Efficient Removal of Strontium from Simulated Radioactive Wastewater by Using Mechanically Modified Dolomite as a Novel Environment-friendly Adsorbent

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Abstract

With similar biochemical properties to calcium, strontium including radioactive ⁹⁰Sr (T₁/₂ = 28.1 year) and stable isotope ⁸⁸Sr, ⁸⁷Sr, ⁸⁶Sr and ⁸⁴Sr can be easily enriched in human body’s bones to cause bone cancer, hematopoietic dysfunction and other diseases for natural decay releasing β-rays. So ⁹⁰Sr removal from radioactive wastewater is necessary from the stances of both human health and environmental protection. To enhance the removal and separation efficiency of Sr ions from simulated radioactive wastewater, we proposed the use of dolomite mineral as environment-friendly absorbent with the aid of ball milling. Due to the easier dissolution of Mg ions after the modification to offer more chance for Sr ions precipitated onto dolomite structure and the remaining Ca carbonate part inside would work as nucleus seeds for easier growth of Sr carbonate crystals as well as the formation of (Sr, Ca)CO₃ solid state solution. Furthermore, the widely available dolomite minerals even with some impurities (gangue minerals) worked in even better performance for Sr removal and offered a low-cost absorbent (without the need to purify dolomite) as another advantage.

Key words: Radioactive Wastewater; Adsorption; Dolomite; Sr(II) Removal; Mechanochemistry.

1. Introduction

There are 16 isotopes for Sr, and most of them are radioactive except 4 stable isotopes including ⁸⁴Sr, ⁸⁶Sr, ⁸⁷Sr and ⁸⁸Sr with relative abundances of 0.56 %, 9.86 %, 7.02 %, and 82.56 % respectively[1,2]. Radioactive ⁹⁰Sr (T₁/₂ = 28.1 year) is typically produced by the nuclear fission of ²³⁵U (about 6 %) and ²³⁹Pu (about 2 %) [1]. It is usually present in the wastest generated by nuclear reactions, unfortunately emitted from nuclear accidents including the Chernobyl nuclear accident, the Fukushima nuclear accident Sr has the similar biochemical properties to Ca and Sr (radioactive Sr and 4 stable isotopes ) can be easily enriched in human body’s bones through the food chain or/and drinking water, to cause bone cancer, hematopoietic dysfunction and other diseases for natural decay releasing β-rays. To protect human health and safeguard a reliable ecological environment, it is necessary to remove ⁹⁰Sr from radioactive wastewater to avoid the easy movement of soluble Sr ions through drinking water or/and food chain to cause possible enrichment in human body.

Since ⁸⁴Sr and ⁹⁰Sr have the same chemical properties and common decontamination properties, ⁸⁴Sr is generally used in many researches instead of ⁹⁰Sr as a reasonable and feasible method. Numerous processes have been studied to remove ⁹⁰Sr, such as evaporation, ion exchange, adsorption [2], chemical precipitation [3], biological method [4], solvent extraction [5] and membrane processes[6]. Chemical precipitation treatment of wastewater is one of the most widely used technologies, due to many advantages such as a simple process, a wide range of removal, feasible economical and practical characteristics. The removal of ⁹⁰Sr by chemical precipitation method occurs based mainly on the principle of solubility product of insoluble strontium salts as shown in Eqs. 1 in the case of SrCO₃. Usually, soluble Na₂CO₃, Na₃PO₄, and Li₃PO₄ have been examined as precipitants. CaCO₃ has to be added as crystal core to promote the growth of SrCO₃ crystalline particles to increase the solid-liquid separation efficiency and to suppress the dissolution of fine particles. However, the use of sodium salts may introduce a large amount of soluble salt and bring solution pH too high to be discharged directly.

\[ Sr^{2+} + CO_3^{2-} = SrCO_3 \]  

(1)
Adsorption appears as another technical option for the treatment of radioactive $^{90}$Sr in wastewater. Many recent publications are available involving various new adsorbent materials including Carbon nanotubes (CNTs), Graphene oxide (GO) [7], activated carbon loaded GO, ZrO$_2$-MnO$_2$, Zr-Sb oxide/ poly-acrylonitrile (PAN) and so on. Since the synthesis process are usually complicated and expensive, there exists the need to reduce the cost by using cheap absorbent instead. Combining both advantages of chemical precipitation and adsorption operation together, we proposed a new approach to use carbonate minerals for the removal of Sr ions by introducing both chemical precipitation and adsorption of Sr ions with the minerals. The reactivity of carbonate minerals themselves may be too low to be useful for engineering applications. Modification of the minerals was introduced to increase the reactivity to serve both purposes.

Mechanochemistry has received much attention for potential applications in wide ranges, including materials syntheses, co-crystallisation, solvent-free synthesis as well as increasing mineral reactivity and ion dissolution after surface modification [8, 9]. The surface modification is one of the main processing technologies of natural mineral processing, which plays an important role in improving application value and performance of natural mineral in treatment of heavy metal wastewater, et c. Repeated impact from ball movement leads to various changes with the target sample around the balls as the results of lattice damage, increased specific surface area and deepened amorphous degree, et c. In the previous studies, when minerals including calcite and serpentine were modified with ball-milling, reactivity with heavy metal sulfates were increased high enough to allow a reaction at nearly equal molar ratio for effective precipitations of heavy metals [9,10]. In case of copper, the formation of Cu$_4$(SO$_4$)$_3$(OH)$_6$*H$_2$O was observed in alkaline solution.

It is interesting to note there exists a clear difference in the solubility product constants (Ksp) of four carbonates with the data at 25°C as MgCO$_3$ (6.82*10$^{-6}$), CaCO$_3$ (3.36*10$^{-9}$), BaCO$_3$ (2.58*10$^{-9}$), SrCO$_3$ (5.6*10$^{-10}$). Due to the smallest Ksp of SrCO$_3$, it is possible to use Mg, Ca and Ba carbonates to remove Sr ions from solution by forming SrCO$_3$ precipitation from the easier dissolutions of these carbonates to provide CO$_3^{2-}$ ions as well as chemical adsorption. Mechanochemical modification of the carbonate minerals increased the dissolutions to achieve significant improvement for Sr removal and dolomite gave the best results. In this paper, we proposed the use of modified dolomite for Sr removal and discussed the reaction mechanism. The widely available cheap mineral could be changed into efficient and environment-friendly adsorbent for the purification of Sr containing radioactive wastewater, without concerns for secondary pollution.

2. Materials and Methods

2.1. Materials

CaCO$_3$, BaCO$_3$ and Sr(NO$_3$)$_2$ from Aladdin Industrial Corporation, Sinopharm Chemical Reagent Co., Ltd. in analytical grade (AR) were used as received without further purification. Mineral magnesite and dolomite were obtained from Haicheng City, Liaoning Province, China. After grinding and sieving by sample preparation with crusher and electric screener, samples with particle size below 320 mesh were used as starting samples for modification operation. The chemical compositions of magnesite and dolomite were shown in Table 1.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>SO$_3$</th>
<th>CaO</th>
<th>P$_2$O$_5$</th>
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<td>0.73</td>
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<td>0.27</td>
<td>0.01</td>
<td>0.50</td>
<td>0.03</td>
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<td>dolomite</td>
<td>21.66</td>
<td>0.23</td>
<td>0.09</td>
<td>0.11</td>
<td>0</td>
<td>31.94</td>
<td>0.01</td>
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<table>
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<tr>
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<th>MnO</th>
<th>Cl</th>
<th>BaO</th>
<th>K$_2$O</th>
<th>SnO$_2$</th>
<th>Loss</th>
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<tbody>
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<td>0.01</td>
<td>0.05</td>
<td>0</td>
<td>0.02</td>
<td>0.01</td>
<td>51.13</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0.04</td>
<td>0</td>
<td>45.91</td>
</tr>
</tbody>
</table>

2.2. Methods

Surface modification of carbonate samples: 4.00 g of carbonate sample was put into a planetary ball mill (Pulverisette-7, Fritsch, Germany), with two stainless-steel milling pots (45 cm$^3$ inner volume each) and 7 steel balls (Ø 15 mm, 14 g), and subjected to ball milling with time changed from 0 to 180 min and speed changed from 0 to 600 revolutions per minute (rpm).

Solution chemical properties of the modified carbonate samples and Sr removal test: 0.1 g of the milled samples was agitated in 100 mL ultra-pure water to prepare samples for the measurement of pH and the dissolved concentrations of Ca and Mg ions in water. Different masses of the milled samples were added to 100 mL of 1 mmol Sr(NO$_3$)$_2$ solution (equivalent to 88 mg/L, simulated radioactive wastewater) to conduct experiments of Sr adsorption. The solutions were vigorously shaken at a frequency of 250 rpm at room temperature (25 ± 1°C) with a fixed shaking time of 180 min. The suspensions were filtered and the solid residues were dried in 105°C for 120 min.
2.3. Characterizations

The pH of all solutions was measured by a pH meter (METTLER TOLEDO FE210-FiveEasyTM, Switzerland). The concentrations of Sr, Ca and Mg ions in the solutions were measured with atomic adsorption spectroscopy (Shimadzu AA-6880, Kyoto, Japan). The chemical compositions of magnesite and dolomite were analyzed by X-ray fluorescence spectrometer (Axios advanced, PANalytical B.V., the Netherlands). The particle sizes of dolomite and the modified samples were analyzed by laser particle size analyzer (Malvern Mastersizer 2000, England). X-ray diffraction analysis (XRD: RU-200 B/D/MAE-RB, Tokyo, Japan) was performed to identify the crystalline phases in the carbonates and the modified samples. The scanning electron microscopic analysis (SEM, HITACHI-SU 8010 with EDS accessory, COXEM, EM-30 AX PLUS+) was used for observing the surface morphology of the samples.

The removal efficiency and capacity of Sr (II) was calculated by the following equation:

\[ \eta = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \% \]  
(2)

\[ q = \left( \frac{C_0 - C_e}{m_0} \right) \times 100 \% \]  
(3)

Where, \( C_0 \) represents the initial concentration, \( C_e \) the concentration after treatment and \( m_0 \) the dosage of adsorbent. The unit of \( C_0 \) and \( C_e \) is mg/L, while the unit of \( m_0 \) is g/L.

3. Results and Discussion

3.1. Comparison between Four Carbonates and Modified Ones

Preliminary experiments were conducted to compare original four carbonates and modified ones for the removal effect of Sr\(^{2+}\) at fixed molar ratio of C in carbonate to Sr in the solution as CO\(_3^{2-}\)/Sr\(^{2+}\) ratio of 7:1 and the results are shown in Figure 1, the raw carbonates did not have high ability to remove Sr\(^{2+}\), except dolomite with a relative high removal of 19.02% of Sr\(^{2+}\) from solution. This may be related to the low solubility of the carbonates to dissolve sufficient CO\(_3^{2-}\) to allow an effective reaction with Sr\(^{2+}\). The modified carbonates demonstrated much better removal efficiency of Sr\(^{2+}\) as high as 88.86%, 78.77%, 59.08% and 34.65% corresponding to the modified dolomite, magnesite, calcite and BaCO\(_3\), respectively. By comparison of Sr\(^{2+}\) removal efficiency of the carbonates before and after mechanical modification, it was easy to draw conclusion that mechanical modification promoted the interaction with Sr\(^{2+}\) by the carbonates, with much higher performance than the simple surface adsorption.

![Figure 1](image-url) Changes in the Sr removal efficiency with several carbonates and the modified samples.

Modification Experiment: weight ratio of ball to powder was 49:1, milling time was 60 min, and milling speed was changed from 0 to 600 rpm.

Sr Adsorption Test: Four carbonates and the modified samples with 500 rpm were added to 100 mL of 1 mmol Sr(NO\(_3\))\(_2\) solution (equivalent to 88 mg/L) to conduct experiments of Sr adsorption as CO\(_3^{2-}\)/Sr\(^{2+}\) ratio of 7:1. And the solutions were vigorously shaken at a frequency of 250 rpm at room temperature (25 ± 1 °C) with
a fixed shaking time of 180 min. The upper clarification liquid was pretreated with centrifugation and Sr concentration of supernatant was analyzed by Atomic absorption method (AAS).

The modified BaCO₃ sample gave the lowest improved performance for Sr²⁺ removal. Together with the toxic properties of barium compounds and very rare availability of Ba carbonate minerals, it was not examined in the subsequent researches. Focus was put on the modified dolomite sample, which exhibited best performance for Sr²⁺ removal, with the modified calcite and magnesite as references in subsequent tests for their accessibility.

3.2. Physical and Chemical Changes of the Modified Carbonates

CaCO₃ and MgCO₃ are the main components of dolomite, with less impurities including SiO₂, Al₂O₃, et c.(Table 1) Their molar ratio was 1.06, which is consistent with theoretical calculations of dolomite. The dolomite sample can be used for test with 99.5% purity of main chemical composition (C.P., Chemical Pure, ≥99.5%).

Crystal structure of the modified samples with different milling speed for 60 min was analyzed by XRD and similar changes were observed with three carbonates. Figure 2 shows the patterns of dolomite sample only.

![Figure 2. XRD patterns of the modified dolomite at different milling speed.](image-url)

Modification Experiment: weight ratio of ball to powder was 49:1, milling time was 60 min, and milling speed was changed from 0 to 600 rpm.

The crystal structure of dolomite belongs to trigonal crystal system, the same as calcite and magnesite. Dolomite is an insoluble mineral composed of CaCO₃ and MgCO₃ and the mole ratio of CaCO₃ to MgCO₃ is approximately 1:1 (Table 1). As shown in Figure 2, the peaks of the raw material of dolomite fit well with reported data of PDF 36-0426 (dolomite). When the milling speed was lower than 200 rpm, the crystal structure of the modified dolomite kept steady. With an increase in milling speed up to 600 rpm, the characteristic peaks of the modified dolomite including (104), (113), (202), (018), (116), et c. were weakened correspondingly. Only the characteristic peak (104) could be observed to remain in the pattern, and other peaks tended to disappear after mechanical modification. Although not shown here, similar changes were observed with both patterns of the modified calcite and magnesite.

The particle sizes of dolomite and the modified samples were also analyzed by laser particle size analyzer (Malvern Mastersizer 2000). d₅₀ of dolomite was 12.30 μm, while d₅₀ of the modified samples at 300 and 600 rpm for 60 min were 15.65 and 13.46 μm, which implied that micron particle reunification happened with low milling speed and the reunited particles were broken again with higher milling speed. The particle sizes of the modified samples were bigger than that of dolomite sample, which are easier to overcome Brownian motion in solution and achieve solid liquid separation in less time.

To understand the reason for what had changed with the modified carbonate samples after the milling operation, changes in pH of 0.1 g modified carbonates with different milling speed and time in 100 mL ultrapure water were monitored. The effect of milling time was first examined with milling speed fixed at 500 rpm and the results are shown in Figure 3.
With an increase in milling time, similar change patterns were observed with all three carbonates. Increase in pH was obtained at the beginning of milling operation up to 60 min and levelled off without further large change with milling time prolonged to 180 min. 60 min of milling time was used for experiments to examine other parameters. With the original sample without milling operation, the pH of calcite was higher than that of magnesite. However, the milled magnesite sample gave much higher pH in water than the modified calcite, indicating that much stronger change occurred in the structure of magnesite by milling operation than that of calcite, to demonstrate easy dissolution of the modified magnesite. It was more interesting to note that dolomite, whether the raw or the milled one, demonstrated higher pH in water than both simple Mg and Ca carbonate. Such different properties would be the main reason of the best performance for Sr\(^{2+}\) removal shown in Figure 1 and discussed further with support of other data.

Figure 3. Changes in pH of three modified carbonates in ultrapure water with different milling time.
Modification Experiment: weight ratio of ball to powder was 49:1, milling speed was 500 rpm, and milling time was changed from 0 to 180 min.
Determination of pH: 0.1g modified carbonates was added to 100 ml ultrapure water at room temperature (25 ± 1 °C), then gently vibrate the bottle so that the solution was evenly mixed. 10 min later, sensitive glass bubble was put into upper of mixed solution and pH value was recorded in 2 min.

With milling time fixed at 60 min, the changes in pH of the solution with milling speed are shown in Figure 4. All three samples demonstrated relatively large increase in pH value with the prolonged milling operation. Compared with the solution pH from high to low of the raw dolomite, calcite and magnesite in order, the milled sample of Mg carbonate gave higher pH than Ca carbonate. Dolomite sample gave the highest pH value up to 10.3. All three carbonate underwent similar changes with the increased mechanochemical modification and showed difference also to some degree.

Figure 4. Changes in pH of three modified carbonates in ultrapure water with different milling speed.
Modification Experiment: weight ratio of ball to powder was 49:1, milling time was 60 min, and milling speed was changed from 0 to 600 rpm. And determination of pH was consistent with previous description in Figure 3.

MgCO$_3$ and CaCO$_3$ are hardly water-soluble substances, so their solution was in weakly alkaline for hydrolysis reaction of trace elements including Mg$^{2+}$, Ca$^{2+}$ and CO$_3^{2-}$. During the surface modification process by the ball-milling, the carbonate minerals were continuously dissociated by the external mechanical force, and the highly active and unsaturated particles Mg$^{2+}$, Ca$^{2+}$ and CO$_3^{2-}$ were exposed on surface, which can react with the water adsorbed on surface, thereby pH of the solution were increased for hydrolysis reaction.

The pH changes implied different dissolution characteristics of the milled samples and the changes in the dissolved Ca$^{2+}$ and Mg$^{2+}$ concentration with different milling speed were measured and the results are shown in Figure 5.

**Figure 5.** Changes in ion concentrations of the modified carbonates in water with different milling speed

Ion dissolving experiment: 0.1 g of three carbonates and the modified samples with different milling speed at 60 min was added to 100 ml ultrapure water at room temperature (25 ± 1 ℃), then the solutions were vigorously shaken at a frequency of 250 rpm at room temperature with a fixed shaking time of 180 min. The upper clarification liquid was pretreated with centrifugation and ion concentrations of supernatant were analyzed by Atomic absorption method (AAS).

In the case of the modified calcite, the dissolved Ca$^{2+}$ concentration increased slowly with an increase in milling speed, consistent well with the gradually increase in pH as shown in Figure 4, suggesting that Ca carbonate underwent quite mild structural change without much dissolution when agitated in water. In case of the modified magnesite, evident increase in Mg$^{2+}$ concentration was observed with the increase in milling speed. It was worthy of noticing that the Mg$^{2+}$ concentration from Mg carbonate was even higher than Ca$^{2+}$ from Ca carbonate in ppm, a much higher value in mmol, consistent with the change patterns in pH, together indicating the easier dissolution of Mg carbonate than Ca carbonate after milling operation. In case of the modified dolomite, quite different results were obtained. Significant increase in Mg$^{2+}$ concentration was observed with the increase in milling speed, with a result of 10 times higher at 600 rpm than that of the raw sample. It was also much higher than that from the modified magnesite. It was more interesting to note that the Ca$^{2+}$ dissolution from the modified dolomite gave a much lower value than Mg$^{2+}$ and even lower than the Ca$^{2+}$ concentration from the modified calcite. Furthermore, no evident change in Ca$^{2+}$ dissolution from dolomite happened with milling operation. Mg$^{2+}$ and Ca$^{2+}$ did not perform an even dissolution at 1:1 as the compositional constitution of both carbonates, but a preferential Mg$^{2+}$ dissolution to a much higher degree than the single magnesite.

In detail, 0.1 g of the modified dolomite dissolved out 57.5 ppm Mg$^{2+}$, and 4.2 ppm Ca$^{2+}$ in 100 mL ultrapure water while 0.1 g of the modified magnesite and modified calcite dissolved out 16.6 ppm Mg$^{2+}$, 11.8 ppm Ca$^{2+}$ respectively. Since it was not easy to measure the exact concentration of carbonate anions in water, the molar amount of CO$_3^{2-}$ was calculated from the Ca$^{2+}$ and Mg$^{2+}$ concentrations based on the equimolar ratio of the carbonate dissolution, ignoring its further hydrolysis to HCO$_3^-$. CO$_3^{2-}$ dissolved out by the modified dolomite (0.230 mmol) were nearly 2 times of the modified magnesite (0.122 mmol), and 10 times of the modified
calcite (0.023 mmol). This was a strong proof for different effects of removing Sr\(^{2+}\) by three modified carbonates and dolomite gave the best performance (Figure 1).

3.3. Enhanced Sr\(^{2+}\) Removal by the Modified Carbonates

The removing capacity of Sr\(^{2+}\) by the modified carbonates were evaluated through the decrease in Sr ion concentration of its nitrate solution with the addition of the carbonates. The changes in Sr removing efficiency with milling speed are shown in Figure 6 with a fixed molar ratio of CO\(_3^{2-}\)/Sr\(^{2+}\) (7:1). All three carbonates demonstrated similar increase pattern for Sr\(^{2+}\) removal and the removal efficiency by the modified calcite was increased from 29.54 % to 59.08 %, a relatively slow pattern, while the data by the modified magnesite increased higher to close 80 %. The modified dolomite gave the best results close to 90 %. It was evident that the patterns were similar to that of pH change shown in Figure 4 and the changes in the dissolved Mg\(^{2+}\) and Ca\(^{2+}\) shown in Figure 5, indicating that the dissolution of the modified carbonates was the key factor for the Sr removal from the solution.

![Figure 6. Sr removal efficiency with three carbonates at different milling speed.](image)

Sr adsorption test was consistent with previous description in Figure 1 and more modified samples with different milling speed were analyzed here.

The amounts of the carbonates required for the efficient Sr\(^{2+}\) removal were examined as the CO\(_3^{2-}\)/Sr\(^{2+}\) ratio, namely the carbonate amounts to Sr in mole, and Figure 7 shows the changes in Sr removal efficiency with the CO\(_3^{2-}\)/Sr\(^{2+}\) ratio. Although all three carbonates demonstrated some increases in Sr\(^{2+}\) removal efficiency from the high CO\(_3^{2-}\)/Sr\(^{2+}\) ratio, there existed clear difference in the curve patterns. In the case of the modified calcite, the Sr\(^{2+}\) removal efficiency remained as low as around 20 % with CO\(_3^{2-}\)/Sr\(^{2+}\) ratio increased from 2.8 to 5.6, and showed relatively quick increase in Sr\(^{2+}\) removal efficiency with further increase in CO\(_3^{2-}\)/Sr\(^{2+}\) ratio to reach 68.46 % at CO\(_3^{2-}\)/Sr\(^{2+}\) of 9.8. In the case of the modified magnesite, quick increase in Sr\(^{2+}\) removal efficiency was obtained with the increase in CO\(_3^{2-}\)/Sr\(^{2+}\) ratio from 2.8 to 5.6, close to 80 % and further increase in CO\(_3^{2-}\)/Sr\(^{2+}\) ratio did not promote removal performance. In the case of the modified dolomite, the best performance in Sr\(^{2+}\) removal efficiency was obtained among three carbonates and over 80 % was simply achieved: the efficiency at CO\(_3^{2-}\)/Sr\(^{2+}\) ratio of 2.8 was even higher than that from the modified magnesite at CO\(_3^{2-}\)/Sr\(^{2+}\) ratio of 5.6. Dolomite allowed a good Sr\(^{2+}\) removal efficiency even at a quite low added dosage and could serve as a good absorbent for treating radioactive wastewater containing Sr\(^{2+}\).
Sr removal efficiency by three modified carbonates at different mole ratio of CO$_3^{2-}$/Sr$^{2+}$.

Sr adsorption test was consistent with previous description in Figure 7 and the difference was mole ratio of CO$_3^{2-}$/Sr$^{2+}$ changed from 2.8 to 9.8.

To Sr adsorption capacity by the modified dolomite, it could be calculate according to equation (3), which ranged from 1898 to 625 mg/g with increased dosage of the modified dolomite. The average value was 1078 mg/g. Meanwhile, the Sr removal amount by the modified dolomite ranged from 69.0 ~79.7 mg/L, and the average value was 75.6 mg/L. Therefore, there was around 12.4 mg/L Sr in effluent, which was failure to meet discharge requirements. There were multiple options for in-depth processing of low concentration wastewater including membrane separation, multi-effect evaporation, etc. So Sr removal test may need to be developed in a combination process including adsorption, filtration and nanofiltration.

3.4. Mechanism Discussion

In order to observe the microstructure with the existence and distributions of Sr in the sediment after reaction of the modified dolomite with Sr nitrate solution, SEM-EDS analyses and the elemental mappings of Sr, Ca, Mg, C and O of the sediment sample were carried out and the results are shown in Figure 8. There was a disordered crystal structure of the modified dolomite (Figure 8-a) in a heavy agglomeration state, resulting from the regular platy structure of the raw dolomite. It is interesting to note from the EDS quantitative analysis that the mole ratio of Mg:Ca of the modified dolomite was 390:1, while mole ratio of Mg/ Ca is close to 1.0 in original mineral. Changed mole ratio of Mg/ Ca indicated that mechanical forces promoted crystal structure to be disordered and structural rearrangement of surface ions, then more Mg than Ca was transferred to surface of the modified dolomite.

After reaction with Sr$^{2+}$ in the solution, a heavier agglomeration of particles appeared as the main morphology in the sediment (Figure 8-b), indicating the phase change from dolomite to new one. The EDS analysis (Figure 8-c) and elemental mappings clearly showed that the Sr, Ca, Mg, C and O elements were evenly distributed with the sediment solid, which could prove that the uniform dispersion of Sr existing in a crystal phase rather than a surface adsorption with concentrated existence of Sr around the particle surface. Formation of Sr carbonate inside the structure of dolomite with Ca carbonate to give the even distribution is believed to be the main mechanism, demonstrating superiority over the commonly observed surface adsorption. It is more interesting to note from the EDS quantitative analysis that the mole ratio of Ca : Mg : Sr was 0.48: 0.40: 0.05, with the mole ratio of Ca: (Mg + Sr) was approximately 1:1, in compliance with the approximately 1:1 mole ratio of Ca: Mg shown in Table 1. The less existence of Mg than Ca indicated the dissolution of Mg into solution, and hole left on surface was filled by Sr, and SrCO$_3$ was formed into the sediment.
Figure 8. SEM image (a) of the modified dolomite; SEM image (b), EDS analysis (c) and elemental mapping of sediment.

The sediment was obtained after vacuum filtration of solution, and dried at 105°C for 2~5 hours in electric drying oven with forced convection before characterization analysis.

The modified dolomite at 500 rpm and the solid sediment after its reaction with Sr²⁺ in the solution were analyzed by XRD and the results are shown in Figure 9. Compared with peaks of MgCa(CO₃)₂ phase, several new diffraction peaks belonging to Ca-rich-strontianite (Sr, Ca) CO₃ [PDF44-1421] appeared and were attributed as lattice planes (111), (021), (112), (130), (221), respectively. The formation of Sr and Ca carbonate solid state solution as (Sr, Ca) CO₃ was a clear indication for the occurrence of ion exchange between Sr from solution with Mg and Ca from the dolomite.
Sr ions react with soluble carbonate salts to form Sr carbonate precipitate, the newly formed small particles tend to hydrolyze to give back Sr ions. The use of modified dolomite may work in a different reaction pathway to offer host position with Ca carbonate and unpaired carbonate anions to accept Sr ions from the solution to form (Sr, Ca) CO$_3$.

Although MgCO$_3$ and CaCO$_3$ are hardly soluble in water, they may hydrolyze partially in water as equation (4) and (5). Further hydrolysis of CO$_3^{2-}$ as equation (6) and (7) would lead to the generation of more OH$^-$ to give pH increase as shown in Figure. 3 and 4. Ball milling of these carbonates to generate smaller particle and broken structures would accelerate the four hydrolysis reactions further to very high degree to give more dissolved Ca$^{2+}$ and Mg$^{2+}$ shown in Figure. 5 and pH increase correspondingly. Since the Ksp of MgCO$_3$ is much larger than that of CaCO$_3$, hydrolysis reaction (4) may go further to give more ions of Mg and CO$_3^{2-}$ than reaction (5).

\[
\begin{align*}
MgCO_3 & \rightleftharpoons Mg^{2+} + CO_3^{2-} \quad (4) \\
CaCO_3 & \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad (5) \\
CO_3^{2-} + H_2O & \rightleftharpoons OH^- + HCO_3^- \quad (6) \\
HCO_3^- + H_2O & \rightleftharpoons OH^- + H_2CO_3^- \quad (7) \\
Mg^{2+} + H_2O & \rightleftharpoons Mg(OH)_2 + H^+ \quad (8) \\
Mg(OH)^{2+} + H_2O & \rightleftharpoons Mg(OH)_2 + H^+ \quad (9)
\end{align*}
\]

When the Mg ions and OH anions are concentrated high enough in the solution, insoluble Mg(OH)$_2$ would precipitate from the solution as equation (8) and (9) to prevent the further increase of them so that the pH kept constant around 10.3 as the highest value from dolomite dissolution (Figure. 3–4).

Depending on the gap in Ksp of alkaline earth carbonate, there exists a potential for Sr precipitation as carbonate through the ion exchange with Mg and/or Ca carbonates. Modification of the carbonates accelerated such exchanging reaction to give quite high Sr removal efficiency by both Mg and Ca carbonates. It was very interesting to note dolomite, a double carbonate, having an alternating structural arrangement of calcium and magnesium ions, demonstrated much better performance than single Mg or Ca carbonate, rather than an average of two carbonate.

From the XRD and SEM analyses (Figure. 8–9), Sr$^{2+}$ was immobilized by the modified dolomite in form of (Sr, Ca)CO$_3$ and the purification of wastewater containing Sr$^{2+}$ was realized. In (Sr, Ca)CO$_3$, Sr$^{2+}$ took the place of Mg$^{2+}$ in the modified dolomite, which indicated that ions exchange happened between Sr$^{2+}$ and Mg$^{2+}$. For Sr$^{2+}$ having a similar ionic radius as Ca$^{2+}$ and Mg$^{2+}$ (Table 2), (Sr, Ca)CO$_3$ was easily formed for Sr$^{2+}$ replacing Ca$^{2+}$ and Mg$^{2+}$ in CaMgCO$_3$. What’s more, the modified dolomite dissolving out more Mg$^{2+}$ than...
Ca$^{2+}$ in the solution (Figure 5), and holes left by Mg$^{2+}$ provided binding sites for Sr$^{2+}$. In summary, ions exchange made it right for the formation of (Sr, Ca) CO$_3$.

### Table 2. Ion Radius of the Alkaline Earth Metal Elements and others in Chemical Periodic Table

<table>
<thead>
<tr>
<th>Element</th>
<th>Valencies</th>
<th>Atomic number</th>
<th>Atomic weight</th>
<th>Ion Radius (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>+2</td>
<td>4</td>
<td>8</td>
<td>45</td>
</tr>
<tr>
<td>Mg</td>
<td>+2</td>
<td>12</td>
<td>24</td>
<td>72</td>
</tr>
<tr>
<td>Ca</td>
<td>+2</td>
<td>20</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>Sr</td>
<td>+2</td>
<td>38</td>
<td>88</td>
<td>118</td>
</tr>
<tr>
<td>Ba</td>
<td>+2</td>
<td>56</td>
<td>137</td>
<td>135</td>
</tr>
<tr>
<td>Fr</td>
<td>+1</td>
<td>87</td>
<td>223</td>
<td>180</td>
</tr>
<tr>
<td>Fe</td>
<td>+2/3</td>
<td>25</td>
<td>56</td>
<td>61/55</td>
</tr>
<tr>
<td>Mn</td>
<td>+4/7</td>
<td>26</td>
<td>55</td>
<td>53/46</td>
</tr>
</tbody>
</table>

Isomorphism is a common phenomenon in minerals, which is an important cause of changes in mineral chemical composition. To dolomite, Fe, Mn, Sr and other metal ions can replace Mg in the long process of evolution of the earth, so there are Ca(Fe, Mg, Mn)CO$_3$, (Ca, Sr) CO$_3$ existing in natural. Especially, strontianiferous aragonite was found in Lanping, Yunnan province, and Baiyuneboite, Inner Mongolia Autonomous Region, which was studied in details and strontianiferous aragonite is known as a variant of aragonite, not a new mineral. In strontianiferous aragonite, Ca in natural aragonite may be largely replaced by Sr but does not cause intragranular fundamental changes in the structure of aragonite.

### 3.5. Application of Dolomite with Impurities

Although dolomite resources are rich in reserves and many mines of high quality are available in China, it is needed to examine the possibility of using some tailings with dolomite and other gangue minerals inside. Quartz (SiO$_2$) and many other silicates mineral are widely distributed in nature, and appear in almost all of natural mines. These silicate minerals are quite hard materials against milling operation and are usually chosen as grinding aids in mineral processing for its high Mohs hardness. To explore the effect of purity of dolomite on the removal efficiency of Sr$^{2+}$, dolomite was milled with an addition of SiO$_2$. Figure 10 shows the changes in Sr$^{2+}$ removal efficiency with the adding percentage of SiO$_2$.

![Figure 10. Sr removal efficiency by the modified dolomite with the added SiO2.](image)

Modification Experiment was consistent with previous description in Figure 3 and the difference was that certain amount of SiO$_2$ was added to dolomite and their total weight was always 4g.

The addition of SiO$_2$ gave a very positive effect with obvious higher removal efficiency of Sr$^{2+}$, increased from 90.59 % to 99.93 % by the modified dolomite in fixed mole ratio of CO$_3^2$-/Sr$^{2+}$ (7:1), following the added SiO$_2$ to dolomite from 15 % to 35 %. The mixture of dolomite and SiO$_2$ had better performance than the pure dolomite sample. Dolomite with impurities including SiO$_2$ was preferred for the treatment of 90Sr in radioactive wastewater rather than the pure dolomite. This provided a new idea for the resource utilization of the dolomite.
in some mining tailings. It is understood that the existence of quartz may work as a milling aid to the target dolomite sample to facilitate its structural change to allow easier dissolution to give Mg ions for Sr ion-exchange. The phenomena will be investigated further in the future researches.

Compared with the reported natural mineral and synthetic modified carbon materials, there was the highest removal ability of Sr ions by the modified dolomite (1078 mg/g), while there were only around 10 mg/g by tourmaline, attapulgite and pecan shell-based activated carbon. Moreover, the cost of materials for the purification of 1g Sr in this study was 1.27 CNY, which was about 1/4 of the cost of materials by sodium carbonate and taking calcium carbonate as the crystalline seeding (5.27 CNY/g Sr) reported in reference. The modified dolomite had clear advantages with higher adsorption capacity and lower cost, which provide a good application prospect to purify a large amount of waste water.

4. Conclusions

Mechanochemical modification of dolomite allowed easier dissolution to give higher pH in water and higher Mg ions dissolved, which contributed to an efficient Sr ion removal by forming carbonate precipitation. Compared with other carbonates, dolomite exhibited the most interesting characteristic, to dissolve Mg ion preferentially rather than evenly for both Mg and Ca, therefore, to precipitate Sr ion efficiently through a synergetic effect resulting from the easy exchange between Mg ions to Sr ions and the nucleus seeding of the Ca carbonate part remaining in the dolomite structure to form Sr-Ca carbonate solid state solution. After simple ball-milling for modification, the widely available cheap dolomite mineral particularly with some silicate impurities may serve as an excellent environment-friendly absorbent for Sr ion removal from typical radioactive wastewater without any concern for the occurrence of secondary pollution.

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References