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Remediation of Acid Mine Drainage in the Haizhou Open-Pit Mine through Coal-Gangue-Loaded SRB Experiments

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Abstract: To address the pollution problem of acid mine drainage (AMD) characterized by high concentrations of Fe^{2+}, Mn^{2+}, and $SO_4{}^{2-}$, a combination of coal gangue (CG) and sulfate-reducing bacteria (SRB) was employed. The effects of coal-gangue dosage, SRB inoculation concentration, and temperature on AMD treatment with coal-gangue-loaded SRB were determined through single-factor experiments and response surface methodology (RSM) experiments. By considering the principles of adsorption isotherms, adsorption kinetics, and reduction kinetics, the removal mechanisms of $SO_4{}^{2-}$, Fe^{2+}, and Mn^{2+} in AMD using coal gangue-loaded SRB in the the Haizhou open-pit mine was revealed. The results showed that the overall effectiveness of the four types of coal-gangue-loaded SRB in repairing AMD was as follows: 3# CG-loaded SRB > 2# CG-loaded SRB > 1# CG-loaded SRB > 4# CG-loaded SRB, with coal-gangue-loaded SRB in the the Haizhou open-pit mine showing the best performance. According to the RSM test, the optimum conditions for repairing AMD with coal-gangue-loaded SRB in the open-pit mine were a coal-gangue dosage of 52 g, SRB inoculation concentration of 11.7%, and temperature of 33.4 °C. The order of factors affecting the removal of $SO_4{}^{2-}$ and Fe^{2+} from AMD by SRB loaded on coal gangue was SRB inoculation concentration > temperature > coal-gangue dosage. For Mn^{2+}, the order of influence was temperature > SRB inoculation concentration > coal-gangue dosage. In the process of repairing Fe^{2+} with coal-gangue-loaded SRB in the the Haizhou open-pit mine, the biological activity metabolism of SRB played a leading role, while the adsorption isotherm of Mn^{2+} followed the Freundlich model. The adsorption kinetics of coal-gangue-loaded SRB in the the Haizhou open-pit mine for Fe^{2+} and Mn^{2+} in AMD conformed to Lagergren's second-order kinetic model, while the reduction kinetics of $SO_4{}^{2-}$ conformed to a first-order reaction model.

Keywords: sulfate-reducing bacteria (SRB); the Haizhou open-pit mine; coal gangue; acid mine drainage (AMD); load

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1. Introduction

Acid mine drainage (AMD) refers to acidic wastewater formed by the oxidation, weathering, rainfall, and other physical and chemical processes of sulfur-containing minerals in mining areas. AMD is characterized by high concentrations of $SO_4{}^{2-}$, Fe^{2+}, Mn^{2+}, and Al^{3+}, making it a significant environmental pollution problem faced by the global mining industry [1–3]. Furthermore, the instability of the water environment during mining process can easily lead to geological disasters [4,5]. For example, the Peșteana open-pit mine in Romania was affected by factors such as water injection speed, duration, and AMD, which increased the risk of geological disasters such as floods [6]. Currently, the main methods used for AMD remediation include neutralization, adsorption, biological treatment, and coagulation [7,8]. The adsorption method involves capturing ions present in AMD onto the surface of porous materials. While this method is effective at adsorbing metal ions, its efficiency in adsorbing SO_4^{2-} is poor. Therefore, the remediation of AMD containing SO_4^{2-}, Fe^{2+}, Mn^{2+}, and other metal ions remains a significant challenge in the field of environmental treatment in mining areas [9]. Specifically, it is necessary to focus on the remediation of pollution caused by AMD (including SO_4^{2-}, Fe^{2+}, and Mn^{2+}) in the water environment of mining areas. Finding a cost-effective and efficient adsorption material is the key to mine water environment remediation.

Coal gangue is a type of hard rock associated with coal and is the largest industrial solid waste generated during the coal mining and processing process [10–12]. In China, the average annual output of coal gangue is approximately 400 million tons, and the cumulative coal gangue total has exceeded 3.8 billion tons [13]. In recent years, efforts have been made to strengthen the treatment and utilization of coal gangue, mine water, and fly ash, aiming to develop a circular economy suitable for the coal industry cluster in accordance with the principles of reduction, reuse, and recycling. Yanlong Li et al. [14] demonstrated that by using a sludge: coal gangue: magnesite tailings ratio of 4.5:4:1.5 and sintering at 1250 °C, the prepared coal gangue ceramsite exhibited good performance with a compressive strength of 11 MPa. Chenxu Liu et al. [15] calcined coal gangue at 800 °C as a partial replacement of slag to prepare alkali-activated cement. Xinyu Li et al. [16] prepared alkali-activated foam using spontaneously combusted coal gangue as a raw material. Currently, coal gangue is primarily used to prepare ceramics, backfill materials, and additives for cement-based materials, but its utilization rate remains low, resulting in products with low added value [17,18]. Therefore, it is particularly important to develop new utilization methods for coal gangue and produce high-value coal gangue products [19]. It has been reported that coal gangue can be used as an inexpensive adsorbent in industrial wastewater pretreatment [20]. Jiushuai Deng et al. [21] prepared coal gangue using ammonium salt as a raw material and applied it in mine water treatment. The results showed that the material effectively removed over 50% of fluoride from both high-concentration (50 mg/L) and low-concentration fluoride wastewater (5 mg/L). The adsorption rate of fluoride was fast (1 min), and the pH value range of mine water was wide (4–11).

Ruifang Qiu [22] used calcined coal gangue as an adsorbent to remove Mn^{2+} from industrial wastewater. In view of the urgency of comprehensive utilization of coal gangue and the demand for organic pollution control in coal chemical water bodies, Chunquan Li [23] prepared a coal-gangue-based persulfate catalytic material using coal gangue as the raw material. The material demonstrated a degradation rate of 82.6% for phenol within 25 min. Xuying Guo and other researchers have shown that coal gangue can serve as the adsorption material for Fe^{2+} and Mn^{2+} in AMD. NaOH-modified spontaneous combustion coal gangue has a significant treatment effect on Fe^{2+} and Mn^{2+} in AMD, but it has a poor treatment effect on SO_4^{2-} [24,25]. Therefore, while coal gangue can be an effective absorbant for remedying Fe^{2+} and Mn^{2+} pollution in AMD, it exhibits a poor repairing effect on SO_4^{2-} in AMD. To address this, coal gangue can be combined with other materials. SRB in the microbial method can reduce SO_4^{2-} to sulfide [26] under anaerobic conditions, thus achieving the purpose of repairing SO_4^{2-} pollution in AMD. Xianjun Wang et al. [27] showed that SRB can effectively remove SO_4^{2-} in AMD and improve the pH value of AMD. Junzhen Di et al. [28] showed that SRB can efficiently repair AMD pollution and metabolize SO_4^{2-} to form metal sulfide precipitation. However, SRB is sensitive to the environmental pH value and concentration of heavy metal ions [29]. Therefore, the combination of coal gangue and SRB not only effectively removes metal ions in AMD but also removes SO_4^{2-}, reducing the environmental pollution of AMD. Coal-gangue-loaded SRB not only improves the inadequate removal of SO_4^{2-} in AMD by coal gangue but also mitigates the adverse influence of the surrounding environment on SRB growth by using the adsorption performance of coal gangue. Additionally, coal gangue is readily available as a solid waste in mining areas, making it a convenient and cost-effective material for remediating AMD. The remediation of AMD using coal-gangue-loaded SRB exemplifies the concept of “treating waste with waste”. Consequently, coal-gangue-loaded SRB is a convenient and affordable solution for repairing AMD.

In this study, coal gangue and SRB were used as materials to prepare coal-gangue-loaded SRB materials by the combined adsorption method and microbial method to solve the pollution problem of AMD with a high content of Fe^{2+}, Mn^{2+} and SO_4^{2-}. Based on the single-factor experiment and response surface experiment, the effects of coal-gangue dosage, SRB inoculation concentration and temperature on AMD treatment with coal-gangue-loaded SRB were determined. Based on the principles of adsorption isotherms, adsorption kinetics and reduction kinetics, the removal mechanism of SO_4^{2-}, Fe^{2+} and Mn^{2+} in AMD using coal-gangue-loaded SRB in the Haizhou open-pit mine was revealed. This was performed in order to obtain a convenient, cheap and efficient AMD repair material, and provide a new technology for environmental pollution remediation in mining areas.

2. Materials and Methods

2.1. Test Materials

Coal gangue: the spontaneous-combustion of coal gangue from Gaode mine in Fuxin City (42°0′39.43″ N, 121°42′4.85″ E), Liaoning Province (1# CG); the spontaneous combustion of coal gangue from the Haizhou open-pit mine in Fuxin City (42°0′9.90″ N, 121°41′12.36″ E), Liaoning Province (2# CG); coal gangue from the Haizhou open-pit mine (3# CG); and coal gangue from a mine in Jincheng City (112°43′ E, 35°47′ N), Shanxi Province (4# CG) were crushed and screened, respectively, soaked with distilled water three times, and dried at 80 °C. A picture of the samples is shown in Figure 1a.

(**a**) (**b**)

Figure 1. Sludge samples and cultured SRB samples taken from the foot of a coal gangue mountain. (**a**) Sludge samples taken from the foot of a coal gangue mountain. (**b**) Cultured SRB samples.

SRB: The wet mud from the lower part of the coal gangue hill in the Haizhou open-pit mine (42°0′9.90″ N, 121°41′12.36″ E) was taken as the seed mud, and the SRB was anaerobically cultured using Starkey medium [25,28]. SRB, after separation and purification, was used in this study. The SRB used in this experiment belongs to Desulfotomaculum; the NCBI accession number is MT804386. The main components of Starkey medium were K_2HPO_4, 0.5 g/L; NH_4Cl, 1.0 g/L; $MgSO_4 \cdot 7H_2O$, 2.0 g/L; Na_2SO_4, 0.5 g/L; $CaCl_2 \cdot H_2O$, 0.1 g/L; yeast extract, 1.0 g/L; sodium lactate, 4 mL/L; $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, 0.5 g/L; ascorbic acid, 0.1 g/L; pH = 7.0. The cultured SRB is shown in Figure 1b.

2.2. Test Methods

2.2.1. Completely Randomized Design

A completely randomized design was used to explore the influence of five factors, namely, the type of coal gangue (1–4# CG), the dosage of coal gangue (20, 30, 40, 50 and 60 g), the amount of SRB inoculation (5%, 10%, 15%, 20% and 25%), the cultural temperature (20, 25, 30, 35 and 40 °C) and the oscillation frequency (0, 50, 100, 150 and 200 r/min), on the effect of coal-gangue-loaded SRB on AMD remediation. Coal gangue, 20 mL culture medium and 80 mL sterile water were added to a conical flask, respectively. SRB was inoculated and sealed with liquid paraffin and a rubber stopper to form an anaerobic environment. The container was put in a constant temperature oscillator at 35 °C and 150 r/min for 24 h. A volume of 400 mL AMD solution was added, and it was placed in a constant-temperature oscillator for a certain period of time. The supernatant was then filtered, and the pH value (GB 6920-86 [30]), ORP value (SL 94-1994 [31]), and the concentrations of SO_4^{2-} (HJ/T 342-2007 [32]), Fe^{2+} (HJ/T 345-2007 [33]) and Mn^{2+} (GB 11906-1989 [34]) were measured. Based on the research results of Guo Xuying et al. [24,25], AMD was prepared by experimental simulation. The pH of AMD was 5, and the concentrations of Fe^{2+}, Mn^{2+} and SO_4^{2-} were 50, 20 and 1000 mg/L, respectively. The test was repeated 3 times to calculate the removal rate.

2.2.2. Response Surface Methodology (RSM)

Based on the randomized design results, three factors, the amount of coal gangue, the amount of SRB inoculation, and the culture temperature, were selected, and compared with the removal rate changes of SO_4^{2-}, Fe^{2+}, and Mn^{2+} after repairing the AMD for 4 d with coal-gangue-loaded SRB from the Haizhou open-pit mine, under optimum conditions. At the same time, we analyzed the influence of the interaction of the different factors (coal-gangue dosage, SRB inoculation concentration, culture temperature and other factors) on the remediation of AMD using coal-gangue-loaded SRB in the Haizhou open-pit mine. The RSM parameters and test results are shown in Table 1.

Table 1. Response surface test results of coal-gangue-loading SRB to treat AMD in the Haizhou open-pit mine.

Number	Variable			Response Value		
	A: Coal-Gangue Dosage (g)	B: SRB Inoculation Concentration (%)	C: Temperature (°C)	SO_4^{2-} Removal Rate (%)	Fe^{2+} Removal Rate (%)	Mn^{2+} Removal Rate (%)
1	40	5	30	63.61	90.65	80.13
2	60	5	30	70.87	93.94	81.44
3	40	15	30	78.21	96.82	81.43
4	60	15	30	79.54	98.34	80.72
5	40	10	20	66.95	89.87	62.19
6	60	10	20	68.18	91.26	70.22
7	40	10	40	64.58	94.33	85.55
8	60	10	40	82.08	99.21	83.09
9	50	5	20	68.23	93.87	64.23
10	50	15	20	69.73	98.34	67.75
11	50	5	40	73.02	96.12	73.11
12	50	15	40	85.17	98.22	79.17
13	50	10	30	88.57	98.54	87.63
14	50	10	30	87.23	98.25	86.85
15	50	10	30	89.71	99.69	86.31
16	50	10	30	88.16	99.24	85.51
17	50	10	30	87.13	98.32	85.97

2.2.3. Tests to Reveal the Mechanism

To reveal the mechanism of coal-gangue-loaded SRB in repairing Fe^{2+}, Mn^{2+}, SO_4^{2-} in AMD, we produced an adsorption isotherm test and an adsorption kinetics test for Fe^{2+} and Mn^{2+}, respectively, and a reduction kinetics test for SO_4^{2-}. The specific methods were as follows:

The test method for the adsorption isotherm of Fe^{2+} and Mn^{2+} in AMD repaired using coal-gangue-loaded SRB in the Haizhou open-pit mine was as follows: 50 g coal-gangue-loaded SRB material from the Haizhou open-pit mine was added into 5 volumes of 100 mL Fe^{2+} solution with different initial concentrations (50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L). After oscillating for 4 d at 35 °C and 100 r/min, the residual Fe^{2+} concentration in the system was measured, and the Fe^{2+} adsorption capacity was calculated. Each test was repeated three times, and the average value was taken to plot the results. The steps of the Mn^{2+} isothermal adsorption test were similar to those of the Fe^{2+} isothermal adsorption test. The initial Mn^{2+} concentrations were 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L, respectively.

The adsorption kinetics test method for repairing Fe^{2+} and Mn^{2+} in AMD with coal gangue-loaded SRB from the Haizhou open-pit mine was as follows: 50 g of coal-gangue-loaded SRB material and 100 mL of AMD (containing 1000 mg/L $SO_4{}^{2-}$) were added into several conical flasks. These were shaken at 35 °C and 100 r/min for 1 d, 2 d, 3 d, 4 d, 5 d, and 6 d, respectively. Then, they were allowed to stand for a period of time before being filtered. The concentration of residual Fe^{2+} and Mn^{2+} in the wastewater system was measured, and the adsorption concentration of Fe^{2+} and Mn^{2+} in the AMD was calculated. Each test was repeated three times, and the average value was taken to plot results.

The reduction kinetics test method for repairing $SO_4{}^{2-}$ in the AMD with coal-gangue loaded-SRB was as follows: 50 g of coal-gangue-loaded SRB material and 100 mL of AMD (containing 1000 mg/L $SO_4{}^{2-}$), respectively, were added into several conical flasks. These were then shaken at 35 °C and 100 r/min for 1 d, 2 d, 3 d, 4 d, 5 d, and 6 d, respectively, then allowed to stand for a while before being filtered. The residual $SO_4{}^{2-}$ concentration was measured, and the concentration reduction of $SO_4{}^{2-}$ in the AMD using coal-gangue-loaded SRB the Haizhou was calculated. Each test was repeated three times, and the average value was taken for plotting the results.

2.3. Test Apparatus

The main instruments used in the experiment were a thermostatic incubator (Changzhou Kaihang Instrument Co., Ltd., Changzhou, China, HZ-9811K type); an ultra-clean bench (Suzhou, China, VD-650 type); a CO_2 anaerobic incubator (Shanghai Likang Co., Ltd., Shanghai, China, HF151 type); a portable pressure steam sterilizer (Shanghai Boxun Biomedical Instrument Co., Ltd., Shanghai, China, YXQ-LS-18SI type); an electronic balance (Shanghai Ligu Instrument Co., Ltd., Shanghai, China, BS-224-S type); an electric hot-blast drying oven (Shanghai Boxun Medical Biological Instrument Co., Ltd., Shanghai, China, GZX-9246MBE type); a PHS-3C pH meter (Shanghai Yidian Scientific Instrument Co., Ltd., Shanghai, China); a CT-8022 ORP meter (Shanghai Hechen Energy Technology Co., Ltd., Shanghai, China); a V-1600PC visible spectrophotometer (Shanghai Yuanwang Liquid Level Meter Co., Ltd., Shanghai, China); and a Z-2000 flame atomic spectrophotometer (Hitachi Co., Japan) among other instruments.

3. Results and Discussion

3.1. Analysis of Single-Factor Test Results

It can be seen from Figure 2 that the type of coal gangue had a definite impact on the remediation of AMD pollution using coal-gangue-loaded SRB. The comparison of the effect of the type of gangue-loaded SRB at repairing the AMD was as follows: 3# CG-loaded SRB > 2# CG-loaded SRB > 1# CG-loaded SRB > 4# CG-loaded SRB. Among them, 3# CG-loaded SRB had the best remediation effect on AMD; the removal effect was better on the 4th day and increased slowly in the later period. After AMD was treated by 3# CG-loaded SRB for 4 d, the pH increased to 6.90, and the removal rates of $SO_4{}^{2-}$, Fe^{2+} and Mn^{2+} were 84.9%, 99.3% and 85.4%, respectively. After being treated for 6 d, the pH value increased to 7.71, and the ORP value decreased from 243 mV to −160 mV, indicating that the weak alkalinity and the trace elements released by 3# CG promoted the growth of SRB, resulting in an alkalinity and ORP reduction in the SRB metabolism. It has been shown that the activity of anaerobic bacteria such as SRB can reduce the ORP value, and the process of SRB metabolizing sulfate is accompanied by an increase in pH [35,36].

When the microbial growth conditions result in an ORP < −100 mV and 5 < pH < 9, SRB organisms are dominant [37]. The neutral pH is beneficial to the growth and metabolism of SRB [38]. The reports above have also reflected that SRB can grow well on the surface of coal gangue. Therefore, the environment provided by 3# CG could continuously promote SRB metabolism, enabling SRB to cooperate with 3# CG to remove SO_4^{2-}, Fe^{2+} and Mn^{2+} from AMD continuously. Previous studies have shown that the sulfur content in 1# CG and 4# CG was high, and the pH of 1# CG and 4# CG leachate was acidic, which is not conducive to the initial growth of SRB [39]. At the same time, previous studies have also shown that 2# CG and 3# CG contained more alkali metal compounds such as K, Na, Ca and Mg, and the release of some soluble alkaline substances caused the leaching solution of 2# CG and 3# CG to become alkaline. The alkalinity of the 3# CG leachate was stronger than that of 2# CG [39]. The alkaline environment of the 3# CG leaching solution was more conducive to the growth and propagation of SRB, which caused the pH value of the 3# CG-loaded SRB-repaired AMD effluent to increase faster, and the ORP value to decrease faster; the SO_4^{2-} removal was more obvious. According to the report of Kyoungkeun, a decrease in the ORP value can reflect the activity of SRB and the efficiency of SRB at metabolizing SO_4^{2-} [40]. The increase in pH, the decrease in ORP and the obvious removal of SO_4^{2-} can indicate that SRB is thriving in the 3# CG environment. Combined with the removal rate of SO_4^{2-}, Fe^{2+} and Mn^{2+}, the overall effect of the four types of coal-gangue-loaded--SRB to remove SO_4^{2-}, Fe^{2+} and Mn^{2+} was as follows: 3# CG-loaded SRB > 2# CG-loaded SRB > 1# CG-loaded SRB > 4# CG-loaded SRB. We performed a comprehensive analysis of the effluent change in the pH and ORP values, and the SO_4^{2-}, Fe^{2+}, and Mn^{2+} removal rates after application of the four types of coal-gangue-loaded SRB, reflecting the reparation of AMD pollution. Therefore, 3# CG was selected as the research material for subsequent tests.

The effects of the dosage of coal cangue, SRB inoculation, culture temperature and oscillation frequency on the remediation of AMD using coal-gangue-loaded SRB in the Haizhou open-pit mine are shown in Figure 3. It can be seen from Figure 3a that the remediation effect of coal-gangue-loaded SRB on pollutants in AMD gradually increased with the increase in coal-gangue dosage, but that the rate of increase decreased. When 50 g coal gangue was added for treat for 4 d, the pH value reached 6.99, and the removal rates of SO_4^{2-}, Fe^{2+} and Mn^{2+} were 85%, 99.26% and 85.6%, respectively. It can be seen from Figure 3b that with the increase in SRB inoculation concentration, the pH value gradually increased, and the removal rates of SO_4^{2-}, Fe^{2+}, and Mn^{2+} also increased. When inoculated with 5% SRB for 4 days, the Fe^{2+} removal rate was 89.71%. When the SRB inoculation concentration was $\geq$ 10%, the removal rate of Fe^{2+} was stable at above 99%, and the repair of pH, SO_4^{2-} and Mn^{2+} showed an increasing trend. However, based on the fact that SRB can reproduce in large quantities after adapting to a new environment, 10% SRB was selected as the optimal inoculation concentration. It can be seen from Figure 3c that when the temperature increased from 20 °C to 35 °C, the ability of coal-gangue-loaded SRB to remedy AMD showed an increasing trend. Treatment at 35 °C for 4 days produced the best remediation effect. The pH value of the system was 6.90, and the removal rates of SO_4^{2-}, Fe^{2+} and Mn^{2+} were 84.88%, 99.25% and 85.40%, respectively. The remediation effect showed an integral decreasing trend at 40 °C, indicating that excessive temperature inhibited SRB metabolism, which was not conducive to the remediation of AMD. In addition, a high temperature was not conducive to the adsorption of metal ions by coal gangue. According to Mansoor et al. [41], at a higher temperature, Fe ions obtain more kinetic energy, which enables Fe ions to overcome potential adsorption, leading to a decrease in their removal rate. Therefore, 35 °C was selected as the optimal cultural temperature. It can be seen from Figure 3d that the coal-gangue-loaded SRB could remedy AMD in standing conditions, and that the remediation effect firstly increased and then decreased with the increase in oscillation frequency. The removal rates of SO_4^{2-} and Fe^{2+} were 85.87% and 99.30%, respectively, at 100 r/min for 4 days. When at 150 r/min, the pH value increased to 6.9, and the removal rate of Mn^{2+} reached 85.40%. Optimally increasing the oscillation frequency enlarged the contact areas between SRB and AMD, and improved the remediation effect. However, when the oscillation frequency was too fast, it prevented SRB from attaching to the surface of the coal gangue, which limited its growth. Therefore, 100 r/min was selected as the optimal oscillation frequency. By comparing the removal rates of Fe^{2+} and Mn^{2+}, it can be seen that the removal effect of gangue-loaded SRB on Fe^{2+} in the the Haizhou open-pit mine was obviously better than that of Mn^{2+}. It has been previously reported that the removal of Fe^{2+} and Mn^{2+} by SRB is mainly in the form of metal sulfide precipitation. Due to $K_{sp}(MnS) > K_{sp}(FeS)$, Mn^{2+} is inhibited from forming stable sulfides [42,43] in the presence of Fe^{2+}. At the same time, there were differences in the adsorption between Fe^{2+} and Mn^{2+} ions by the coal gangue. Previous research has shown that the adsorption of Fe^{2+} by the coal gangue was noticeably better than that of Mn^{2+} [24,25]. At the same time, Liu Fabang et al. [44] found a similar conclusion when adsorbing Co^{2+}/Mn^{2+} using Co^{2+}/Mn^{2+}-imprinted adsorbent grafted by cysteine (Cys-Co/Mn-CCTS). The adsorption of Co^{2+} was significantly better than that of Mn^{2+} using Cys-Co/Mn-CCTS [44]. The difference between SRB and the coal gangue in removing Fe^{2+} and Mn^{2+} allows us to conclude that the removal efficiency of Fe^{2+} using coal-gangue-loaded SRB in the Haizhou open-pit mine was obviously better than that of Mn^{2+}.

3.2. Analysis of the RSM Results

The RSM results of using coal-gangue-loaded SRB to treat AMD in the Haizhou open-pit mine are shown in Table 1 and Figure 4.

The experimental parameters in Table 1 were evaluated using the quadratic multiple regression model of Design-Expert 8.0 software created by Stat-Ease(Minneapolis, MN 55413-2561, US). The quadratic multiple regression model between the response value and the factors of the Design-Expert 8.0 software is:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \beta_{ij} X_i X_j$$

where Y represents response value, β_0 represents the offset migration coefficient, β_i represents the independent-variable linear offset coefficient, β_{ii} represents the second-order offset coefficient of the independent-variable, β_{ij} represents the independent-variable interaction effect coefficient, and X_i, X_j, X_iX_j represent the level values of each factor used to analyze the main effects and interaction effects of each factor.

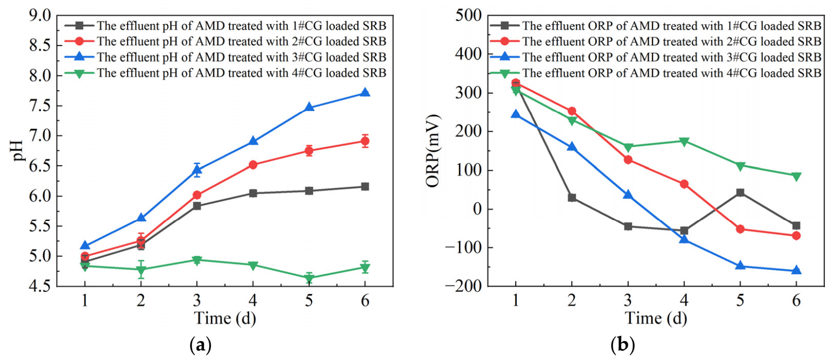


Figure 2. *Cont.*

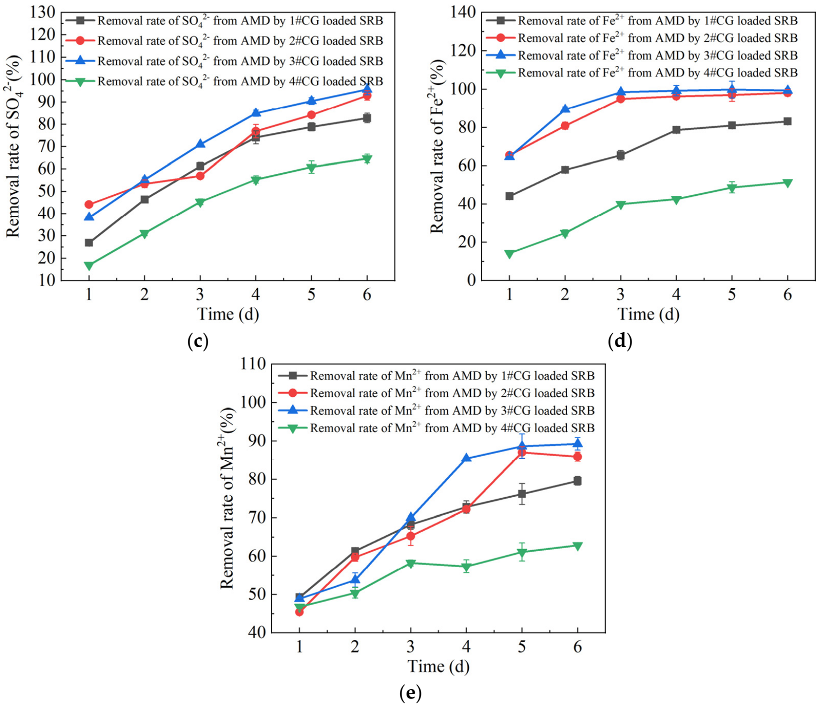


Figure 2. Impact of coal gangue type. (**a**) The effluent pH of AMD treated with 1#CG~4#CG-loaded SRB. (**b**) The effluent ORP of AMD treated with 1#CG~4#CG-loaded SRB. (**c**) Removal rate of $SO_4{}^{2-}$ from AMD by 1#CG~4#CG-loaded SRB. (**d**) Removal rate of Fe^{2+} from AMD by 1#CG~4#CG-loaded SRB. (**e**) Removal rate of Mn^{2+} from AMD by 1#CG~4#CG-loaded SRB.

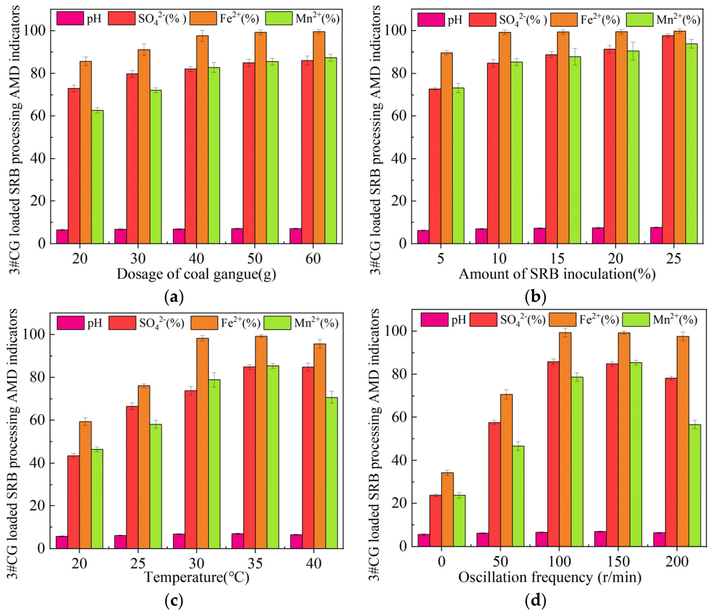


Figure 3. Inoculation concentration (**a**) Effects of gangue dosage, (**b**) SRB inoculation concentration, (**c**) culture temperature, and (**d**) oscillation frequency. The pH in the figure refers to the pH value of water after AMD treatment under different 3#CG-loaded SRB conditions. $SO_4{}^{2-}$ (%) refers to the removal percentage of $SO_4{}^{2-}$ in water after AMD treatment under different 3# CG-loaded SRB conditions, %. Fe^{2+} (%) refers to the removal percentage of Fe^{2+} in water after AMD treatment under different 3# CG-loaded SRB conditions, %. Mn^{2+} (%) refers to the removal percentage of Mn^{2+} in water after AMD treatment under different 3# CG-loaded SRB conditions, %.

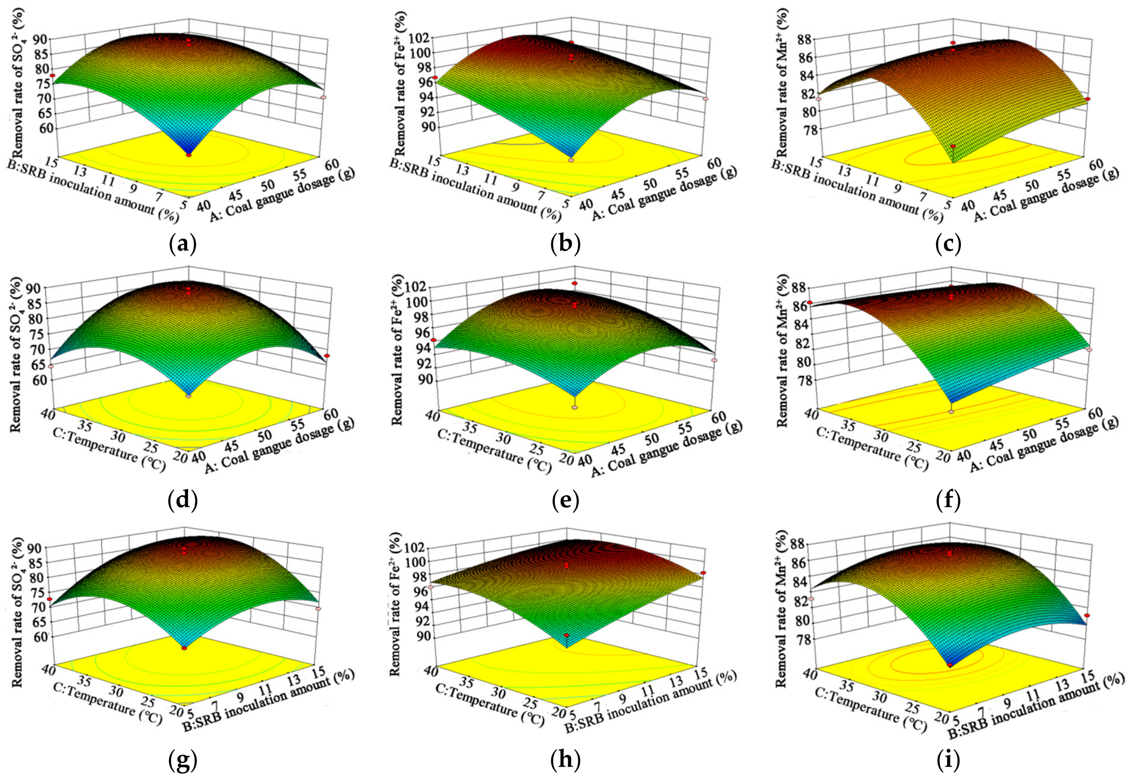


Figure 4. Response of gangue dosage (A), SRB inoculation concentration (B) and temperature (C) on the AMD removal effect of gangue-loaded SRB. (**a**) Response of A and B to SO_4^{2-} removal. (**b**) Response of A and B to Fe^{2+} removal. (**c**) Response of A and B to Mn^{2+} removal. (**d**) Response of A and C to SO_4^{2-} removal. (**e**) Response of A and C to Fe^{2+} removal. (**f**) Response of A and C to Mn^{2+} removal. (**g**) Response of B and C to SO_4^{2-} removal. (**h**) Response of B and C to Fe^{2+} removal. (**i**) Response of B and C to Mn^{2+} removal.

Through the above Design-Expert 8.0 software model, the quadratic multiple regression model was obtained; the removal rate of SO_4^{2-}, Fe^{2+}, and Mn^{2+} in AMD using coal-gangue-loaded SRB the Haizhou open-pit mine were are as follows:

$$SO_4^{2-}\text{ removal rate (\%)} = 88.16 + 3.42 \times A + 4.62 \times B + 3.97 \times C - 1.48 \times A \times B + 4.07 \times A \times C + 2.66 \times B \times C - 9.35 \times A^2 - 5.76 \times B^2 - 8.37 \times C^2,\ R^2 = 0.9730.$$

$$Fe^{2+}\text{ removal rate (\%)} = 98.81 + 1.39 \times A + 2.14 \times B + 1.82 \times C - 0.44 \times A \times B + 0.87 \times A \times C - 0.59 \times B \times C - 3.42 \times A^2 - 0.45 \times B^2 - 1.72 \times C^2,\ R^2 = 0.8982.$$

$$Mn^{2+}\text{ removal rate (\%)} = 86.45 + 0.77 \times A + 1.27 \times B + 7.07 \times C - 0.51 \times A \times B - 2.62 \times A \times C + 0.64 \times B \times C - 0.66 \times A^2 - 4.86 \times B^2 - 10.53 \times C^2,\ R^2 = 0.9565.$$

In the formula above, A represents coal-gangue dosage; its unit is g. B represents the SRB inoculation concentration; its unit is %. C represents temperature; its unit is °C.

The F value of the second-order model of the SO_4^{2-}, Fe^{2+}, Mn^{2+} removal rates in AMD were 28.06, 6.86, and 17.11, respectively. Additionally, the p values were 0.0001, 0.0094, and 0.0006, respectively, which indicated that the regression of the three models above was good and the model was highly significant. The accuracies of the three models were 13.71, 7.55 and 11.54, respectively, all of which were >4, and the fit of the models was reasonable. The variation coefficients of the three models were 2.47%, 1.57% and 0.59%, respectively, all of which were less than 10%, indicating that the models had credibility and precision. Therefore, the three models above were suitable for predicting and analyzing the removal rates of SO_4^{2-}, Fe^{2+} and Mn^{2+} in AMD using coal-gangue-loaded SRB.

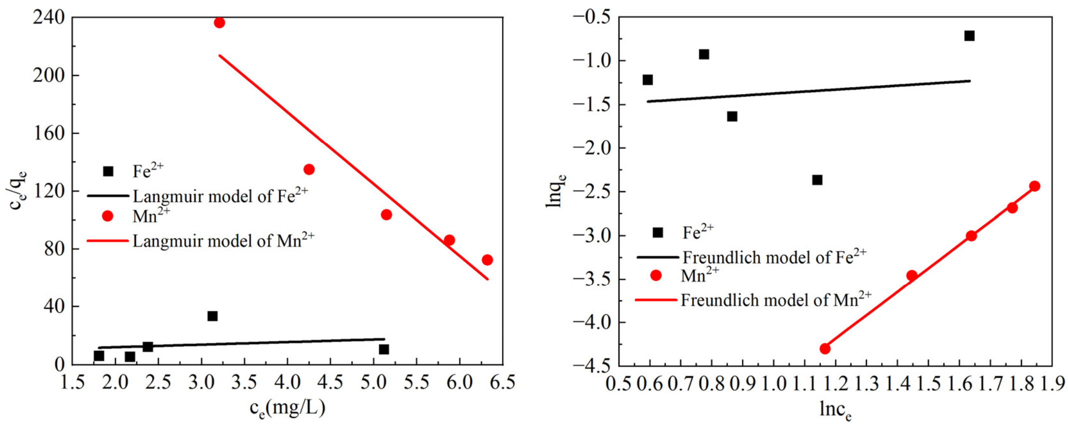
The effects of coal-gangue dosage (A), SRB inoculation concentration (B) and temperature (C) on the removal of SO_4^{2-}, Fe^{2+} and Mn^{2+} in AMD using coal-gangue-loaded SRB are shown in Figure 4. Figure 4a–c shows the effect of the coal-gangue dosage and SRB inoculation concentration on the AMD removal capacity using coal-gangue-loaded SRB. Variance analysis showed that the effects of the single-factor coal-gangue dosage on the removal rates of SO_4^{2-}, Fe^{2+} and Mn^{2+} were highly significant, significant and insignificant, respectively. There were interactions between the coal-gangue dosage and the SRB inoculation concentration, but these were not significant. The significance levels were 0.2459, 0.5885 and 0.5885, respectively, which were higher than 0.05. Figure 4d–f shows the effect of coal-gangue dosage and temperature on the AMD removal capacity of coal-gangue-loaded SRB. The effect of single-factor temperature on the SO_4^{2-}, Fe^{2+} and Mn^{2+} removal rates reached highly significant, significant and extremely significant levels, respectively. There were interactions between coal-gangue dosage and temperature on the SO_4^{2-} removal rate which were significant ($p = 0.0103$). There were also interactions between coal-gangue dosage and temperature on the removal rate of Fe^{2+} and Mn^{2+} which were not significant. Figure 4g–i shows the effect of the SRB inoculation concentration and temperature on the AMD removal capacity of coal-gangue-loaded SRB. The effect of single-factor SRB inoculation concentration on the SO_4^{2-}, Fe^{2+} and Mn^{2+} removal rates reached extremely significant, highly significant and insignificant levels, respectively. There were interactions between the SRB inoculation concentration and temperature on SO_4^{2-}, Fe^{2+}, Mn^{2+} removal rates but these were not significant.

The RSM results indicated that the best conditions for remedying AMD using coal-gangue-loaded SRB in the Haizhou open-pit mine were as follows: a coal-gangue dosage of 52 g, an SRB inoculation concentration of 11.7%, and a temperature of 33.4 °C. In this condition, after repairing AMD for 4 d using coal-gangue-loaded SRB in the Haizhou open-pit mine, the theoretical removal rates of SO_4^{2-}, Fe^{2+} and Mn^{2+} were 90.2%, 100% and 87.5%, respectively. Under the conditions of 52 g of coal-gangue dosage, an SRB inoculation concentration in 11.7%, and a temperature of 33–34 °C, the actual removal rates of SO_4^{2-}, Fe^{2+} and Mn^{2+} in AMD using coal-gangue-loaded SRB were 89.76%, 99.66% and 87.95%, respectively. The difference between the experimental value and the theoretical value was small, and the error was within the allowable range, which showed that the model can analyze and predict the effect of treating AMD using coal-gangue-loaded SRB in the Haizhou open-pit mine truly and accurately. After conducting a comprehensive analysis for the F value in Figure 4, the influence order of the single-factor coal-gangue dosage, the SRB inoculation concentration and the temperature on the removal of SO_4^{2-} and Fe^{2+} in AMD was as follows: SRB inoculation concentration > temperature > coal-gangue dosage. The influence order of single factors on the removal of Mn^{2+} in AMD using coal-gangue-loaded SRB was as follows: temperature > SRB inoculation concentration > coal-gangue dosage.

3.3. Analysis of AMD Characteristic Test Results of Coal-Gangue-Loaded SRB Treatment in the Haizhou Open-Pit Mine

3.3.1. Analysis of the Fe^{2+} and Mn^{2+} Adsorption Isotherm Test Results

Langmuir and Freundlich adsorption isotherm models were used to fit the Fe^{2+} and Mn^{2+} adsorption when using coal-gangue-loaded SRBthe Haizhou, and the fitting results are shown in Figure 5.



(**a**) (**b**)

Figure 5. Adsorption isotherm fitting of Fe^{2+} and Mn^{2+} removal using coal gangue loaded with SRB in the Haizhou open-pit mine. (**a**) Langmuir fitting curve. (**b**) Freundlich fitting curve.

Langmuir adsorption model:

$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m}$$

Freundlich adsorption model:

$$lnq_e = lnk_f + \frac{1}{n} lnc_e$$

In the formulae above, q_e represents the equilibrium adsorption capacity, and its unit is mg/g; c_e represents the equilibrium concentration, and its unit is mg/L; k_L is the Langmuir adsorption constant; q_m is the saturated adsorption capacity; k_f is the Freundlich adsorption equilibrium constant, and is related to the types and characteristics of adsorbents; and n is Freundlich adsorption equilibrium constant.

It can be seen from Figure 5 that the Langmuir fitting curve of the coal-gangue-load SRB with the Fe^{2+} concentration in the Haizhou open-pit mine was

$$c_e/q_e = 8.32173 + 1.78008c_e, R^2 = -0.27727.$$

The Freundlich fitting curve was:

$$\ln q_e = -1.59769 + 0.22575 \ln c_e, R^2 = -0.30737.$$

The value of $R^2{}_{\text{Langmuir}}(Fe^{2+})$ and $R^2{}_{\text{Freundlich}}(Fe^{2+})$ were both negative numbers, indicating that the adsorption model of Fe^{2+} when using coal-gangue-loaded SRB was neither the Freundlich model nor the Langmuir model, suggesting that the adsorption process of Fe^{2+} using coal-gangue-loaded SRB mainly depended on the dominant role of SRB bioactivity The Langmuir fitting curve of the coal-gangue-load SRB concentration to the Mn^{2+} concentration in the Haizhou open-pit mine was:

$$c_e/q_e = 373.55453 - 49.75181\ c_e, R^2 = 0.87338.$$

The Freundlich fitting curve was:

$$\ln q_e = -7.40145 + 2.68525\ \ln c_e, R^2 = 0.99962.$$

By comparison we could found that $R^2{}_{\text{Langmuir}}$ (Mn^{2+}) < $R^2{}_{\text{Freundlich}}$ (Mn^{2+}), indicating that the adsorption model of Mn^{2+} using coal-gangue-loaded SRB in the Haizhou open-pit mine was more in line with the Freundlich model, and the adsorption process of Mn^{2+} was mainly multi-molecular layer adsorption. Wu et al. [11] discovered that coal gangue has obvious adsorption characteristics toward Pb^{2+} and Zn^{2+}, and that the Langmuir model can fit coal gangue's adsorption level of Pb^{2+} and Zn^{2+} better. Compared with the studies above, the previous studies only used coal gangue to adsorb metal ions. In our study, the adsorption of Mn^{2+} using coal-gangue-loaded SRB was mainly multi-molecular layer adsorption. The main reason for this is that there are a large number of pores in coal gangue; SRB can be loaded onto the surface and into the internal voids, resulting in the adsorption of Mn^{2+} in accordance with the Freundlich model.

3.3.2. Analysis of the Results of the Fe^{2+} and Mn^{2+} Adsorption Kinetics Test

Lagergren's first-order and second-order adsorption kinetic equations, the origin 2023 software and a particle expansion model were used to analyze the adsorption kinetic process of Fe^{2+} and Mn^{2+} while using coal-gangue-loaded SRB in the Haizhou open-pit mine. The results are shown in Figure 6 and Table 2.

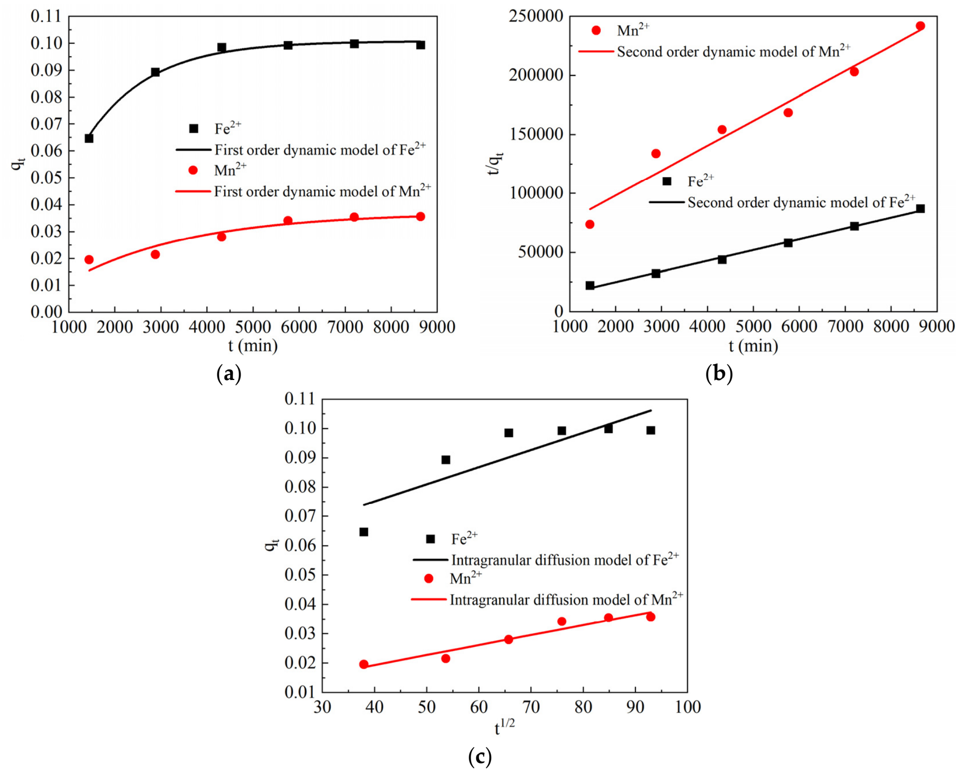


Figure 6. Dynamic fit diagram of Fe^{2+} and Mn^{2+} adsorption using coal-gangue-loaded SRB in the Haizhou open-pit mine. (**a**) First order dynamic model. (**b**) Second order dynamic model. (**c**) Intragranular diffusion model.

Table 2. Kinetic parameters of the adsorpbtion of Fe^{2+} and Mn^{2+} by coal-gangue-loaded SRB in the Haizhou open-pit mine.

Dynamic Model	Parameter	Adsorbent Fe^{2+}	Adsorbent Mn^{2+}
First-order dynamic model	k_1	7.33171×10^{-4}	3.76372×10^{-4}
	q_e	0.10081	0.03716
	R^2	0.99038	0.85009
Second-order dynamic model	k_2	0.01197	0.00792
	q_e	0.11027	0.04740
	R^2	0.99371	0.95363
Intraparticle diffusion model	k_3	5.86623×10^{-4}	3.41275×10^{-4}
	c	0.05164	0.00569
	R^2	0.67433	0.91709

Lagergren's first-order adsorption kinetic model is

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

and the formula can be changed into:

$$q_t = q_e(1 - \mathrm{e}^{-k_1 t})$$

Lagergren's second-order adsorption kinetic model:

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

The intraparticle diffusion model:

$$q_t = k_3 \cdot t^{1/2} + c$$

In the formulae above, q_t represents the adsorption capacity at time t, mg/L; t represents the adsorption time, min; k_1 represents the first-order kinetic rate constant, 1/min; k_2 represents the second-order kinetic rate constant, mg/(g·min); and k_3 represents the intraparticle diffusion rate constant, mg/(g·min$^{1/2}$).

It can be seen from Figure 6 and Table 2 that when adsorbing Fe^{2+} and Mn^{2+} using coal-gangue-loaded SRB the Haizhou open-pit mine, $R^2_{\text{Second order}}(Fe^{2+}) > R^2_{\text{First order}}(Fe^{2+}) > R^2_{\text{Intraparticle diffusion}}(Fe^{2+})$, $R^2_{\text{Second order}}(Mn^{2+}) > R^2_{\text{Intraparticle diffusion}}(Mn^{2+}) > R^2_{\text{Second order}}(Mn^{2+})$, which shows that the adsorption of Fe^{2+} and Mn^{2+} using coal-gangue-loaded SRB fitted into the second-order kinetic fitting model. Among them, the adsorption kinetic fitting equation of Fe^{2+} using coal-gangue-loaded SRB was as follows

$$t/q_t = 9.0683t + 6870.02498,\ R^2 = 0.99371.$$

The adsorption kinetic fitting equation of Mn^{2+} absorption using coal-gangue-loaded SRB the Haizhou open-pit minewas

$$t/q_t = 21.09779\mathrm{t} + 56220.56189,\ R^2 = 0.95363.$$

It has been reported that the adsorption of Pb^{2+} and Zn^{2+} by coal gangue fitted in the second-order kinetic model [8]. Previous experiments have shown that the adsorptions of Fe^{2+} and Mn^{2+} by spontaneous-combustion gangue and chemically modified spontaneous-combustion gangue fitted into the second-order kinetic model [24]. Zhang et al. [45] reported that the Mn^{2+} can be removed effectively by akhtenskites and that the removal process conformed to the second-order kinetic model. In this study, we found that the adsorption of Fe^{2+} and Mn^{2+} using coal-gangue-loaded SRB conformed to the second-order kinetic fitting model, which was similar to the research conclusions above, indicating that the treatment of Fe^{2+} and Mn^{2+} in AMD using coal-gangue-loaded SRB in the Haizhou open-pit mine was mainly in the form of chemical reactions.

3.3.3. Analysis of Reduction Kinetics Test Results of $SO_4{}^{2-}$

Adopting the fitting models of zero-order kinetics and first-order kinetics, respectively, we used Origin 2023 software and analyzed the reduction process of $SO_4{}^{2-}$ through coal-gangue-loaded SRB; the results are shown in Figure 7.

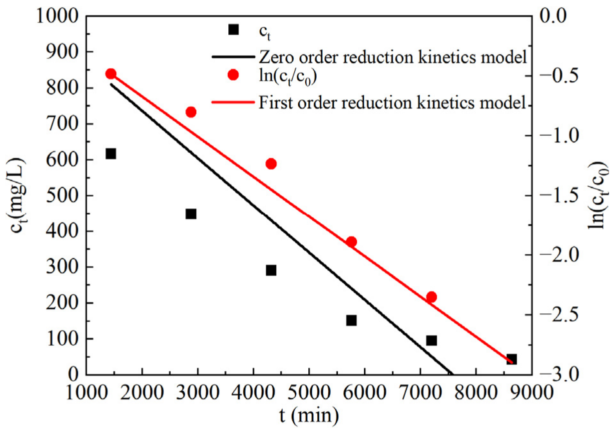


Figure 7. Kinetic fitting diagram of SO_4^{2-} reduction using coal-gangue-loaded SRB in the Haizhou open-pit mine.

The zero-order dynamic model:

$$c_t = c_0 - k_0 \cdot t$$

The first-order kinetic fitting model:

$$\ln c_t = \ln c_0 - k'_1 \cdot t$$

In the formulae above, c_0 represents the initial SO_4^{2-} concentration, mg/L; c_t represents the concentration of SO_4^{2-} at any given time, mg/L; k_0 represents the rate constant of the zero-order reaction, mg/(L min); and k'_1 represents the rate constant of the first-order reaction, 1/min.

It can be seen in Figure 7 that the zero-order dynamic fitting equation of SO_4^{2-} reduction using coal-gangue-loaded SRB was as follows:

$$c_t = 1000 - 0.13181t, R^2 = 0.77797$$

Additionally, the first-order kinetic fitting equation was

$$\ln c_t = \ln 1000 - 3.35358 \times 10^{-4}t, R^2 = 0.99247.$$

$R^2_{\text{First order}}(SO_4^{2-}) > R^2_{\text{Zero order}}(SO_4^{2-})$, indicating that the reduction process of SO_4^{2-} using coal-gangue-loaded SRB in the Haizhou open-pit mine was more in line with first-order kinetics. Since the first-order reaction kinetic process is mainly affected by the electron acceptor, this further explains why the electron acceptor is the main factor affecting the reduction in SO_4^{2-} levels by SRB. Schwarz et al. [46] reported that when the iron concentration was 10 mg/L, the removal rates of ions from potato starch and corn starch reached 96% and 92%, respectively, but no sulfate adsorption was observed. Compared with the studies above, the coal-gangue-loaded SRB material the Haizhouin this study could not only remove Fe ions, but could reduce SO_4^{2-} effectively as well. At the same time, the reduction in SO_4^{2-} using coal-gangue-loaded SRB involved the processes of electron gain and loss, which was only available in the processes of SRB biological and metabolic reactions. Therefore, it is necessary to enhance the SRB activity, improve the reduction levels of SO_4^{2-} in AMD using coal-gangue-loaded SRB in the Haizhou open-pit mine, and thus improve the removal effect.

3.4. Discussion

AMD formed by mining activities has a serious impact on the water environment of the mining area. In particular, open-pit mining causes serious damage to water, soil and plants in the mining area, resulting in the large-scale diffusion of pollutants in AMD in the mining area. In this study, coal gangue and SRB were used as materials to prepare coal-gangue-loaded SRB, by combining adsorption and microbial methods, to solve the pollution problem of coal-mine acid wastewater with a high content of Fe^{2+}, Mn^{2+} and $SO_4{}^{2-}$. As waste, coal gangue can be used to remove heavy metals from water mixtures, but its adsorption capacity is not high. Therefore, many scholars have improved the adsorption capacity of coal gangue towards heavy metals by means of modification and compounding, and have achieved outstanding results. Ramin Mohammadi prepared alginate-combustion coal gangue (ACCG) composites. The maximum adsorption capacities of ACCG for zinc and manganese were 77.68 mg/g and 64.29 mg/g, respectively. The adsorption process followed the Langmuir isotherm model and the intraparticle diffusion model [47]. Gao Xiang et al. used coal gangue as the main raw material: when chitosan and calcined coal gangue were mixed to prepare ceramsite, the removal rate of Cr(VI) reached 75.6% [48]. Zhanhu Zhang et al. [49] prepared modified coal gangue adsorbent using a calcination–chelator modification. Under the conditions of an adsorption time of 2 h and a dosage of 0.8 g/L, the optimum removal rates of 50 mg/L of Cu^{2+} and Pb^{2+} in mineral processing wastewater were 69.34% and 79.98%, respectively [49]. An adsorbent analcime-activated carbon (ANA-AC) was synthesized from coal gangue [50]. The adsorption of Pb^{2+} in the solution by ANA-AC conformed to the Langmuir isotherm model and a pseudo-second-order kinetic model [50]. Qizheng Qin et al. [51] used coal gangue as the raw material, and coal gangue was modified based on low-temperature method combining roasting-dewatering and leaching. The adsorption capacity of the modified-coal-gangue adsorption material towards lead ions was higher than that of the original coal gangue and kaolinite [51]. Cheng Wang et al. [52] used coal gangue as the raw material, synthesizing sodium silicate using a hydrothermal method. The maximum adsorption capacities of sodium silicate towards Cd^{2+} and methylene-blue were 60 mg/g and 17.3 mg/g, respectively [52]. Above all, the adsorption capacity of coal gangue toward heavy metals can be improved by modification and compounding. Compared with the above research, the coal-gangue-loaded SRB material used in this study can not only remove metal ions such as Fe^{2+} and Mn^{2+}, but can also remove $SO_4{}^{2-}$, especially in AMD, such a unique form of wastewater pollution where the $SO_4{}^{2-}$ is higher. Therefore, coal-gangue-loaded SRB can not only improve the problem of poor removal rates of $SO_4{}^{2-}$ in AMD by coal gangue, but also reduce the adverse influence of the surrounding environment on SRB growth by using the adsorption performances of coal gangue, and in this way can improve the removal effect of heavy metals.

Focusing on the treatment of wastewater containing iron and manganese, some scholars have analyzed the treatment effect of various adsorption materials on iron and manganese by using coal gangue combined with other materials, such as bentonite and new composite materials. Liping Zhang et al. [53] showed that the use of coal gangue, sandy soil and clay (mass ratio 45:4:1) as a goaf filling material can effectively remove iron and manganese in coal mining drainage. The maximum adsorption capacities of iron and manganese were 163.79 μg and 15.25 μg, respectively [53]. Bentonite can adsorb and remove Fe(II) [54]. The maximum removal rate of Fe(II) using 0.5 g bentonite was more than 98% [54]. Maria K. Doula synthesized a high-surface-area clinoptilolite-iron-oxide system (Clin-Fe) using clinoptilolite, and found that the adsorption capacity of clinoptilolite toward Mn was 7.69 mg/g, while the adsorption capacity of Clin-Fe toward Mn was 27.12 mg/g [55]. Ibrahim M. El-Sherbiny et al. [56] combined sodium alginate with different proportions of calcareous soil to form new-composite microparticles (NCM). The removal rate of 0.5–16.0 mg/L Fe by these NCMs was almost 100%, and the removal rate of 0.5 mg/L Mn (II) was about 89% [56]. Xuying Guo et al. [24,25] showed that the effective concentration of spontaneous-combustion coal gangue was 8 g/100 mL, which could adsorb Fe^{2+} and Mn^{2+} when incorporated in AMDs. The removal efficiencies of Fe^{2+} and Mn^{2+} in AMDs using NaOH-modified spontaneous-combustion coal gangue was noticeably better than that when using spontaneous-combustion coal gangue alone [25]. The average removal rates of Fe^{2+} and Mn^{2+} by NaOH-modified spontaneous-combustion coal gangue were 97.73% and 44.82%, respectively [24,25]. Compared to the above research, the removal rates of SO_4^{2-}, Fe^{2+} and Mn^{2+} using coal-gangue-loaded SRB material in the Haizhou open-pit mine remained at a higher level. Under the conditions of a coal-gangue dosage of 52 g, an SRB inoculation concentration of 11.7% and a temperature of 33–34 °C, the removal rates of SO_4^{2-}, Fe^{2+} and Mn^{2+} in AMD using coal-gangue-loaded SRB were 89.76%, 99.66% and 87.95%, respectively, after treating AMD for 4 days. Zhuxiang Liu [57] reported that under the condition of an initial pH of 6.0 and an initial SO_4^{2-} concentration of 2000 mg/L, the removal efficiency of Fe by SRB using an expanded granular sludge bed reactor was 95.2–100%. Mingliang Zhang et al. [29] reported that the maximum reduction rate of sulfate in AMD using SRB-immobilized particles, prepared with SRB as the main component, was 2.67 g/(L·d). It was difficult to remove the manganese in AMD; the removal efficiency was only 42–99% [29]. Compared to the above studies on the treatment of AMD by SRB, the process of building an expanded granular sludge bed reactor and preparing SRB-immobilized particles was relatively complicated. The coal-gangue-loaded SRB material prepared in this study only required the mixing of coal gangue with microorganisms in a certain proportion, and the preparation process was relatively simple. In summary, coal-gangue-loaded SRB can achieve the effect of "treating waste with waste", making it a type of convenient and cheap AMD-repair material. This study only focused on the removal effect of SO_4^{2-}, Fe^{2+} and Mn^{2+} using coal-gangue-loaded SRB; the removal effect of other heavy metals in wastewater using coal-gangue-loaded SRB will be analyzed in the future. At the same time, the application effect of coal-gangue-loaded SRB in other industrial fields will be analyzed, and its application range of will be further promoted.

4. Conclusions

In this study targeting the pollution problem of AMD, with high contents of Fe^{2+}, Mn^{2+} and SO_4^{2-}, coal gangue and SRB were used as materials to prepare a coal-gangue-loaded SRB material, which solved the problem of the pollution of coal-mine acid wastewater with high contents of Fe^{2+}, Mn^{2+} and SO_4^{2-}. Coal-gangue-loaded SRB can not only improve the problem of poor SO_4^{2-} removal rates in AMD by coal gangue, but also reduce the adverse influences of the surrounding environment on the SRB growth by using the adsorption qualities of coal gangue. At the same time, the coal gangue in this technology originated from the solid waste of the mining area, and hence was easy to obtain. AMD is a type of polluted wastewater in mining areas. The remediation of AMD using coal-gangue-loaded SRB can achieve the effect of "treating waste with waste". Coal-gangue-loaded SRB is a convenient, cheap and efficient AMD-repairing material. Use of the remediation technology within coal-gangue-loaded SRB for other types of contaminated wastewater still needs to be further explored in the future.

(1) The overall effect order of repairing AMD with four types of coal-gangue-loaded SRB was as follows: 3# CG-loaded SRB > 2# CG-loaded SRB > 1# CG-loaded SRB > 4# CG-loaded SRB. Moreover, the best conditions for repairing AMD using coal-gangue-loaded SRB were by adding 50 g of 3# CG, inoculating with 10% SRB, at 35 °C and 100 r/min.

(2) The RSM test indicated that the best condition for repairing AMD with coal-gangue-loaded SRB in the Haizhou open-pit mine was as follows: using a coal-gangue dosage of 52 g, an SRB inoculation concentration of 11.7%, and a temperature of 33.4 °C. In this condition, the removal rates of SO_4^{2-}, Fe^{2+} and Mn^{2+} were 89.76%, 99.66% and 87.95%, respectively. After repairing AMD using coal-gangue-loaded SRB the Haizhoufor 4 d, the influence order of the single-factor coal-gangue dosage, the SRB inoculation concentration and the temperature on the removal of SO_4^{2-} and Fe^{2+} in AMD using coal-gangue-loaded SRB was as follows: SRB inoculation concentration > temperature > coal-gangue dosage. The order that affects the removal of Mn^{2+} in AMD using coal-gangue-loaded SRB was the temperature > the SRB inoculation concentration > the coal-gangue dosage.

(3) In the process of repairing Fe^{2+} with coal-gangue-loaded SRB in the Haizhou open-pit mine, the biological-activity metabolism of SRB played a dominant role, and the adsorption kinetics conformed to Lagergren's second-order kinetic model:

$$t/q_t = 9.0683t + 6870.02498, R^2 = 0.99371.$$

The adsorption isotherms of Mn^{2+} when using coal-gangue-loaded SRB in the Haizhou open-pit mine obey the Freundlich model:

$$\ln q_e = -7.40145 + 2.68525\ln c_e, R^2 = 0.999625.$$

The adsorption kinetics of Mn^{2+} conformed to the Lagergren second-order kinetic model:

$$t/q_t = 21.09779t + 56220.56189, R^2 = 0.95363.$$

The reduction Kinetics of ${SO_4}^{2-}$ in AMD when using coal-gangue-loaded SRB conformed to the first-order reaction model:

$$\ln c_t = \ln 1000 - 3.35358 \times 10^{-4}t, R^2 = 0.99247$$

Author Contributions: Conceptualization, Y.D.; methodology, Y.D.; validation, Y.D. and Z.G.; formal analysis, Y.D. and Z.G.; investigation, Y.D., Z.G., J.D., D.W., Z.Y., X.G., Y.L., G.W. and X.Z.; data curation, Y.D. and Z.G.; writing—original draft preparation, Y.D., Z.G., J.D., D.W., Z.Y. and X.Z.; writing—review and editing, Y.D.; visualization, Z.Y.; supervision, Z.G.; project administration, Y.D., J.D. and D.W.; funding acquisition, Y.D., J.D. and D.W. All authors have read and agreed to the published version of the manuscript.

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