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Study on the Treatment of Acid Mine Drainage Containing Fe^{2+} and Mn^{2+} Using Modified Spontaneous Combustion Gangue

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Received: 26 June 2020 Accepted: 26 August 2020

ABSTRACT

The high concentrations of Fe^{2+} and Mn^{2+} in acid mine drainage make it difficult and expensive to treat. It is urgent that we find a cheap and efficient adsorption material to treat Fe^{2+} and Mn^{2+} . As a solid waste in mining areas, coal gangue occupies a large area and pollutes the surrounding environment during the stacking process. Developing a method of resource utilization is thus a research hotspot. In this study, we modified spontaneous combustion gangue using NaOH, NaCl, and HCl by chemically modifying the minerals. We determined the optimal conditions for treating Fe^{2+} and Mn^{2+} in acid mine drainage with spontaneous combustion gangue and modified coal gangue using the single factor test method. Based on results of the static test, two dynamic test columns, column No. 1 (spontaneous combustion gangue) and column No. 2 (NaOH modified spontaneous combustion gangue), were constructed, and the repair effects of acid mine drainage were compared and analyzed using dynamic experiments. The results show that overall, NaOH modified spontaneous combustion gangue is the most efficient at removing the Fe^{2+} and Mn^{2+} in acid mine drainage. The optimal conditions for NaOH modification are an NaOH concentration of 3 mol/L, a liquid to solid ratio of 2 L/kg, and a modification time of 8 h. The overall efficiency of column No. 2 at removing Fe^{2+} and Mn^{2+} from acid mine drainage is better than that of column No. 1. Among them, the average removal efficiency of Fe^{2+} and Mn^{2+} from acid mine drainage in column No. 2 were 97.73% and 44.82%, respectively. The above results show that NaOH modified spontaneous combustion gangue is a good adsorbent, which has application potential in wastewater remediation, as it can achieve the purpose of “treating dust with waste”.

KEYWORDS

Acid mine drainage; chemical modification; dynamic experiments; single factor test; spontaneous combustion gangue

1 Introduction

Acid mine drainage is formed by the oxidation and weathering of sulfides. The pH value of acid mine drainage is low, and its Fe^{2+} , Fe^{3+} , Al^{3+} , Mn^{2+} , and SO_4^{2-} contents are high [1–3], which seriously affects the water resources and soil ecosystem surrounding mining areas. Thus, acid mine drainage has become a global



environmental pollution problem [4]. At present, the heavy metals in acid mine drainage are removed using physical and chemical treatment technologies, such as adsorption [5], ion exchange [6], and permeable membranes [7], or using biological treatment technologies [8]. Among these techniques, the adsorption method uses porous solid substances to cause one or more substances in the water to be adsorbed onto the solid's surface and be removed. Mokgehle et al. [9] used fly ash to synthesize dicarboxylic acid zeolite and analyzed its efficiency at removing Cd^{2+} from acid mine drainage using column experiments. Igberase et al. [10] found that chitosan derivatives can be used as adsorbents in the treatment of acid mine drainage. Li et al. [11] used red mud as an adsorbent to treat Mn^{2+} in acid mine drainage and analyzed the difference between the column experiment and batch experiment treatment effects. Etale et al. [12] studied the adsorption and removal effects of maghemite nanoparticles on Cu(II), Mn(II), and U(VI) ions in acid mine drainage, and their results revealed that sulfate ions in acid mine drainage can improve the target ion adsorption capacity of maghemite nanoparticles. At present, many types of adsorption materials have been developed and utilized but using the adsorption method to treat wastewater has the disadvantages of large material consumption and high treatment costs. If suitable solid adsorbent materials can be selected on-site in the mining area, the cost of environmental restoration in the mining area can be effectively reduced, and the secondary utilization of the waste in the mining area can be achieved.

Coal gangue is a solid waste produced in the process of coal mining and washing, and its average output accounts for about 10–15% of the output of raw coal [13]. Coal gangue occupies a large amount of land resources and spontaneously combusts easily during the stacking process, so the utilization rate of coal gangue needs to be improved [14]. According to statistics, the utilization rate of coal gangue in 2013 was only about 64% [15]; it was mainly used for power generation [16], backfilling material [17,18], and traditional building materials [19,20]. Coal gangue has a certain adsorption property after modification and can be used as an adsorbent and flocculant in the field of water treatment. Jablonska et al. [21] demonstrated that chemical modification expands the total pore volume and the specific surface area of coal gangue, and modified coal gangue can be used as a cheap adsorbent in industrial drainage pretreatment. Yan et al. [22] used 3-mercaptopropyl to prepare mercapto-modified coal gangue, which can effectively remove heavy metal cations from water; its maximum Pb^{2+} , Cd^{2+} , and Hg^{2+} adsorption capacities can reach 332.8, 110.4, and 179.2 mg/g, respectively. Silas et al. [23] activated coal gangue using HCl, and the resulting modified coal gangue was used to adsorb methylene blue in wastewater. Qiu et al. [24] mixed coal gangue with $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and heated it at 500°C for 2 h to prepare modified coal gangue. This modification method increased the maximum Mn^{2+} adsorptive capacity of the coal gangue by seven times. These studies show that using chemically modified coal gangue as an adsorbent to treat wastewater has a certain feasibility. Therefore, if coal gangue can be used as a raw material and can be chemically modified to repair acidic mine water pollution, it will have an important environmental protection significance.

Because the silicon to aluminum ratio of coal gangue is similar to that of zeolite, several researchers have made zeolite after the chemical modification of coal gangue, thereby improving the ability of the coal gangue to treat acid mine drainage. Bu et al. [25] used alkali fusion and hydrothermal methods to synthesize NaY zeolite from coal gangue. The Pb^{2+} removal efficiency of the synthesized NaY zeolite reached 100% and more than 63.71% after five adsorption and desorption cycles. Lu et al. [26] converted coal gangue into NaX zeolite with a low silicon to aluminum ratio and used the Langmuir's model to determine that the Cu^{2+} and CO^{2+} adsorption capacities of zeolite can reach 45.05 and 44.53 mg/g, respectively. Ge et al. [27] prepared NaX zeolite from coal gangue powder with a particle size of less than 150 mesh. Under the conditions of a pH of 6, a reaction temperature of 45°C , a reaction time of 40 min, and an initial Pb^{2+} concentration of 200 mg/L, the Pb^{2+} adsorption capacity reached 457 mg/g. However, there are some limitations with these studies, such as their complex modification processes and high preparation

condition requirements. For example, the preparation process requires additional materials such as Al_2O_3 to maintain the silicon to aluminum ratio required for the synthesis of zeolite, and high temperature heating is required for the modification process. Furthermore, the aging process of the materials takes an additional 12 h, which also makes it difficult for the existing production conditions of the mining area to meet the requirements of the coal gangue modification process. Thus, the efficient use of coal gangue is not possible, and the cost of environmental restoration is high. It is therefore important that we find a simple and fast chemical modification method that can not only improve the wastewater treatment capacity of coal gangue but can also facilitate large-scale preparation in mining areas.

Based on the above considerations, this study focuses on the following aspects: (1) Using the chemical modification method, NaOH, NaCl, and HCl were used to modify spontaneous combustion coal gangue. The modified coal gangue was analyzed using SEM and XRD, and the influence of the different modification methods on the morphology and composition of the coal gangue was investigated. (2) The single factor test was used to explore the application conditions of the spontaneous combustion coal gangue as an adsorbent, to optimize the preparation conditions of the modified spontaneous coal gangue, and to obtain the best modification method. (3) Dynamic experiments were conducted to verify the long-term adsorption performance of NaOH modified spontaneous combustion gangue. Through the above research, a new method of converting coal gangue into an inexpensive, green adsorbent was developed, which can generate local materials for the treatment of acid mine drainage, thereby reducing the cost of wastewater treatment, effectively solving the problem of large amounts of waste coal gangue, and making it possible to reuse coal gangue.

2 Materials and Methods

2.1 Experimental Materials

Spontaneous combustion gangue (SCG), was collected from the Gaode mining area, Fuxin City, Liaoning Province, China. Its main chemical composition is presented in [Tab. 1](#). The SCG samples were broken and screened out. The 75–96, 96–120, 120–180, 180–425, and 425–1,700 μm particle size fractions were soaked in distilled water 3 times and dried at 60°C .

Table 1: Chemical composition of the spontaneous combustion gangue (%)

Constituent	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	SO_3	CO_2	Loss on ignition
SCG	60.16	16.56	6.26	3.63	3.4	1.84	3.09	0.71	0.16	0.19	0.73	2.50	0.79

The modified spontaneous combustion gangue (MSCG) samples were prepared using NaOH, NaCl, and HCl soaking modification. These samples were labeled as NaOH-MSCG, NaCl-MSCG, and HCl-MSCG. The SCG was placed in different modified solutions according to the liquid to solid ratio set in the single factor test, soaked in an oven at 100°C for several hours, taken out of the modified solution, washed with distilled water until neutral, and dried in an oven at 105°C to obtain MSCG.

Because most acid mine drainage pollution has high Fe^{2+} and Mn^{2+} contents, we used the Fe^{2+} , Mn^{2+} , and SO_4^{2-} concentrations as the acid mine drainage quality indicators measured in Rumbel City, Inner Mongolia Autonomous Region, China. We simulated the acid mine drainage in the laboratory. In the field samples, the acid mine drainage contained 947–1118 mg/L of SO_4^{2-} , 52.85–86.31 mg/L of Fe^{2+} , and 13.42–28.51 mg/L of Mn^{2+} , and it had a pH of 4.84–5.36. In order to ensure that the simulated acid mine drainage was realistic, we ensured that the simulated acid mine drainage contained 1000 mg/L of SO_4^{2-} , 65 mg/L of Fe^{2+} , and 20 mg/L of Mn^{2+} and had a pH of 5. All the chemicals used in the experiments were of analytical reagent grade.

2.2 Static Experimental Method

The SCG was weighed and placed in a conical flask containing 50 mL of simulated acid mine drainage at 25°C. The flask was shaken at 100 r/min for 30 min, and then the supernatant was extracted and passed through a 0.45 µm filter membrane. Finally, the residual concentrations of Fe²⁺ and Mn²⁺ were measured. The effects of the particle size of the SCG (75–96, 96–120, 120–180, 180–425, and 425–1,700 µm), the dosing amount (1, 2, 3, 4, and 5 g/50 mL), and the reaction time (30, 60, 90, 120, 150, 180, and 240 min) on the adsorption of Fe²⁺ and Mn²⁺ from the acid mine drainage by the SCG were investigated using the static single factor test method [28], which was used to determine the optimal particle size, dosing amount, and reaction time of the SCG.

The MSCG was prepared according to the optimal particle size of the SCG determined from the experiment described above, and the experiment to investigate the adsorption of Fe²⁺ and Mn²⁺ from acid mine drainage by MSCG was carried out using the previously determined optimal dosage amount and reaction time. The effects of the NaOH concentration (1, 2, 3, and 4 mol/L), the liquid-solid ratio (2, 4, 6, and 8 L/kg), and the modification time (1, 2, 3, 4, 6, 8, 10, and 12 h) on the adsorption of Fe²⁺ and Mn²⁺ from acid mine drainage by NaOH-MSCG were investigated using the static single factor test method [28], which was used to determine the optimal modifying condition of the NaOH-MSCG. The optimum conditions of the NaCl-MSCG and HCl-MSCG were determined using a method similar to that used for the NaOH-MSCG. The difference from the method used for the NaOH-MSCG is that the modification time for the NaCl-MSCG and HCl-MSCG experiments was extended to 24 h.

Based on the optimum modification conditions of the NaOH-MSCG, NaCl-MSCG, and HCl-MSCG, the efficiencies of the three types of modified spontaneous combustion gangue at removing different concentrations of Fe²⁺ and Mn²⁺ were determined and compared with that of SCG to determine the best modification method for the removal of Fe²⁺ and Mn²⁺.

2.3 Construction and Method of the Dynamic Experimental Apparatus

As shown in Fig. 1, two plexiglass tubes with inner diameters of 56 mm and heights of 500 mm were used as the reactor. Column No. 1 was used as the control group and column No. 2 was used as the experimental group. Each end of the column was filled with 210 g of quartz sand as a protective layer. The height of the quartz sand was 50 mm. Column No. 1 was filled with 2.4 kg of SCG, and column No. 2 was filled with 2.4 kg of NaOH-MSCG. The height of the SCG and NaOH-MSCG was 400 mm.

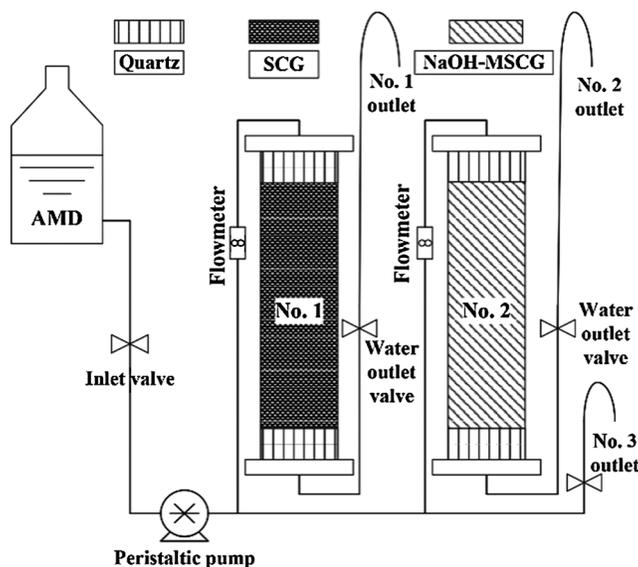


Figure 1: Experimental device system

A peristaltic pump was used to pass the simulated acid mine drainage through the column from top to bottom. The flowmeter in the influent path was adjusted so that the flow rate in each dynamic column was maintained at approximately 12 mL/h. The dynamic column experiment was operated at room temperature for 30 days. Samples of incoming and outgoing water were collected regularly at 8:00 am every morning. The residual concentrations of Fe^{2+} and Mn^{2+} in the effluent were determined after being passed through a 0.45 μm filter membrane. The removal efficiencies η of Fe^{2+} and Mn^{2+} were calculated using Eq. (1):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%. \quad (1)$$

where C_0 (mg/L) is the initial concentration of Fe^{2+} and Mn^{2+} ; and C_t (mg/L) is the residual concentration of Fe^{2+} and Mn^{2+} in the effluent of the dynamic column at time t .

2.4 Analysis and Material Characterization Methods

The Fe^{2+} content was determined using o-phenanthroline spectrophotometry (HJ/T 345–2007), and the Mn^{2+} content was determined using potassium periodate spectrophotometry (GB 11906-89). The SCG and MSCG were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD) using a Quanta 250 field emission scanning electron microscope and an XRD-6100 X-ray diffractometer, respectively.

3 Results and Discussion

3.1 SEM and XRD Analysis of the Experimental Materials

3.1.1 SEM Analysis

As shown in Fig. 2a, the surfaces of the spontaneous combustion coal gangue are rough and uneven, and there are obvious groove marks. These grooves increase the specific surface area, provide more adsorption sites for metal ions, improve the surface free energy of the SCG, and enhance its reaction activity [29]. Compared with the SCG, the surface roughness of the NaOH-MSCG in Fig. 2b is larger, and there is an obvious pore structure. This is because the silica to aluminum ratio of the coal gangue is closer to that of zeolite, and the NaOH reacts with the aluminosilicates to change the silica to aluminum ratio of the coal gangue and to synthesize a zeolite material with a strong adsorption capacity and a good pore structure [30]. As shown in Fig. 2c, compared with the SCG, the morphology of the NaCl-MSCG is similar, and the surface is relatively smooth, without excessive groove marks. This is because the main mechanism of NaCl modification is that Na^+ adsorbs the negative charges on the surface of the coal gangue, increases the number of cations on the surface, increases the cation exchange capacity, and does not corrode its structure [31]. High concentrations of HCl are corrosive to coal gangue and can react with the Fe_2O_3 , Al_2O_3 , and other oxides in the coal gangue. Therefore, as shown in Fig. 2d, there are many grooves on the surface of the HCl-MSCG, and the surface is relatively rough. However, due to the acid resistance of the coal gangue, unlike the NaOH-MSCG, the HCl-MSCG has no obvious pore structure [32].

3.1.2 XRD Analysis

As shown in the XRD diffraction pattern (Fig. 3), the main components of the SCG are quartz, albite, kaolinite, calcite, hematite, illite, and pyrite. The MSCG still contains the silica tetrahedron skeleton of the quartz, but according to the change in the diffraction peak, its main composition has changed. The diffraction peaks of the NaOH-MSCG were significantly enhanced at $2\theta = 21^\circ$, 27° , and 42° , and the peak shape at $2\theta = 28^\circ$ was changed, indicating that the quartz and albite crystals in the sample were dissolved during the modification process [33]. Therefore, the change in the XRD image after NaOH modification may be related to the dissolution of the oxides in the coal gangue. The strength of the NaCl-MSCG becomes weaker at $2\theta = 26.6^\circ$, and a new peak appears at $2\theta = 66.70^\circ$. The intensity of the quartz diffraction peak of the HCl-MSCG was weakened at $2\theta = 26.6^\circ$. The diffraction peak of the calcite in HCl-MSCG

disappears and the intensity of the diffraction peak of pyrite becomes weaker at $2\theta = 40.8^\circ$. This is consistent with the results of Peng et al. [34], who found that after acid leaching of the coal gangue, the calcite, pyrite, and kaolinite diffraction peaks of the residue were significantly reduced.

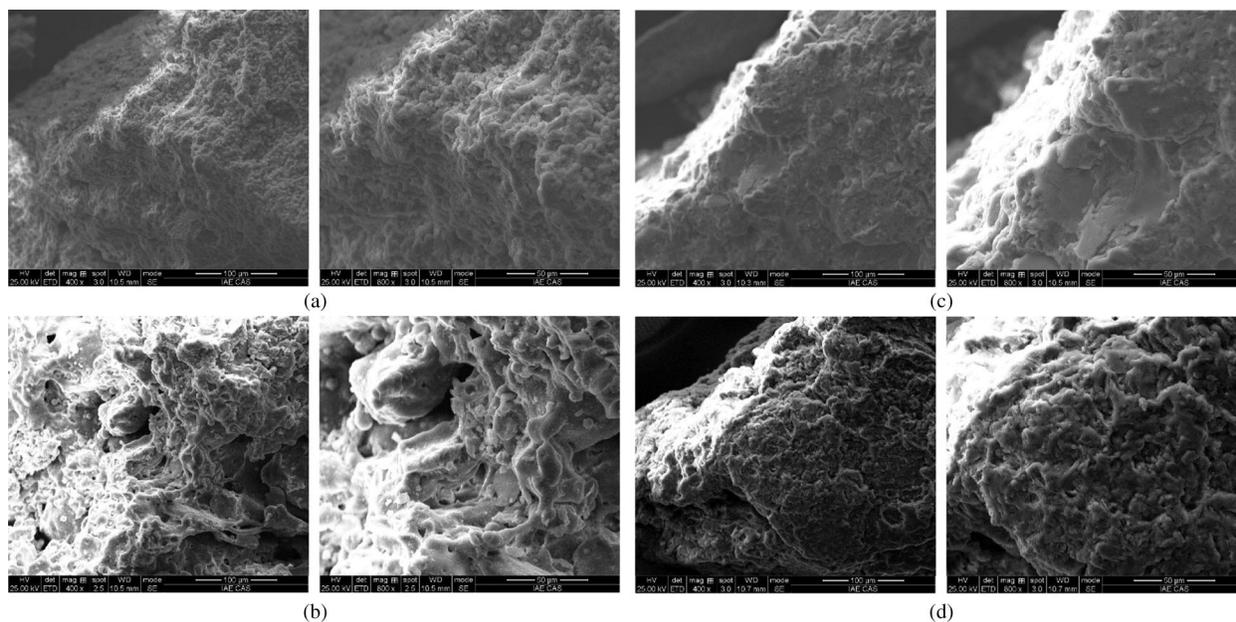


Figure 2: SEM images. (a) SCG, (b) NaOH-SCG, (c) NaCl-SCG and (d) HCl-SCG

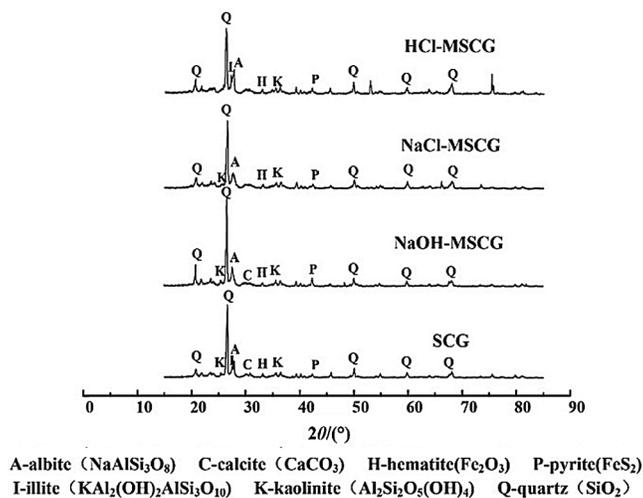


Figure 3: XRD diffraction patterns

3.2 Efficiency of SCG and MSCG at Removing Fe^{2+} and Mn^{2+} from Acid Mine Drainage

3.2.1 Efficiency of SCG at Removing Fe^{2+} and Mn^{2+} from Acid Mine Drainage

The effects of the particle size, dosage, and adsorption time of the efficiency of SCG at removing Fe^{2+} and Mn^{2+} in acid mine drainage were investigated using single factor experiments. The results are shown in

Fig. 4. As shown in Fig. 4a, the removal efficiency of Fe^{2+} from acid mine drainage gradually increased with decreasing grain size. The smaller the grain size of the SCG, the greater the damage to the silicon lattice, i.e., the silicon activity improved. Furthermore, the specific surface area and surface energy both increase with decreasing grain size, which is conducive to the adsorption process [35]. When the particle size of SCG was decreased from 425–1700 μm to 180–425 μm , the removal efficiency of Mn^{2+} increased significantly. However, as the grain size continued to decrease, the removal efficiency of Mn^{2+} tended to remain relatively stable and even decreased slightly. This is likely because the small amount of Mn^{2+} contained in the SCG is released during the oscillation process, which is not conducive to the adsorption of Mn^{2+} by the SCG. Tang et al. [36] found that the Mn^{2+} contained in gangue is gradually released and migrates outward. Through experimental observations, it was found that when the particle size is too small, the SCG does not settle easily. Based on a comparison of the influence of particle size of the SCG on the removal of Fe^{2+} and Mn^{2+} , SCG with a particle size of 120–180 μm was selected as the experimental material for the other experiments.

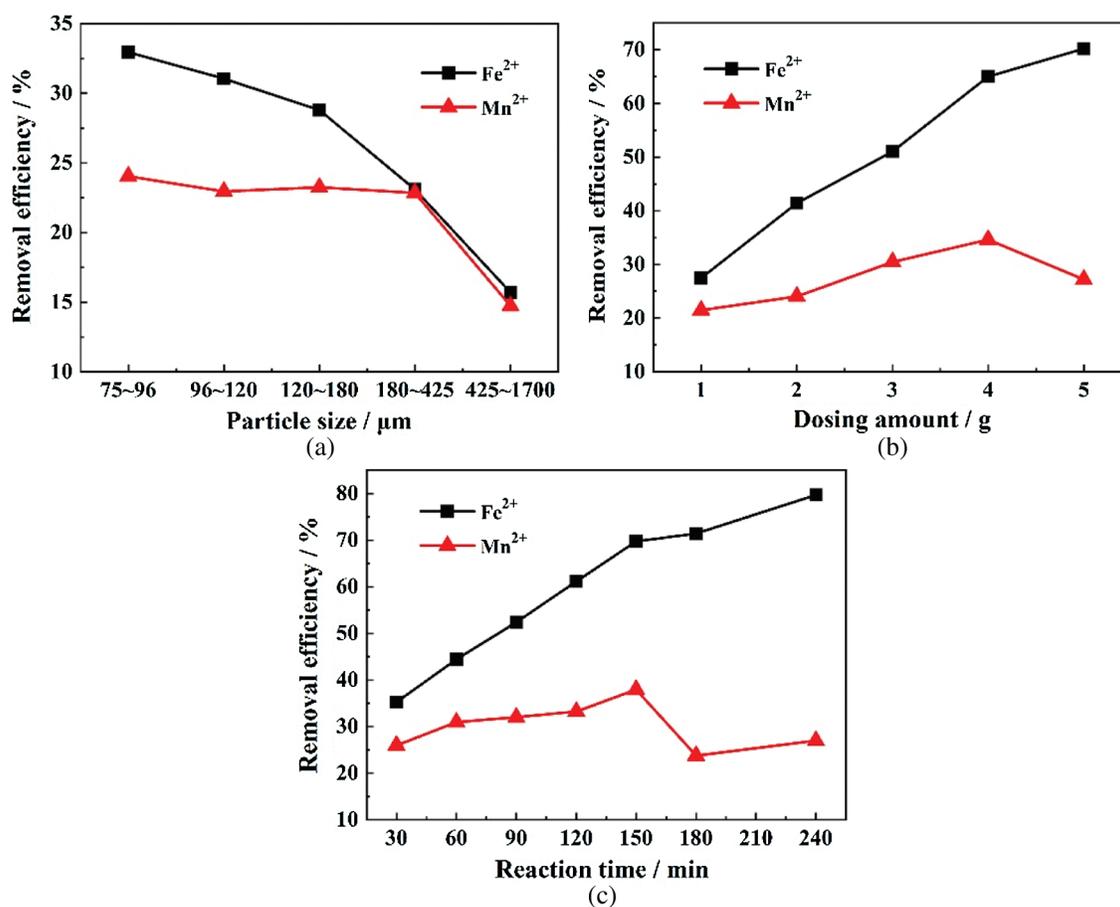


Figure 4: Fe^{2+} and Mn^{2+} removal efficiency of SCG

As shown in Fig. 4b, the Fe^{2+} removal efficiency gradually increased from 27.47% to 70.20% as the amount of SCG added was increased. This is because the spontaneous combustion process of coal gangue is similar to the decarburization and activation process of coal gangue, which causes some of the stable crystals in the coal gangue to decompose and be converted into amorphous α -quartz, amorphous SiO_2 , κ - Al_2O_3 , amorphous Al_2O_3 , and other active amorphous crystals [37]. When the amount of SCG was

increased, the number of active crystals in the system increased, and the adsorption effect was enhanced. As the amount of SCG added was increased, the removal efficiency of Mn^{2+} increased from 21.46% to 34.62% and then decreased back to 27.2%. This is because increasing the amount of SCG increased the amount of released Mn^{2+} . When the dosing amount of the SCG was 4 g/50 mL, the removal efficiency of Fe^{2+} was higher and the removal efficiency of Mn^{2+} did not decrease. Thus, 4 g/50 mL was selected as the optimal dosing amount.

According to Fig. 4c, the removal efficiency of Fe^{2+} increases with increasing reaction time. This is because the extension of the reaction time enables the SCG to fully interact with the Fe^{2+} , thereby increasing the removal efficiency of Fe^{2+} . The removal efficiency of Mn^{2+} increased gradually when the reaction time was less than 150 min, decreased from 150 to 180 min, and increased again after 180 min. This may be because the adsorption capacity of the SCG for Mn^{2+} reaches saturation after 150 min, and as the reaction time increases, shaking the beaker causes the adsorption-resolution phenomenon of Mn^{2+} . Therefore, the removal efficiency of Mn^{2+} fluctuated between 150 and 180 min. Thus, 150 min was selected as the optimal reaction time.

The optimal conditions for SCG to absorb Fe^{2+} and Mn^{2+} in acid mine drainage are particle sizes of 120–180 μm , a dosing amount of 4 g/50 mL, and a reaction time of 150 min.

3.2.2 Efficiency of MSCG at Removing Fe^{2+} and Mn^{2+} from Acid Mine Drainage

In the SCG modification experiments, the influence of the modification solution concentrations, the liquid to solid ratio of the modification solutions and the SCG, and the modification time on the efficiency of the MSCG at removing Fe^{2+} and Mn^{2+} from acid mine drainage were studied. The results are shown in Figs. 5–7. The efficiency of the SCG and MSCG at removing Fe^{2+} and Mn^{2+} from wastewater with different concentrations of Fe^{2+} and Mn^{2+} were compared. The results are shown in Fig. 8.

As shown in Fig. 5, the removal efficiencies of Fe^{2+} and Mn^{2+} were significantly improved with increasing NaOH concentration, but the removal efficiencies tended to become stable when the NaOH concentration exceeded 3 mol/L, which indicates that high concentrations of NaOH can more fully dissolve the aluminosilicates in the coal gangue and can improve the cation adsorption capacity. With an increasing liquid to solid ratio, the removal efficiency of Fe^{2+} fluctuated slightly, exhibiting an overall upward trend, while the removal efficiency of Mn^{2+} decreased gradually. This may be because the ionic radius of Fe^{2+} is smaller than that of Mn^{2+} , so the interaction between the Fe^{2+} and the gangue structure is stronger, and the competitive Fe^{2+} adsorption capacity is stronger under the condition of multi-ion co-existence.

Increasing the modification time had little effect on the efficiency of the removal of Fe^{2+} , but it effectively improved the efficiency of the removal of Mn^{2+} . Therefore, the optimal conditions for NaOH modification are an NaOH concentration of 3 mol/L, a liquid to solid ratio of 2 L/kg, and a modification time of 8 h.

As shown in Fig. 6, the Fe^{2+} and Mn^{2+} removal efficiencies initially increased and then decreased as the NaCl concentration and the liquid to solid ratio increased. The reason for this is that Na^+ combines with the negative charge on the surface of the coal gangue during the modification process, which increases the number of cations on the surface of the coal gangue. Na^+ has a low valence and a large ionic radius, and the interaction between Na^+ and the gangue is weak, resulting in Na^+ being easily replaced by Fe^{2+} and Mn^{2+} during acid mine drainage treatment. Thus, the Fe^{2+} and Mn^{2+} removal efficiencies gradually increase [31]. The Fe^{2+} and Mn^{2+} removal efficiencies decrease when excessive amounts of NaCl are present, which indicates that the surface charge point of the coal gangue has reached saturation, and increasing the amount of NaCl interferes with the adsorption of Fe^{2+} and Mn^{2+} by the NaCl-MSCG. Furthermore, increasing the modification time promoted the removal of Fe^{2+} and Mn^{2+} , but the removal efficiency gradually leveled off with increasing modification time. Therefore, the optimal conditions for NaCl modification are an NaCl concentration of 2 mol/L, a liquid to solid ratio of 4 L/kg, and a modification time of 16 h.

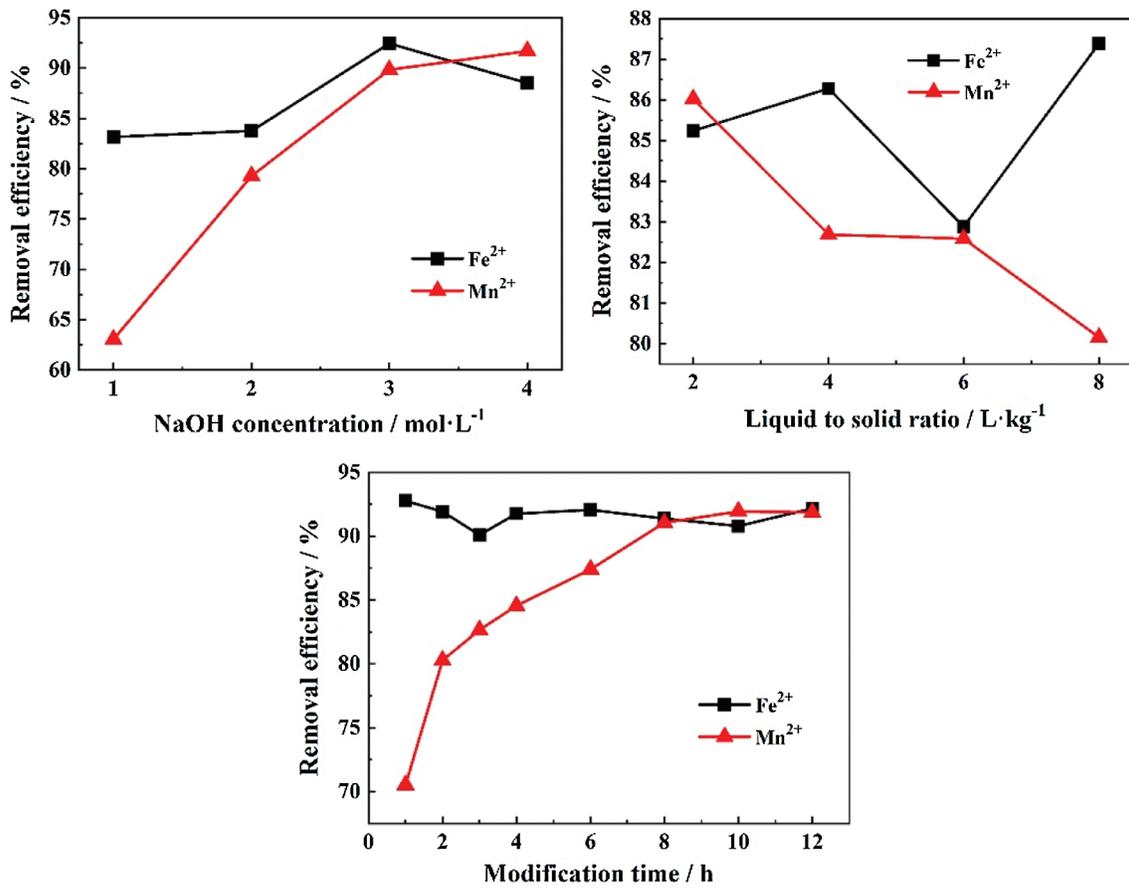


Figure 5: Fe²⁺ and Mn²⁺ removal efficiencies of the NaOH modification conditions

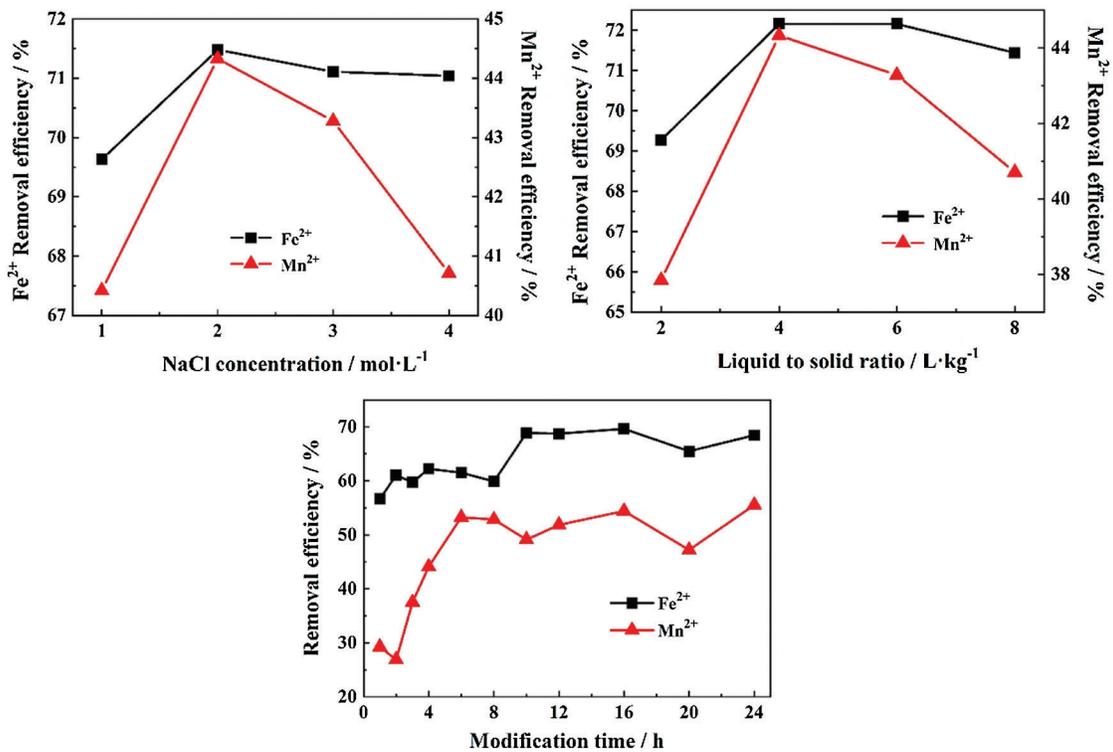


Figure 6: Fe²⁺ and Mn²⁺ removal efficiencies under NaCl modification conditions

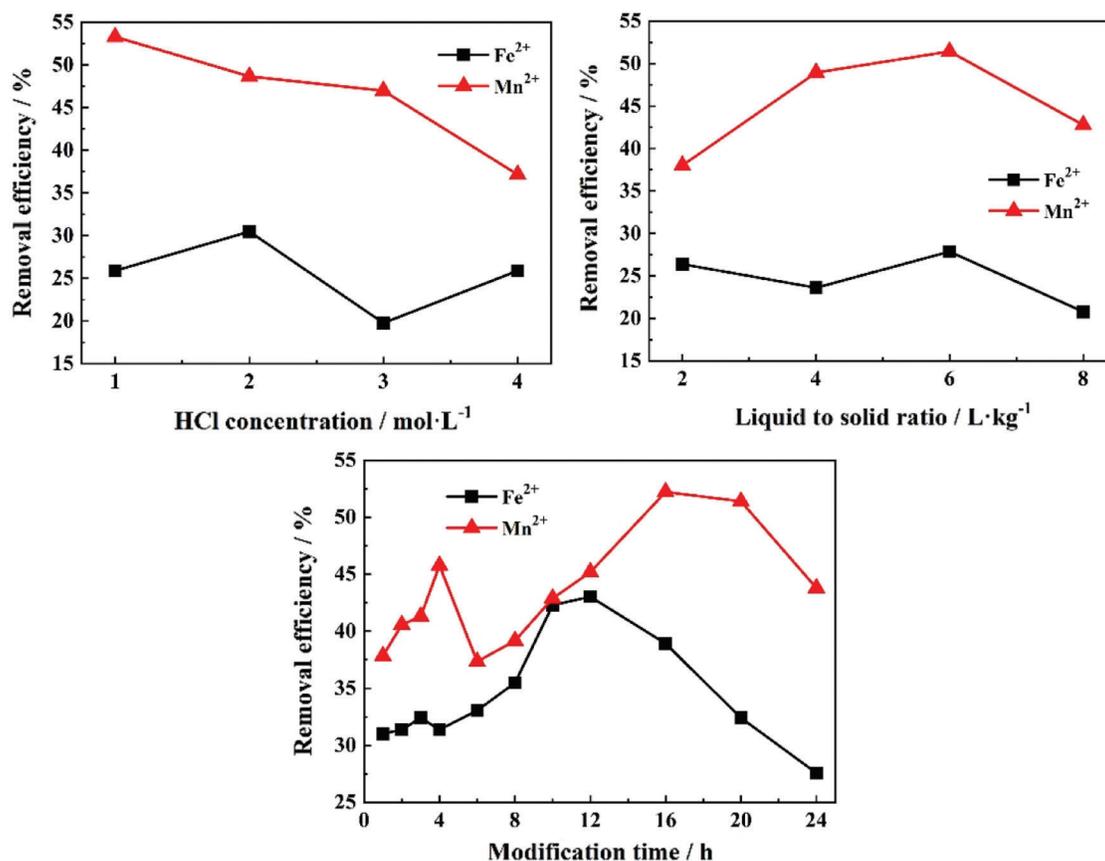


Figure 7: Fe^{2+} and Mn^{2+} removal efficiencies under HCl modification conditions

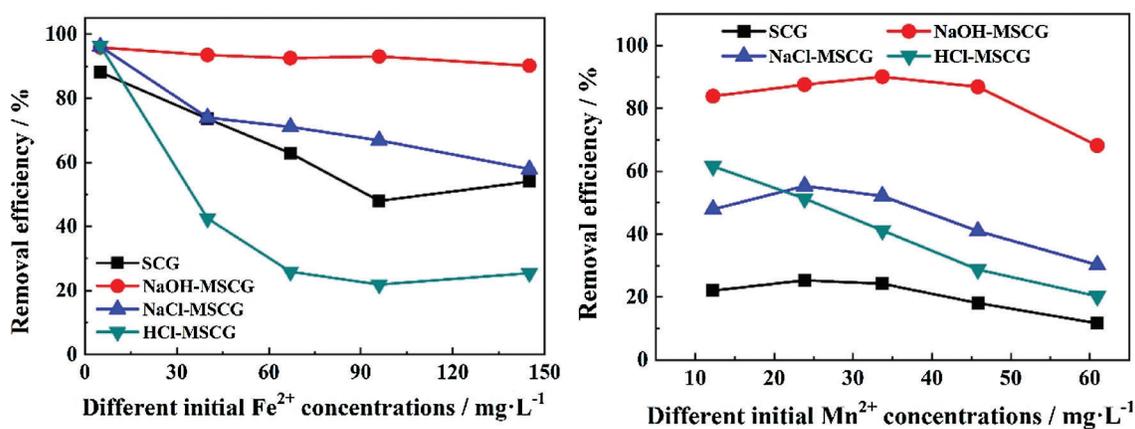


Figure 8: Efficiency of MSCG at removing different concentrations of Fe^{2+} and Mn^{2+}

As shown in Fig. 7, the HCl-MSCG has a low Fe^{2+} removal efficiency and is not as effective as NaOH-MSCG and NaCl-MSCG at removing Mn^{2+} . Chen et al. [38] found that the concentration of alkali metal oxides, such as iron and Al_2O_3 , in coal gangue can be reduced by soaking coal gangue in HCl. The pores on the surface of the HCl-MSCG can absorb Fe^{2+} and Mn^{2+} . Moreover, H^+ will also replace the Ca^{2+} , Mg^{2+} , and other cations on the surface of the coal gangue during the modification process, which

improves the cation exchange capacity of the HCl-MSCG [32]. However, during the modification process, some pore impurities that are firmly bound to the minerals and do not easily react with acid are difficult to remove, so the effect of the acid modification is limited, and the Fe^{2+} and Mn^{2+} removal efficiencies are 43.37% and 52.20%, respectively, which are lower than those of the NaOH-MSCG and NaCl-MSCG. In addition, the initial concentration of Mn^{2+} was lower than that of Fe^{2+} , so the Mn^{2+} removal effect was better than that of Fe^{2+} . Taking Mn^{2+} as the standard, the optimal conditions for HCl modification are an HCl concentration of 1 mol/L, a liquid to solid ratio of 6 L/kg, and a modification time of 16 h.

As shown in Fig. 8, the removal efficiency of Fe^{2+} and Mn^{2+} decreased with increasing metal ion concentration. The Fe^{2+} removal effects were as follows: NaOH-MSCG > NaCl-MSCG > SCG > HCl-MSCG. The Mn^{2+} removal effects were as follows: NaOH-MSCG > NaCl-MSCG > HCl-MSCG > SCG. Zhou et al. [39] found that in the process of the alkali modification of gangue, some of the metal oxides in the gangue, e.g., $(\text{HO})_3\text{SiO}^-$ and $\text{Al}(\text{OH})_4^-$, are dissolved due to the increased number of capillary pores and the increased specific surface area. They determined that alkali modification can not only dissolve some metal oxides, but that the alkali solution also reacts with the aluminosilicates in the coal gangue to create zeolites with a higher adsorption capacity [30]. Under the alkali modification conditions, the Al^{3+} , Fe^{2+} , Fe^{3+} , and Mg^{2+} in the gangue are hydrolyzed to generate $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, and other colloidal flocculent particles. In addition, many complexation ions were formed, removing some of the ions from the wastewater [40]. Therefore, NaOH modified spontaneous combustion gangue has a stronger ability to absorb metal ions in wastewater. The efficiencies of the three modification methods at removing Fe^{2+} and Mn^{2+} are as follows: NaOH-MSCG > NaCl-MSCG > HCl-MSCG. Therefore, NaOH-MSCG was selected for the next experiment.

3.3 Dynamic Removal of Fe^{2+} and Mn^{2+} from Acid Mine Drainage Using NaOH-MSCG

Based on the results of the single factor experiments, two dynamic experimental columns were constructed for the dynamic test: column No. 1 was loaded with SCG, and column No. 2 was loaded with NaOH-MSCG. The dynamic removal of Fe^{2+} and Mn^{2+} from acid mine drainage by NaOH-MSCG was analyzed. The results are shown in Fig. 9.

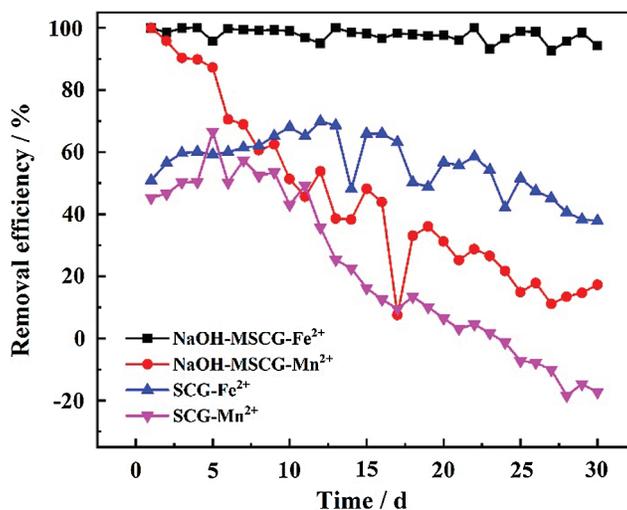


Figure 9: Dynamic removal of Fe^{2+} and Mn^{2+} from acid mine drainage by NaOH-MSCG

According to Fig. 9, the two dynamic experimental columns showed good and relatively stable Fe^{2+} removal capabilities; the average removal efficiency of Fe^{2+} for column No. 1 and column No. 2 were 55.91% and 97.73%, respectively. The SCG mainly removed the Fe^{2+} in acid mine drainage through surface pore adsorption and ion exchange reactions with albite. The removal efficiency initially increased and then decreased because there are more adsorption sites and ion exchange points on the coal gangue's surface at the beginning of the adsorption period. Thus, the adsorption effect tends to increase, while the removal efficiency tends to decrease slowly as the number of available adsorption sites decreases. By comparing the efficiencies of the SCG and the NaOH-MSCG at removing Fe^{2+} , we determined that the NaOH modification improved the Fe^{2+} adsorption capacity of the SCG. This may be because the alkali modification can dissolve some of the metal oxides, forming more pores inside and on the surface of the coal gangue, thereby increasing the number of adsorption sites on the surface. In addition, the alkali compound reacts with the aluminosilicates to synthesize a small amount of zeolite with a higher adsorption capacity, thus improving the removal of Fe^{2+} .

The removal of the Mn^{2+} in acid mine drainage in the two dynamic experimental columns showed a general downward trend, with average Mn^{2+} removal efficiency of column No. 1 and column No. 2 were 21.64% and 44.82%, respectively. As the reaction time increased, the removal efficiency of Mn^{2+} in column No. 2 showed a downward trend, from an initial removal efficiency of 99.99% to 17.28%, indicating that there were many Mn^{2+} adsorption sites because of the initial amount of NaOH-MSCG. As the reaction progressed, the adsorption sites gradually became occupied, and the amount of Mn^{2+} adsorbed by the NaOH-MSCG gradually decreased as the gangue became saturated. The Mn^{2+} removal efficiency of column No.1 increased from 45.25% to 66.58% and then decreased to -17.27%. Zhang et al. [41] found that increasing the amount of coal gangue provides more available adsorption sites for Mn^{2+} adsorption, so the Mn^{2+} removal efficiency for the column increased in the initial stage of the reaction. However, when the adsorbent is sufficient, the adsorption effect mainly depends on the ability of the adsorbent molecules to migrate sufficiently to the surface [42]. As the amount of Mn^{2+} adsorbed by the SCG increases and gradually becomes saturated, adsorption-analysis of the Mn^{2+} occurs, which is not conducive to the adsorption of Mn^{2+} . Therefore, the removal efficiency of Mn^{2+} by the column decreases in the later stage of adsorption.

Based on our experiments, we determined that NaOH-MSCG has a better dynamic Fe^{2+} and Mn^{2+} removal efficiency than SCG.

4 Conclusions

The accumulation of spontaneous combustion gangue poses large safety risks to the daily production and environmental protection of mining areas. In the process of acid mine drainage treatment, efficient and cheap adsorption materials are always scarce resources. Therefore, this paper uses spontaneous combustion gangue from the Gaode mining area as the raw material, and through NaOH, NaCl, and HCl chemical modification, we conducted a comparative study of the effects of modified coal gangue on acid mine wastewater treatment. The following conclusions were drawn based on the results of this study.

- (1) The effectiveness of spontaneous combustion gangue at removing Fe^{2+} is better than its effectiveness at removing Mn^{2+} , and the optimal conditions for spontaneous combustion gangue to absorb Fe^{2+} and Mn^{2+} include a particle size of 120–180 μm , a dosing amount of 4 g/50 mL, and a reaction time of 150 min.
- (2) Compared with spontaneous combustion gangue and modified coal gangue, NaOH modification significantly improves the efficiency of the spontaneous combustion gangue at removing Fe^{2+} and Mn^{2+} from acid mine drainage. The optimal modification conditions are an NaOH concentration of 3 mol/L, a liquid to solid ratio of 2 L/kg, and a modification time of 8 h.

- (3) Based on the results of the single factor test, the dynamic adsorption performance of the NaOH modified gangue was verified using column experiments. The results show that the dynamic treatment of Fe^{2+} and Mn^{2+} removal from acid mine drainage is as follows: NaOH modified gangue in column No. 2 > unmodified gangue in column No. 1. The average removal efficiencies of Fe^{2+} and Mn^{2+} by the NaOH modified gangue in column No. 2 were 97.73% and 44.82%, respectively.
- (4) Using spontaneous combustion gangue to prepare an adsorbent has the advantages of numerous raw materials and low cost. It not only achieves recycling and utilization of coal gangue, but it also solves the pollution problem posed by nearby acid mine drainage. The results of our study provide new ideas for addressing solid waste and wastewater issues in mining areas, promoting clean production in mining areas, and fulfilling the research purpose of “treating dust with waste”.

This study introduces a new application of spontaneous combustion gangue, optimizes the preparation conditions of modified coal gangue, verifies the feasibility of the application of NaOH modified spontaneous coal gangue to wastewater remediation, provides a research basis for the secondary utilization of coal gangue in Fuxin, and is conducive to sustainable development in mining areas.

Funding Statement: This work was supported by the National Natural Science Foundation of China (Nos. 51304114, 41672247), and the Scientific Research Fund of the Liaoning Provincial Education Department (No. LJ2017FAL016).

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

References

1. Masindi, V., Akinwekomi, V., Maree, J. P., Muedia, K. L. (2017). Comparison of mine water neutralisation efficiencies of different alkaline generating agents. *Journal of Environmental Chemical Engineering*, 5(4), 3903–3913. DOI 10.1016/j.jece.2017.07.062.
2. Crafton, E., Pritchard, C., Guo, L., Senko, J. M., Cutright, T. J. (2019). Dynamics of Mn removal in an acid mine drainage treatment system over 13 years after installation. *Environmental Earth Sciences*, 78, 10. DOI 10.1007/s12665-018-8008-z.
3. Dong, Y., Di, J., Yang, Z., Zhang, Y., Wang, X. et al. (2020). Study on the effectiveness of sulfate-reducing bacteria combined with coal gangue in repairing acid mine drainage containing Fe and Mn. *Energies*, 13(4), 995. DOI 10.3390/en13040995.
4. Naidu, G., Ryu, S., Thiruvengkatahari, R., Choi, Y., Jeong, S. et al. (2019). A critical review on remediation, reuse, and resource recovery from acid mine drainage. *Environmental Pollution*, 247, 1110–1124. DOI 10.1016/j.envpol.2019.01.085.
5. Shen, X., Xie, Y., Wang, Q., Yi, X., Shamshina, J. L. et al. (2019). Enhanced heavy metal adsorption ability of lignocellulosic hydrogel adsorbents by the structural support effect of lignin. *Cellulose*, 6(6), 4005–4019. DOI 10.1007/s10570-019-02328-w.
6. Bezzina, J. P., Ruder, L. R., Dawson, R., Ogden, M. D. (2019). Ion exchange removal of Cu(II), Fe(II), Pb(II) and Zn(II) from acid extracted sewage sludge–resin screening in weak acid media. *Water Research*, 158, 257–267. DOI 10.1016/j.watres.2019.04.042.
7. Du, R., Gao, B., Men, J. (2018). Microfiltration membrane possessing chelation function and its adsorption and rejection properties towards heavy metal ions. *Journal of Chemical Technology & Biotechnology*, 94(5), 1441–1450. DOI 10.1002/jctb.5915.
8. Hwang, S. K., Jho, E. H. (2018). Heavy metal and sulfate removal from sulfate-rich synthetic mine drainages using sulfate reducing bacteria. *Science of the Total Environment*, 635, 1308–1316. DOI 10.1016/j.scitotenv.2018.04.231.

9. Mokgehele, T. M., Gitari, W. M., Tavengwa, N. T. (2019). Synthesis of di-carboxylic acid functionalized zeolites from coal fly ash for Cd (II) removal from acid mine drainage using column studies approach. *Journal of Environmental Chemical Engineering*, 7(6), 103473. DOI 10.1016/j.jece.2019.103473.
10. Igberase, E., Osifo, P., Ofomaja, A. (2017). Mathematical modelling of Pb^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Cr^{6+} and Cd^{2+} ions adsorption from a synthetic acid mine drainage onto chitosan derivative in a packed bed column. *Environmental Technology*, 39(24), 3203–3220. DOI 10.1080/09593330.2017.1375027.
11. Li, Y., Huang, H., Xu, Z., Ma, H., Guo, Y. (2020). Mechanism study on manganese(II) removal from acid mine wastewater using red mud and its application to a lab-scale column. *Journal of Cleaner Production*, 253, 119955. DOI 10.1016/j.jclepro.2020.119955.
12. Etale, A., Tutu, H., Drake, D. C. (2016). Application of maghemite nanoparticles as sorbents for the removal of Cu (II), Mn(II) and U(VI) ions from aqueous solution in acid mine drainage conditions. *Applied Water Science*, 6(2), 187–197. DOI 10.1007/s13201-014-0217-3.
13. Qian, T., Li, J. (2015). Synthesis of Na-A zeolite from coal gangue with the *in-situ* crystallization technique. *Advanced Powder Technology*, 26(1), 98–104. DOI 10.1016/j.apt.2014.08.010.
14. Liu, X., Yang, X., Du, H., Wu, Y., Zhang, X. et al. (2018). Preparation and characterization of a porous silicate material using a CO_2 -storage material for CO_2 adsorption. *Powder Technology*, 333, 138–152. DOI 10.1016/j.powtec.2018.04.022.
15. Wu, H., Wen, Q., Hu, L., Gong, M., Tang, Z. (2017). Feasibility study on the application of coal gangue as landfill liner material. *Waste Management*, 63, 161–171. DOI 10.1016/j.wasman.2017.01.016.
16. Zhao, J., Wang, D., Liao, S. (2015). Effect of mechanical grinding on physical and chemical characteristics of circulating fluidized bed fly ash from coal gangue power plant. *Construction and Building Materials*, 101, 851–860. DOI 10.1016/j.conbuildmat.2015.10.144.
17. Zhang, J., Li, M., Liu, Z., Zhou, N. (2017). Fractal characteristics of crushed particles of coal gangue under compaction. *Powder Technology*, 305, 12–18. DOI 10.1016/j.powtec.2016.09.049.
18. Qi, W., Huang, Y., He, H., Zhang, J., Qiao, M. (2019). Potential pollution of groundwater by dissolution and release of contaminants due to using gangue for backfilling. *Mine Water and the Environment*, 38(2), 281–293. DOI 10.1007/s10230-018-00585-y.
19. Yang, Z., Zhang, Y., Liu, L., Seetharaman, S., Wang, X. et al. (2016). Integrated utilization of sewage sludge and coal gangue for cement clinker products: promoting tricalcium silicate formation and trace elements immobilization. *Materials*, 9(4), 275–288. DOI 10.3390/ma9040275.
20. Zhang, N., Li, H., Liu, X. (2016). Hydration mechanism and leaching behavior of bauxite-calcination-method red mud-coal gangue based cementitious materials. *Journal of Hazardous Materials*, 314, 172–180. DOI 10.1016/j.jhazmat.2016.04.040.
21. Jabłońska, B., Kityk, A. V., Busch, M., Huber, P. (2017). The structural and surface properties of natural and modified coal gangue. *Journal of Environmental Management*, 190, 80–90. DOI 10.1016/j.jenvman.2016.12.055.
22. Shang, Z., Zhang, L., Zhao, X., Liu, S., Li, D. (2019). Removal of Pb(II), Cd(II) and Hg(II) from aqueous solution by mercapto-modified coal gangue. *Journal of Environmental Management*, 231, 391–396. DOI 10.1016/j.jenvman.2018.10.072.
23. Nadiye-Tabbiruka, M. S., Lungani, L. (2018). Removal of dyes from waste waters through adsorption using HCl activated coal. *International Journal of Materials and Chemistry*, 8(2), 23–30. DOI 10.5923/j.ijmc.20180802.01.
24. Qiu, R., Cheng, F. (2016). Modification of waste coal gangue and its application in the removal of Mn^{2+} from aqueous solution. *Water Science and Technology*, 74(2), 524–534. DOI 10.2166/wst.2016.235.
25. Bu, N., Liu, X., Song, S., Liu, J., Yang, Q. et al. (2020). Synthesis of NaY zeolite from coal gangue and its characterization for lead removal from aqueous solution. *Advanced Powder Technology*, 31(7), 2699–2710. DOI 10.1016/j.apt.2020.04.035.
26. Lu, X., Shi, D., Chen, J. (2017). Sorption of Cu^{2+} and Co^{2+} using zeolite synthesized from coal gangue: isotherm and kinetic studies. *Environmental Earth Sciences*, 76, 591. DOI 10.1007/s12665-017-6923-z.

27. Ge, Q., Moeen, M., Tian, Q., Xu, J., Feng, K. (2020). Highly effective removal of Pb^{2+} in aqueous solution by Na-X zeolite derived from coal gangue. *Environmental Science and Pollution Research*, 27(7), 7398–7408. DOI 10.1007/s11356-019-07412-z.
28. Di, J., Wang, M., Zhu, Z. (2018). Experiment on the treatment of acid mine drainage with optimized biomedical stone particles by response surface methodology. *Environmental Science and Pollution Research*, 25(8), 7978–7990. DOI 10.1007/s11356-017-1135-3.
29. Buyanov, R. A., Molchanov, V. V., Boldyrev, V. V. (2009). Mechanochemical activation as a tool of increasing catalytic activity. *Catalysis Today*, 144(3–4), 212–218. DOI 10.1016/j.cattod.2009.02.042.
30. Li, H., Zheng, F., Wang, J., Zhou, J., Huang, X. et al. (2020). Facile preparation of zeolite-activated carbon composite from coal gangue with enhanced adsorption performance. *Chemical Engineering Journal*, 390, 124513. DOI 10.1016/j.cej.2020.124513.
31. Ellersdorfer, M. (2017). The ion-exchanger–loop-stripping process: ammonium recovery from sludge liquor using NaCl-treated clinoptilolite and simultaneous air stripping. *Water Science and Technology*, 77(3), 695–705. DOI 10.2166/wst.2017.561.
32. Hor, K. Y., Chee, J. M. C., Chong, M. N., Jin, B., Saint, C. et al. (2016). Evaluation of physicochemical methods in enhancing the adsorption performance of natural zeolite as low-cost adsorbent of methylene blue dye from wastewater. *Journal of Cleaner Production*, 118, 197–209. DOI 10.1016/j.jclepro.2016.01.056.
33. Zhang, Y., Yang, X., Tighe, S. (2019). Evaluation of mechanical properties and microscopic structure of coal gangue after aqueous solution treatment. *Materials*, 12(19), 3207. DOI 10.3390/ma12193207.
34. Peng, B., Li, X., Zhao, W., Yang, L. (2018). Study on the release characteristics of chlorine in coal gangue under leaching conditions of different pH values. *Fuel*, 217, 427–433. DOI 10.1016/j.fuel.2017.12.123.
35. Yan, S., Zhang, F., Wang, L., Rong, Y., He, P. et al. (2019). A green and low-cost hollow gangue microsphere/geopolymer adsorbent for the effective removal of heavy metals from wastewaters. *Journal of Environmental Management*, 246, 174–183. DOI 10.1016/j.jenvman.2019.05.120.
36. Tang, Q., Li, L., Zhang, S., Zheng, L., Miao, C. (2018). Characterization of heavy metals in coal gangue-reclaimed soils from a coal mining area. *Journal of Geochemical Exploration*, 186, 1–11. DOI 10.1016/j.gexplo.2017.11.018.
37. Li, L., Zhang, Y., Zhang, Y., Sun, J., Hao, Z. (2016). The thermal activation process of coal gangue selected from Zhungeer in China. *Journal of Thermal Analysis and Calorimetry*, 126(3), 1559–1566. DOI 10.1007/s10973-016-5711-4.
38. Chen, J., Lu, X. (2017). Synthesis and characterization of zeolites NaA and NaX from coal gangue. *Journal of Material Cycles and Waste Management*, 20(1), 1–7. DOI 10.1007/s10163-015-0396-5.
39. Zhou, J., Zheng, F., Li, H., Wang, J., Bu, N. et al. (2020). Optimization of post-treatment variables to produce hierarchical porous zeolites from coal gangue to enhance adsorption performance. *Chemical Engineering Journal*, 381, 122698. DOI 10.1016/j.cej.2019.122698.
40. Quan, X., Wang, H. (2014). Preparation of a novel coal gangue–polyacrylamide hybrid flocculant and its flocculation performance. *Chinese Journal of Chemical Engineering*, 22(9), 1055–1060. DOI 10.1016/j.cjche.2014.06.032.
41. Zhang, L., Chen, A., Qu, H., Xu, S., Zhang, X. et al. (2015). Fe and Mn removal from mining drainage using goaf filling materials obtained from coal mining process. *Water Science and Technology*, 72(11), 1940–1947. DOI 10.2166/wst.2015.322.
42. de Sales, P. F., Magriotis, Z. M., Rossi, M. A., Tartuci, L. G., Papini, R. M. et al. (2013). Study of chemical and thermal treatment of kaolinite and its influence on the removal of contaminants from mining effluents. *Journal of Environmental Management*, 128, 480–488. DOI 10.1016/j.jenvman.2013.05.035.