 \mu\text{m}$. Furthermore, the specific surface area of the powder was determined using a Brunauer–Emmett–Teller (BET) measuring device (MicrotracBEL, BELSORP-mini II).

3. Results and discussion

3.1 Sr^{2+} removability of scallop shell powder

The Sr^{2+} removability of the reagent CaCO_3 has been previously reported at an initial Sr^{2+} concentration of 1.1 g/dm^3 .¹²⁾ Figure 1 shows the Sr^{2+} removability of both CaCO_3 and scallop shell powder at various initial concentrations, after suspending 3.0 g of powder in 0.050 dm^3 (concentration of the powder 60 g/dm^3) of a SrCl_2 aqueous solution for 15 h at 25°C .

At an initial concentration of $\geq 0.50 \text{ g/dm}^3$ Sr^{2+} , both scallop shell powder and CaCO_3 showed similar Sr^{2+} removability. However, with an initial concentration $< 0.50 \text{ g/dm}^3$, the Sr^{2+} removability of the scallop shell powder was far higher than that of the reagent CaCO_3 : at an initial concentration of 0.010 g/dm^3 , the reagent CaCO_3 still had a residual Sr^{2+} rate of almost 100%, whereas the residual Sr^{2+} concentration in the solution with scallop shell powder was below the detection limit of AAS, indicating the superior removability of the scallop shell powder at low initial concentrations.

Figure 2 shows the change over time of the residual rate of Sr^{2+} concentration in a high-concentration aqueous solution of SrCl_2 (1.1 g/dm^3 Sr^{2+}), to which the powder was suspended. Measurements were taken by adding 30 g

Fig. 1. Sr^{2+} adsorption capacity depending on Sr^{2+} initial concentration. ($\blacktriangle$, a dotted line) CaCO_3 , ($\bullet$, a solid line) scallop shell. Initial concentration of Sr^{2+} 0.010 to 2.4 g/dm^3 , 25°C , concentration of the powder 60 g/dm^3 , 15 h suspended.

Fig. 2. Change in Sr^{2+} residual rate over time in suspension. ($\blacktriangle$, a dotted line) CaCO_3 and ($\bullet$, a solid line) scallop shell. Initial concentration of Sr^{2+} 1.1 g/dm^3 , 25°C , concentration of the powder 60 g/dm^3 .

Fig. 3. XRD patterns of (a) CaCO_3 and (b) scallop shell after 15 h suspension in an aqueous solution of SrCl_2 ($1.1 \text{ g/dm}^3 \text{ Sr}^{2+}$). (c) is calcite peaks.¹³⁾

of powder to 0.50 dm^3 (concentration of the powder 60 g/dm^3) of solution at 25°C . At this high concentration, there was no significant difference between the Sr^{2+} removability over time of scallop shell powder and CaCO_3 .

3.2 Sr present in the scallop shell powder

Since the Sr^{2+} concentration in the aqueous solution was decreasing, we hypothesized that the removed Sr^{2+} was contained in the scallop shell powder. We therefore attempted to identify Sr compounds within the solids using XRD, as shown in Fig. 3.

After suspension, the scallop shell powder had peaks at the same positions as CaCO_3 . However, we were unable to identify compounds containing Sr due to the detection limit of the laboratory XRD. Therefore, in order to investigate the presence of trace amounts of Sr compounds, we took measurements with XPS, which is capable of detecting Sr with higher sensitivity (Fig. 4).

Scallop shell was cut into squares weighing 3.0 g using a diamond cutter. This bulk scallop shell sample was added to 0.050 dm^3 of an aqueous solution of SrCl_2 ($1.1 \text{ g/dm}^3 \text{ Sr}^{2+}$) and left for 2 months. To ensure conductivity during XPS measurements, the sample was wrapped in a non-glossy aluminum wheel. The scallop shell has an additional Sr peak after Sr^{2+} removal, showing that it did contain Sr.

3.3 Removal of low concentration Sr^{2+} by scallop shell

Since a previous report mentioned in detail the mechanism of Sr^{2+} removal from an aqueous solution ($1.1 \text{ g/dm}^3 \text{ Sr}^{2+}$), we decided to focus on a Sr^{2+} initial concentration of 0.010 g/dm^3 , where there was a significant difference in the Sr^{2+} removability between scallop shell and the CaCO_3 . Figure 5 shows the change over time in the Sr^{2+} residual rate in a SrCl_2 aqueous solution with a low initial concentration ($0.010 \text{ g/dm}^3 \text{ Sr}^{2+}$). The experiment was conducted by adding 3.0 g of powder to 0.050 dm^3 (con-

Fig. 4. XPS spectra of (a) original scallop shell and (b) after being immersed for 2 months in an aqueous solution of SrCl_2 ($1.1 \text{ g/dm}^3 \text{ Sr}^{2+}$).

Fig. 5. Change of Sr^{2+} residual rate with time in suspension. ($\blacktriangle$, a dotted line) CaCO_3 and ($\bullet$, a solid line) scallop shell. Initial concentration of Sr^{2+} 0.010 g/dm^3 , 25°C , concentration of the powder 60 g/dm^3 .

centration of the powder 60 g/dm^3) of aqueous solution at 25°C .

Within about 3 min of suspension, scallop shell powder was able to remove Sr^{2+} to below the detection limit of the AAS (saturated Sr^{2+} adsorption amount of scallop shell powder at $0.010 \text{ g/dm}^3 \text{ Sr}^{2+}$ initial concentration is 0.35 mg/g). Despite the fact that there was no difference between the two powders at a high initial Sr^{2+} concentration (1.1 g/dm^3), the scallop shell powder demonstrated an entirely different Sr^{2+} removal capability to CaCO_3 at this low initial Sr^{2+} concentration (0.010 g/dm^3). Therefore, we considered the possibility that composition of scallop shell powder and CaCO_3 are different.

Fig. 6. XRD patterns of (a) CaCO_3 and (b) scallop shell powder. (c) is calcite peaks.¹³⁾

Fig. 7. SEM images of (a) CaCO_3 and (b) scallop shell powder.

The results of XRD measurements of the scallop shell powder and the reagent CaCO_3 are shown in Fig. 6.

The scallop shell powder was found to have peaks at the same positions as CaCO_3 . Thus, the crystal structure of the scallop shell powder and CaCO_3 was the same. Therefore, we theorized that the difference in Sr^{2+} removability was attributable to the microstructure of the powder.

Figure 7 shows SEM observations of the microstructure of scallop shell powder had a large amount of long and narrow particles, whereas CaCO_3 had a different particle shape like a cube. There were no other obvious differences; hence, we investigated the presence or absence of pores by measuring nitrogen adsorption and desorption.

Figure 8 shows the nitrogen adsorption–desorption isotherms of scallop shell powder and reagent CaCO_3 . The pre-treatment was carried out at 130°C for 2 h and the temperature at the time of nitrogen desorption was 77 K. Hysteresis of the isotherm was observed only for scallop shell powder. According to the classification of international union of pure and applied chemistry,¹⁴⁾ the type of H3 loop is assumed that particles giving rise to slit-shaped pores. It is therefore presumed that the scallop shell powder has slit-shaped pores, and the CaCO_3 has no pores. Hence, it was considered that the scallop shell powder may have a larger surface area than the reagent CaCO_3 .

The specific surface area is calculated by the BET method. Scallop shell powder had a specific surface area of $4.3 \text{ m}^2/\text{g}$, while that of CaCO_3 was $0.14 \text{ m}^2/\text{g}$. Because the scallop shell powder has pores that are not present in CaCO_3 , and because the specific surface area of scallop

Fig. 8. Adsorption isotherm by the nitrogen adsorption method. (a) CaCO_3 , (b) scallop shell.

Fig. 9. Adsorption isotherm in Sr^{2+} aqueous solution. (▲, a dotted line) CaCO_3 , (●, a solid line) scallop shell. Initial concentration of Sr^{2+} 0.010 to $0.10 \text{ g}/\text{dm}^3$, 25°C , concentration of the powder $60 \text{ g}/\text{dm}^3$.

shell powder is greater than CaCO_3 , the removal of Sr^{2+} by scallop shell powder may be through adsorption.

3.4 Classification of Sr^{2+} removal by scallop shell powder

The adsorption isotherm of scallop shell powder in an aqueous solution of SrCl_2 is shown in Fig. 9. The Sr^{2+} concentration was regarded as equilibrium after suspension for 15 h. The experiment was conducted by adding 3.0 g of powder to 0.050 dm^3 (concentration of the powder $60 \text{ g}/\text{dm}^3$) of an aqueous solution of SrCl_2 (Sr^{2+} concen-

Fig. 10. XRD patterns of (a) CaCO_3 and (b) scallop shell after 15 h suspension in an aqueous solution of SrCl_2 ($0.010 \text{ g/dm}^3 \text{ Sr}^{2+}$). (c) is calcite peaks.¹³⁾

tration: 0.010 to 0.10 g/dm^3), at an aqueous solution temperature of 25°C .

The isotherm curve for scallop shell powder took a convex upward shape, but for CaCO_3 it was in the form of a downward convex shape. Generally, when the shape of the isotherm is upwardly convex, there is strong interaction between the adsorbent and the adsorbate, and a high possibility of chemisorption. Conversely, a downwardly convex curve implies that there is no interaction between the adsorbent and the adsorbate, so it is not possible to say there has been an adsorption phenomenon.¹⁵⁾ Since the graph of scallop shell powder is in the shape of an upwardly convex curve, it is presumed that Sr^{2+} is removed by chemisorption. Since scallop shell powder is highly likely to chemically adsorb Sr^{2+} , we tried to identify compounds containing Sr that formed on the surface of the scallop shell powder particles.

Figure 10 shows the results of using XRD to identify compounds in scallop shell powder that contain Sr after adsorption.

We measured the powders that were suspended in the aqueous solution of SrCl_2 (Sr^{2+} concentration: 0.010 g/dm^3) for 15 h each, then filtered and dried. After suspension, the scallop shell powder had peaks at the same positions as for CaCO_3 , and we observed no peak attributable to the compound containing Sr. However, there is a possibility that a trace amount of Sr compound is present in scallop shell powder below the amount detectable by the laboratory XRD.

Therefore, we measured the powder adsorbed with Sr^{2+} by TOF-SIMS, which provides higher sensitivity (Fig. 11). The powders were suspended in an aqueous solution of SrCl_2 ($0.010 \text{ g/dm}^3 \text{ Sr}^{2+}$) for 15 h, then filtered and dried. Since scallop shell naturally contains trace amounts of Sr which are present in the ocean,¹⁶⁾ in order to clarify whether or not Sr is adsorbed onto the scallop shell powder, it is necessary to compare the level of Sr in scallop shell powder before and after suspension.

The TOF-SIMS profile of scallop shell powder after suspension [Fig. 11(b)] is similar to that of the reagent SrCl_2

Fig. 11. Comparison of the Sr spectra of scallop shell powder (a) before and (b) after Sr^{2+} adsorption. (c) Sr spectrum of reagent SrCl_2 .

[Fig. 11(c)] but differs from the profile before suspension [Fig. 11(a)]. Thus, the Sr contained in the suspended scallop shell powder is derived from SrCl_2 .

4. Conclusions

Although Sr^{2+} removal via scallop shell powder is similar to that via CaCO_3 at a high initial Sr^{2+} concentration ($\geq 0.50 \text{ g/dm}^3$), a clear difference in Sr^{2+} removability appears with a low initial concentration ($< 0.50 \text{ g/dm}^3$), where scallop shell powder was superior. The scallop shell powder was found to have slit-shaped pores and a specific surface area of $4.3 \text{ m}^2/\text{g}$. Furthermore, the removed Sr^{2+} was found to be present on the surface of the scallop shell powder by chemisorption.

Acknowledgement The authors are thankful to Dr. Yoshitsugu Akiyama and Mr. Ross Cooper of Liberal Arts in Oshamambe, Faculty of Industrial Science and Technology, Tokyo University of Science. We also thankful to Dr. Naoto Kitamura and Dr. Naoya Ishida of the Department of Pure and Applied Chemistry, Graduate School of Science and Technology, Tokyo University of Science. We are also thankful to Hokusho Fisheries and the Oshamambe Fishery Cooperative Association.

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