Preparation of Selective Adsorption Materials Based on Al₂O₃ and their Adsorption Properties for Sr²⁺

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Abstract. Aiming at the selective adsorption treatment of ⁹⁰Sr in radioactive waste liquid, we need to synthesize MnO₂ and other inorganic ion exchanger with high selectivity for Sr²⁺ in the waste water, find the best material ratio, and prepare the raw material liquid. The feed liquid is blown into the hot dimethylsilicone oil by the self-made spherical particle preparation device and loaded on the Al₂O₃ matrix. The composite adsorbent with appearance and size similar to ion exchange resin was prepared. The physicochemical properties of the composite adsorbent were characterized by SEM, FT-IR and XRD. Different concentrations of strontium ion solution were prepared to study the change of adsorption capacity of Sr²⁺ at different time. The effects of pH on the adsorption properties of the adsorption properties under the influence of different initial concentrations and different coexisting ions were studied. According to the experimental data, the pseudo first order and quasi second order kinetic first order and quasi second order kinetic equations were used to fit the adsorption process. Two typical adsorption isotherm models, Langmuir and Freundlich models, were used to describe the adsorption process of Sr²⁺ by composite adsorbents.

1. Introduction
²⁹Sr is one of the most important radionuclides in radioactive waste liquid, and radioactive cesium¹⁰⁰Sr is produced by ²³⁵U and ²³⁹Pu nuclear fissions and is widely found in radioactive wastewater. The 2011 explosion at Japan's Fukushima nuclear power plant caused radioactive material to leak and discharge a large amount of wastewater containing radioactive cesium. It is a high heat release rate of longer half-life (T₁/₂=28.1a), fission product nuclide, which is a pure β radionuclide that is produced by β decay to produce a submersion that emits high-energy β line. The chemical, biochemical properties of radon and calcium are similar, and after ²⁹Sr enters the body, more than 99% of ²⁹Sr remain in bones and teeth, resulting in high-energy β rays that cause significant radiation damage to bone marrow hematopoietic tissue and bone tissue due to its long physical and biological half-life. Therefore, ²⁹Sr in radioactive waste liquid must be properly removed to avoid entering the environment.

At present, ²⁹Sr in radioactive waste liquid is usually removed at home and abroad using chemical precipitation, ion exchange, membrane separation and biological methods. Vokovich¹¹ studied fission elements in molten salt waste from nuclear fuel reprocessing by phosphate precipitation. The sediments are lithium phosphate and sodium phosphate. I. Smiciklas²² use oblique zeolite adsorption Cs,Co²⁺ and Sr²⁺-zeolite adsorption capacity for 3 metal ions Cs⁺>Sr²⁺>Co²⁺ the maximum adsorption capacity is approximately 11 mg/g when treating simulated wastewater with an initial Sr²⁺ mass concentration of
300mg/L. A. Richards [3] for groundwater with an initial mass concentration of 1.30 mg/L, using a combination of UF and RO, BW30, TFC-S, ESPA4 membranes, respectively, with removal rates of 0.2%(99.6±0.2%) and (95.7±0.9%) and (98.8±1.4%), respectively. N. Ngwenya (SBS) remove Sr2+, Cs+, Co2+ from a single or mixed solution with an initial mass concentration of 25-500mg/L, the experimental data conformed to the Langmuir model, and the maximum adsorption of SBS to 3 metal ions in a single solution was 416.7, 238.1, 204.1 mg/g.

2. Materials and Methods

2.1. Instruments and equipment
Spectrum BX II Fourier Infrared Spectrometer, PerkinElmer Instruments, USA; 3H-2000PS2 Static Capacity Ratio Surface Product and Porosity Analyzer; JSM-5610LV Scanning Electron Microscope, Japan Electronics Co., Ltd.; PHS-3D Precision PH Meter, Shanghai Precision Science Instruments Co., Ltd.; SHA-C thermostatstatic oscillating box, Jiangsu Jintan City, China University Instrument Co., Ltd.; DZ-1BC vacuum drying box, Tianjin Tester Instrument Co., Ltd.

2.2. Preparation of spherical particles
Take 112.5g aluminum nitrate add water to 100ml to make 3mol/L of aluminum nitrate solution. Add 5.12 mlof ammonia to the aluminum nitrate solution and adjust the solution concentration to 2.85mol/L. Take 49.2ml of mixture and add 10.36ml of ammonia to get the mixture A. Take 18g urea and 42g of 6 methylamphetamine add water to 100ml, and the solution concentration of urea and hexamide temimamine is 3mol/L to get solution B. Slowly add solution A to 45ml solution B under constant stirring conditions of the magnetic agitator to obtain the mixture.

![Figure 1 Spherical particle preparation device](image)

A: Air compressor  B: Flowmeter  C: Syringe  D: Injector  E: Solidification  F: Part Water heating

Before making the ball, the manganese dioxide is sufficiently dried and ground, and the screening results in powder less than 150 mesh. An air compressor pumps air into a device that is drying the gas, which flows through the adjustable flow gas flow meter and then into the intake of the needle. After the device is ventilated and the gas flow is adjusted, the previously configured viscous solution is added to the syringe tube, and the solution flows down into the outlet of the needle port under the combined action of the gravity of the liquid itself and the constant current injection device. At the outlet of the needle, the air flow at a fixed uniform flow rate disperses the slurry into uniform droplets, which then fly into the beaker and form in a dimethyl silicone oil. The spherical particles are then dried at 60 degrees C.
2.3. Experimental method

2.3.1 Contact time affects the experiment
Formulated with a water solution with a concentration of 10mg/L, add the solution by solid liquid ratio of 0.02g:150mL in a series of plug triangular flasks, then oscillate in a water bath thermostat oscillator, remove a plug triangle flask from the oscillator at a time, and measure the concentration of the solution Sr\textsuperscript{2+} in the bottle with an atomic absorption diaphotometer.

2.3.2 Solution pH affects the experiment
Formulated with a water solution with a concentration of 10mg/L, the pH of the solution is adjusted with 10% HCl and 2mol/L NaOH to form a series of Sr\textsuperscript{2+} solutions with different pH (2.00 to 12.00) and 0.02g with adsorption material: 150mL is adsorbed in a Sr\textsuperscript{2+} solution with different pH values, and the Sr\textsuperscript{2+} concentration in the solution is determined separately when the adsorption balance is achieved.

2.3.3 Co-existing ions affect the experiment
Formulated with 20 solutions containing Sr\textsuperscript{2+} and one co-existing ion, the concentration of Sr\textsuperscript{2+} in the solution was 10mg/L, and the co-op ion concentration was 10mg/L, 50mg/L, 100mg/L, 200mg/L, 500mg/L, for a total of four surveys co-existing ions, K\textsuperscript+, Na\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+}. According to the solid-liquid ratio of 0.02g:150mL, the adsorption material is added to the solution to determine the concentration of Sr\textsuperscript{2+} in the solution after the adsorption balance.

2.3.4 The initial concentration of radon affects the experiment
The Sr\textsuperscript{2+} solution with concentrations of 10mg/L, 50mg/L, 100mg/L, 200mg/L, 500mg/L is formulated respectively, and the solid-liquid-to-solution ratio of the adsorption material to the solution is 0.02g:150mL when the solid-liquid adsorption system at different Sr\textsuperscript{2+} concentrations is formulated to achieve the adsorption balance. Measure the concentration of Sr\textsuperscript{2+} in the solution separately.

3. Results and Discussions

3.1. Characterization of spherical particles
Figure 2 shows that the adsorption material is approximately spherical, the surface of the microsphere is rough, there are a large number of holes and cracks, this structure is conducive to the rapid process of adsorption.
Figure 2 SEM photo of spherical particles

Figure 2 is a Fourier Infrared Spectroscopy (FT-IR) spectrogram of the adsorbed material. As can be seen from the figure, the absorption peak at 2800-3650 cm$^{-1}$ is caused by gap water and hydroxyl, and the absorption peak at 1650 cm$^{-1}$ belongs to the curved vibration of water molecules, and the absorption peak near 1301 cm$^{-1}$ is the telescopic vibration of C-O.

Figure 3 The Fourier Infrared Spectroscopy (FT-IR) spectra of adsorbed materials

Figure 4 N$_2$ adsorption-de-iso-temperature line of the adsorption material

Figure 4 is the N$_2$ adsorption-de-iso-temperature line of the adsorption material. As can be seen from the figure, the N$_2$ adsorption isohemline of adsorption material is approximate to V-type adsorption.
isohemline, and their N\textsubscript{2} adsorption-de-isohem line is a typical mesopoly-adsorption isohe
tic line, indicating that there are a large number of mesoporidium structures in the adsorption material.

3.2. *Spherical particles absorb the effects of Sr\textsuperscript{2+}*

3.2.1 *Contact time impact*

![Figure 5 Impact of contact time on adsorption material adsorption Sr\textsuperscript{2+}](image)

As can be seen from Figure 5, as the contact time increases, the adsorption capacity of the adsorption material to Sr\textsuperscript{2+} increases and the adsorption balance is reached near 8h, and the adsorption of the adsorption material to the Sr\textsuperscript{2+} is a fast-to-slow rate changing process, the adsorption material adsorption material at the beginning of the adsorption process is faster, at the rate of Sr\textsuperscript{2+} At 2h, the adsorption capacity reaches 77% of the balanced adsorption capacity, and at 3h, the adsorption capacity reaches 93% of the balanced adsorption capacity, after which the adsorption rate slows down until the adsorption balance is reached, and when the adsorption balance is balanced, the adsorption capacity of the adsorption material to Sr\textsuperscript{2+} is approximately 61 mg/g.

In determining the balanced adsorption capacity, the opt-in time is 14hin order for the adsorption material to fully adsorpt Sr\textsuperscript{2+} to achieve the adsorption balance.

3.2.2 *Effect of the pH of the solution*

![Figure 6 Effect of co-existing ions on adsorption material adsorption Sr\textsuperscript{2+}](image)

PH is an important media factor and one of the key factors affecting adsorption. This is due to the fact that, on the one hand, changes in the acidity and alkalinity of the solution affect the morphology of the solute molecules in the solution, and on the other hand, the pH of the solution has a strong influence on the surface condition and ionization of the adsorbent. In addition, hydrogen ions may compete with target ions.
Only solutions containing nitrate have a pH of 5.23, with the largest adsorption capacity, and an increase or decrease in pH will affect the adsorption capacity, with the least adsorption capacity at pH near 9.

### 3.2.3 Effect of the initial concentration of radon ions

![Figure 7](image.png)

As can be seen from the figure, the equilibrium adsorption of $\text{Sr}^{2+}$ changes with the initial concentration of $\text{Sr}^{2+}$ in the solution, i.e. as the initial concentration of $\text{Sr}^{2+}$ increases in the solution, the equilibrium adsorption capacity increases rapidly first, then flattens, when the solution is $\text{Sr}^{2+}$. The initial concentration is greater than 200mg/L when the equilibrium adsorption capacity tends to be constant. This may be because, when the initial concentration of $\text{Sr}^{2+}$ is low, increasing the concentration of $\text{Sr}^{2+}$ significantly increases the chance of contact between $\text{Sr}^{2+}$ and the adsorption bit, making full use of the adsorption bit on the adsorbent, but the number of adsorption bits on the adsorbent is limited, and when the initial concentration of $\text{Sr}^{2+}$ reaches a certain concentration, $\text{Sr}^{2+}$ The concentration continues to increase, leading to gradual saturation of adsorption.

### 3.2.4 The effects of co-existing ions

![Figure 8](image.png)

Absorption material Balanced adsorption capacity for $\text{Sr}^{2+}$ Increased concentration of 4 coexistence ions in the solution There is a similar trend of change, i.e. as the concentration of coexistence ions increases, the adsorption material has a flat adsorption capacity to $\text{Sr}^{2+}$. The volume drops sharply first, and then flattens, indicating that they have a strong inhibitory effect on the adsorption of $\text{Sr}^{2+}$ on the adsorption
material, and at the same concentration, the order of strength and weakness of the adsorption effect of different co-existing ions on the adsorption material adsorption Sr\(^{2+}\) inhibition adsorption is: Ca\(^{2+}\) ≥ Mg\(^{2+}\) > Na\(^{+}\) ≥ K\(^{+}\). There are two reasons for the above inhibition: first, co-existence ions shield the electrostatic gravity between Sr\(^{2+}\) and adsorption materials, and co-existing ions compete with Sr\(^{2+}\) for adsorption positions.

3.3. Spherical particles Adsorption the dynamics of Sr\(^{2+}\)

Using quasi-first-stage dynamic equations and quasi-secondary dynamic equations respectively, the adsorption process of spherical particles to Sr\(^{2+}\) is described and analyzed from the point of view of adsorption dynamics.

The quasi-level dynamic equation\(^{[4]}\) is:

\[
\ln(q_e - q_t) = ln q_e - k_1t
\]

(1)

The quasi-secondary dynamic equation\(^{[5]}\) is:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

(2)

in the formula, \(q_e\) is the balanced adsorption, mg/g; \(q_t\) is the adsorption amount after the adsorption time, mg/g; \(k_1\) is the primary rate constant, h\(^{-1}\); \(k_2\) is the secondary rate constant, g/(mg.h). The relevant dynamic parameters are obtained by plotting and calculating \(\ln(q_e-q_t)\) to \(t\) (Figure 9) and \(t/q_t\) to \(t\) (Figure 10), respectively. The results are listed in Table 1.

![Figure 9 The adsorption material adsorption Sr\(^{2+}\) quasi-primary dynamic fit curve](image)

![Figure 10 The adsorption material adsorption Sr\(^{2+}\) quasi-level second-stage dynamic fit curve](image)

As available from Figures 9, 10 and 1, the correlation coefficient \(R^2\) of the quasi-secondary dynamic equation is 0.9682, which is higher than the correlation coefficient of the quasi-primary dynamic equation 0.862, the balanced adsorption capacity calculated by the quasi-first-level dynamic equation and the quasi-secondary dynamic equation is compared with the experimental value, and the balanced adsorption capacity calculated by the quasi-level-two dynamic equation is closer to the experimental
value, so it can be considered that the quasi-level two dynamic equation can better describe the adsorption of Sr\(^{2+}\) on spherical materials\[^6\].

| Adsorption material adsorption dynamics parameters of Sr\(^{2+}\) |
|---------------------------------------------------------------|
| **quasi-first-level dynamic equations**                      | **quasi-second-level dynamic equation** |
| q(mg/g) | k\(_1\) (h\(^{-1}\)) | R\(^2\) | q(mg/g) | k\(_2\) (g/(mg·h)) | R\(^2\) |
| 33.89 | 0.3463 | 0.826 | 63.73 | 72.9 | 0.0105 | 0.9682 |

3.4. Spherical particles Adsorption of thermodynamic studies Sr\(^{2+}\)

The adsorption of spherical particle to Sr\(^{2+}\) is described in the Langmuir and Freundlich models, where:

The Langmuir model\[^7\] is:

\[
\frac{c_e}{q_e} = \frac{1}{Q_0K_L} + \frac{c_e}{Q_0}
\]

The Freundlich model\[^7\] is:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

Formula: q\(_e\) for balanced adsorption, mg/g; C\(_e\) for balanced concentration, mg/L; Q\(_0\) for saturation adsorption, mg/g; K\(_L\) for Langmuir constant related to adsorption capacity; K\(_F\) for Freundlich constant, 1/n is an unequal phase factor, which is related to adsorption strength. The results are shown in the table in C\(_e\)/q\(_e\) for C\(_e\) (Figure 11) and logq\(_e\) for logC\(_e\) (Figure 12).

![Figure 11 Adsorption material Is the contour of the Langmuir adsorption of Sr\(^{2+}\)](image)

![Figure 12 Adsorption material Adsorption contours for freedlich in Sr\(^{2+}\)](image)
Freundlich constant $K_F$, the non-homogeneous factor $1/n$ can be calculated with a $n$ value of 2.023, and in general, $n>1$ indicates that the adsorption is easy to adsorb by the adsorbent[8].

4. Conclusions

Based on the above findings, the following conclusions can be drawn:

1. Manganese dioxide adsorption materials have a strong adsorption capacity of $\text{Sr}^{2+}$, and at 2h, the adsorption capacity can reach 77 percent of the balanced adsorption capacity.

2. The balance adsorption of $\text{Sr}^{2+}$ changes with the change in the initial concentration of $\text{Sr}^{2+}$ in the solution, i.e. as the initial concentration of $\text{Sr}^{2+}$ increases in the solution, the equilibrium adsorption capacity increases rapidly and then flattens.

3. Absorption material Balanced adsorption capacity for $\text{Sr}^{2+}$ increased concentration of 4 co-existing ions in the solution. There is a similar trend of change, i.e. as the concentration of coexistence ions increases, the adsorption material has a balanced adsorption capacity to $\text{Sr}^{2+}$, the volume drops sharply first, and then flattens.

4. The adsorption dynamic equation describes the adsorption process, and the quasi-secondary dynamic equation can better describe the adsorption of $\text{Sr}^{2+}$ on the adsorption material than the quasi-primary dynamic equation.

5. The analysis results of the integrated particle intra-particle diffusion model and the liquid film diffusion model show that the intra-particle diffusion is the main factor affecting the adsorption rate during the adsorption of the adsorption material, but at the same time the membrane diffusion also has an effect on the adsorption rate.

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