



Ziguo Liu *, Wei Zhou, Xianli Liu 🔎, Xuefen Yang, Wei Yang and Han Zheng

School of Environmental Science and Engineering, Hubei Polytechnic University, Huangshi 435003, China; zhouwei@hbpu.edu.cn (W.Z.); liuxianli@hbpu.edu.cn (X.L.); yangxuefen@hbpu.edu.cn (X.Y.); yangwei@hbpu.edu.cn (W.Y.); zhenghan@hbpu.edu.cn (H.Z.)

* Correspondence: liuziguo@hbpu.edu.cn

Abstract: In this study, the zero-valent iron Fenton reagent (ZVI Fenton-like) system was combined with the chemical precipitation method for the deep treatment of desulfurization wastewater from coal-fired power plants, and the chemical oxygen demand (COD) was used as the evaluation criterion for organic matter in the desulfurization wastewater. The effects of reaction time, H₂O₂ dosage, zero-valent iron dosage, pH, and reaction temperature were also investigated. The results showed that the COD concentration of the effluent was the lowest when the running time of the ZVI Fenton-like reagent system was 1 h, the dosage of H₂O₂ was 33.3 mg·L⁻¹, the dosage of iron was 0.075 g·L⁻¹, the pH was 4.5~6.5, the reaction temperature was 35 °C, the COD concentration of the wastewater was the lowest and its operating conditions were the best, and the internal reaction mechanism was finally deduced. In summary, the zero-valent iron Fenton reagent system provides a new idea for the treatment of desulfurization wastewater from coal-fired power plants.

Keywords: zero-valent iron (ZVI); Fenton-like oxidation; flue gas desulfurization wastewater; chemical oxygen demand



Citation: Liu, Z.; Zhou, W.; Liu, X.; Yang, X.; Yang, W.; Zheng, H. Study on Treatment Performance of Desulfurization Wastewater by Zero-Valent Iron Fenton-like Process. *Separations* **2023**, *10*, 451. https:// doi.org/10.3390/separations10080451

Academic Editors: Guanlong Yu and Wenjing Chen

Received: 18 June 2023 Revised: 31 July 2023 Accepted: 8 August 2023 Published: 14 August 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

1. Introduction

Flue gas desulfurization (FGD) is an effective method widely used in flue gas treatment. According to the form of the desulfurization agent and its byproducts, based on the advantages of wet flue gas desulfurization, it is the most widely used technology at present. Limestone–gypsum desulfurization is the most typical wet process. It has become the first choice for flue gas desulfurization in thermal power plants because of its mature technology, simple and stable operation, and high desulfurization efficiency, but this method generates a large amount of desulfurization wastewater in the process of desulfurization [1–3]. According to statistics, about 92% of the flue gas desulfurization units in Chinese coal-fired power plants use the limestone-gypsum method, so treating desulfurization wastewater is a challenge [4–6]. As the end wastewater of coal-fired power plants, desulphurization wastewater has miscellaneous substances which mainly include chloride, fluoride, high concentrations of sulphite, suspended matter, sulphate, a small amount of heavy metal ions (such as Pb²⁺, Cr²⁺, etc.), ammonia nitrogen, etc. With most of the pollutants transferring from the gas phase to the liquid phase, it is the most difficult to treat within thermal power plants [7–9]. According to the literature, the "neutralization-flocculation-precipitation" triple tank is a common chemical precipitation process to treat desulphurization wastewater, but its process was long and complex. In addition to its large area, various equipment, and complex arrangement, its treatment effect is also average, and it is difficult to achieve the expected effect [10-12]. Hydroxyl free radical (\cdot OH) generated by Fenton reaction (Equation (1)) has been shown to effectively degrade numerous toxic pollutants [13], so the Fenton process is widely used as a complementary step for the advanced treatment, given that it is capable of simultaneously removing organics and heavy metals such as As, Cd, and Hg [14,15]. However, the shortcomings of the Fenton oxidation method are mainly: the large amount of H_2O_2 that will be consumed, the low utilization rate of H_2O_2 , the easy loss of Fe^{2+} , and the ready formation of iron sludge [16], all of which increase the cost of water treatment. In addition, there is the disadvantage of a narrow range of pH. Therefore, the process needs to be further improved. The electrode potential of zero-valent iron (ZVI) is E_0 $(Fe^{2+}/Fe^{0}) = -0.44$ V, which is high electronegativity. It has a strong reduction ability and can reduce oxidizing ions or compounds as well as some organic pollutants. Its chemical property is active, and some inactive heavy metals can be replaced by substitution reaction, which plays a role in removing heavy metal ions in wastewater. Fe²⁺ can be further oxidized into Fe³⁺ and OH⁻ to form precipitation, and the pollutants in the water can be removed by flocculation and precipitation. At the same time, compared with the traditional homogeneous Fenton system (Fe^{2+}/H_2O_2), the heterogeneous Fenton-like system formed by ZVI and H_2O_2 has the advantages of less H_2O_2 consumption and easy recovery of catalytic materials. It can avoid the problems of other Fenton systems such as narrow pH range, catalyst deactivation, and difficulty in regeneration [17]. A novel nanoscale zero-valent iron (AMD-nZVI) produced from the reaction of acid mine drainage (AMD) with NaBH₄ was combined with peroxydisulfate (PDS) for the simultaneous removal of Cr (VI), Cd (II), and atrazine (ATZ) in water. Results demonstrate that the simultaneous removal efficiencies of Cr(VI), Cd(II), and ATZ by the AMD-nZVI/PDS process were high: up to 90% within 40 min [18]. It can be seen that the treatment of all kinds of wastewater by the zero-valent iron Fenton-like process has been widely studied. However, there are few studies on the use of ZVI Fenton-like oxidation to treat desulfurization wastewater from thermal power plants. This research probes into the effects of reaction time, H_2O_2 dosage, iron powder dosage, pH, and reaction temperature on the degradation of chemical oxygen demand (COD) through single-factor experiments. It was designed to find the optimal reaction conditions for the treatment of Fenton oxidation of thermal power plant desulphurization wastewater with zero-valent iron, so as to achieve optimal treatment of desulphurization wastewater.

2. Materials and Methods

2.1. Experimental Equipment and Apparatus

The experimental apparatuses used in the experiment include a pH meter (PHSJ-3F, Shanghai Raycom Sensor Technology Co., Ltd., Shanghai, China), magnetic stirrer (DF-101S, Shanghai Shampo Instruments & Equipment Co., Ltd., Shanghai, China), colorimeter (DR300, HACH, Shanghai, China), spectrophotometer (UV-2600, Shimadzu, Kyoto, Japan), and microwave dissolver, etc.

2.2. Water Quality Conditions and Testing Indicators

The desulfurization wastewater used for the experiment was obtained from a coalfired power plant pretreating with the chemical precipitation method. The light-yellow wastewater was slightly turbid with pungent odor. The current concentrations of the pollutants in the water were: COD 170.6 mg·L⁻¹, SS 38.5 mg·L⁻¹, water color 19, and pH 7.6. The indicators to be measured in the study involved pH, COD, chroma, etc. COD was measured according to the water quality determination of the chemical oxygen demand dichromate method [19].

2.3. Experimental Materials and Reagents

According to the standard assay method, the research had to use the following chemical reagents, namely, $FeSO_4 \cdot 7H_2O$ solid, sodium hydroxide solid, concentrated sulfuric acid solution, 30% hydrogen peroxide solution, COD determination reagent, sponge iron powder, polyacrylamide (PAM), etc. All chemicals used in this study were of analytical grade and were purchased from Sinopharm Reagent Co., Ltd., Shanghai, China.

2.4. ZVI Fenton-like Method for Desulfurization Wastewater

The traditional Fenton method involves the decomposition of H₂O₂ under the catalytic action of Fe²⁺ to produce hydroxyl radicals which oxidize and decompose organic matter into small molecules. At the same time, Fe^{2+} was oxidized to Fe^{3+} to produce coagulation and precipitation, removing a large amount of organic matter. However, the utilization rate of H_2O_2 is not high and cannot fully mineralize the organic matter. Therefore, for the existing desulfurization wastewater treated by the conventional chemical precipitation method, some of the difficult-to-degrade organic matter proved difficult and problematic to remove. It is proposed to use the ZVI Fenton-like oxidation technology as a supplement to the existing process, the desulfurization wastewater for in-depth treatment, to ensure that the final effluent COD can meet the discharge standards. The ZVI Fenton-like oxidation technology introduces Fe^0 into water treatment, which can generate large amounts of Fe^{2+} upon reaction in water, which in turn can catalyze the generation of \cdot OH from H₂O₂ to oxidize and decompose organic matter in a fast and effective manner (Equations (1)-(5)) [20,21]. Regardless, ZVI particles can adsorb organic matter on their surface, where it can directly undergo redox reaction, which contributes to the removal of COD. The Fe^{3+} generated after a series of oxidation reactions can then react with Fe^0 to produce Fe^{2+} constantly, thus decreasing the production of iron sludge and reducing the burdens of sludge treatment and disposal [18].

$$Fe_0(s) + H_2O_2 + 2H^+ \rightarrow Fe(II) + 2H_2O$$

$$\tag{1}$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + \cdot OH + OH^-$$
(2)

$$Fe(II) + H_2O_2 \rightarrow Fe(IV) (e.g., FeO^{2+}) + H_2O$$
(3)

$$Fe(II) + O_2 \to Fe(III) + O_2 \cdot^- \tag{4}$$

$$Fe(II) + O_2 \cdot^- + 2H^+ \rightarrow Fe(III) + H_2O_2$$
(5)

According to the above reaction process, the ZVI Fenton-like oxidation technology produces a small amount of precipitation, is easy to separate, and has a flexible operation method compared with the traditional Fenton reaction. However, there are few research reports on the use of the ZVI Fenton-like oxidation technology to treat desulfurization wastewater. Therefore, in this study, the ZVI Fenton-like oxidation technology was used to treat desulfurization wastewater, and the key lies in how to control the catalytic reaction process and optimize the dosage of each agent, as well as in the operating parameters. The reaction mechanism of the ZVI Fenton-like oxidation technology to degrade COD in desulfurization wastewater was analyzed.

2.5. Experimental Design

In the laboratory, the wastewater was treated by the process shown in Figure 1.

The experiment uses the ZVI Fenton-like method to achieve the removal of organic matter in desulfurization wastewater, and the experiment can be divided into two stages: ZVI Fenton-like reaction and coagulation reaction, and the specific operation process and mechanism are shown in Figure 1. Firstly, the collected desulfurization wastewater needs to go through 0.5 h of aeration and 1 h of static pretreatment. Subsequently, each 500 mL of desulfurization wastewater was loaded into a beaker as a water sample, the solution was continuously stirred with the help of a magnetic stirrer, and ZVI and H_2O_2 were added to the solution in turn. The internal reaction mechanism is shown in Figure 1.



Figure 1. Fenton-like oxidation process for desulfurization wastewater treatment.

After a period of reaction, polyacrylamide (PAM) was added to the beaker and maintained at a concentration of 10 mg/L, left to stand for a period of time. The PAM was mixed with the suspended material to form a homogeneous mixture, resulting in the final bottom sludge and supernatant. A total of 20 groups of experiments were set up, and single-factor experiments were designed according to five factors: reaction time, H_2O_2 dosage, iron powder dosage, pH, and reaction temperature for quantitative analysis. Four groups of parallel experiments were set up for each single-factor experiment to finally determine the best reaction conditions for the treatment of desulfurization wastewater by the ZVI Fenton-like system. In addition, to minimize errors, samples were collected and measured in triplicate.

3. Results and Discussion

3.1. Impact of Reaction Time on COD Removal

In general, with the increase in time, the effect of wastewater treatment is better, but the volume of the equipment will increase, leading to an increase in investment costs. Therefore, it is necessary to choose an appropriate reaction time. When the pH was kept at 6.5, the amount of iron powder was $0.1 \text{ g} \cdot \text{L}^{-1}$, the amount of H₂O₂ was 33.3 mg·L⁻¹, and the reaction temperature was 25 °C. The reaction times for the experiments were set to 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.5, and 2 h. To investigate the effect of reaction time on the COD concentration of the effluent, we measured the COD concentration in the aqueous solution after the reaction and calculated the COD removal rate. The results are shown in Figure 2.

As can be seen from Figure 2, the concentration of COD decreased significantly with the increase in the reaction time. When the reaction time was 1 h, its concentration reached the lowest, 98.2 mg·L⁻¹, and the removal rate reached 42.4%. After extending the reaction time, it was found that the increase in COD removal rate was not obvious. Therefore, the treatment of desulfurization wastewater pretreated by chemical precipitation using ZVI Fenton-like oxidation can be completed within 1 h, and the treatment effect of extending the reaction time is not obvious. On the contrary, it increases the volume of the treatment facility and thus the operating cost, which is not worthwhile. Therefore, the optimal reaction time for this study was determined to be 1 h.



Figure 2. Reaction time impact on the COD removal rate (reaction conditions: iron powder dosage is 0.1 g/L; H₂O₂ dosage is 33.3 mg/L; pH is 6.5; reaction temperature is 25 °C).

3.2. Impact of H₂O₂ Dosage on COD Removal

The dosage of H_2O_2 at the initial stage is crucial; it will directly affect the removal efficiency of COD. At the same time, in the application of Fenton-like technology, the amount of H_2O_2 is an important factor to determine the cost of wastewater treatment, and reducing the dosage of H_2O_2 to reduce the treatment cost is the main consideration of researchers. It is therefore necessary to investigate the optimal H_2O_2 dosage. Ramos et al. studied the degradation of a real textile effluent in the presence of zero-valent iron and H_2O_2 as an oxidant, they discovered that the greatest COD reductions were obtained for H_2O_2 values of between 0.02–0.04 mol·L⁻¹ at 15 °C [22].

Under the conditions of pH 6.5, a reaction time of 1 h, an iron powder dosage of $0.1 \text{ g}\cdot\text{L}^{-1}$, and a reaction temperature of 25 °C, the H₂O₂ dosages of experimental groups were set as 0.01, 0.02, 0.03, 0.04, and 0.05 mL·L⁻¹, respectively. The COD concentration in the aqueous solution was measured after the reaction, and the COD removal rate was calculated to investigate the effect of H₂O₂ dosage on the effluent COD concentration. The results are shown in Figure 3.



Figure 3. H_2O_2 dosage impact on the COD removal rate (reaction conditions: iron powder dosage is 0.1 g/L; pH is 6.5; reaction temperature is 25 °C; reaction time is 1 h).

As shown in Figure 3, when the H_2O_2 dosage was increased from 0.01 mL·L⁻¹ to 0.03 mL·L⁻¹, the COD concentration decreased to 97.8 mg·L⁻¹, and the removal rate was

42.6%; when the H₂O₂ dosage was increased from 0.03 mL·L⁻¹ to 0.05 mL·L⁻¹, the COD concentration increased rather than decreased.

When H_2O_2 was below 0.03 mL·L⁻¹, increased H_2O_2 dosage led to increased ·OH in the system, which promoted the degradation of pollutants [23]. When H_2O_2 was above 0.03 mL·L⁻¹, H_2O_2 may have been excessive, and the excess H_2O_2 would have been consumed in reaction with ·OH [24,25], thus inhibiting the oxidation reaction and resulting in a lower COD removal rate. According to literature reports, when H_2O_2 was excessive, the product ·OH reacted with excess H_2O_2 to form HO_2 · with lower oxidation ability (Equation (6)). In addition, ·OH further reacted with the generated HO_2 · and finally released O_2 (Equation (7)), resulting in some HO_2 · being self-consumed. It was further explained that the reaction degradation rate and degradation rate decrease when the amount of H_2O_2 is excessive. Based on the above analysis, the optimum H_2O_2 dosage was determined to be 0.03 mL·L⁻¹. The H_2O_2 dosages were all determined to be 0.03 mL·L⁻¹ in the subsequent experiments.

$$H_2O_2 + \cdot OH \to H_2O + HO_2 \cdot \tag{6}$$

$$HO_2 \cdot + \cdot OH \to H_2O + O_2$$
 (7)

3.3. Impact of Fe Powder Dosage on COD Removal

In Fe⁰ type Fenton systems, which employ Fe⁰ as a reducing agent, can directly reduce the pollutants in wastewater and simultaneously provide a source of Fe²⁺ ions required in Fenton reaction. However, Fe⁰ also reacts directly with H₂O₂ to consume some H₂O₂. In previous works, the amounts of Fe⁰ initially used for the treatment were larger [22]. Therefore, it is necessary to select the appropriate Fe⁰ dosage under the condition of a certain dosage of H₂O₂ to achieve the best results. In a certain range, the concentration of pollutants increases with the increase in ZVI addition, while the excess Fe affects the removal of pollutants instead, so it is necessary to investigate the Fe dosage.

Under the conditions of pH 6.5, an H_2O_2 dosage of 33.3 mg·L⁻¹, and a reaction temperature of 25 °C, the iron powder dosages of 0.05, 0.075, 0.1, 0.125, and 0.15 g·L⁻¹ were set, the COD concentration in the aqueous solution was measured after the reaction, and the final COD removal rate was calculated. The results are shown in Figure 4.



Figure 4. Fe powder dosage impact on the COD removal rate (reaction conditions: H_2O_2 dosage is 33.3 mg/L; pH is 6.5; reaction temperature is 25 °C; reaction time is 1 h).

Figure 4 shows that when the Fe powder dosage was increased from $0.05 \text{ g}\cdot\text{L}^{-1}$ to 0.075 g·L⁻¹, the COD concentration decreased to 100.6 mg·L⁻¹; when the Fe powder dosage was increased from 0.075 g·L⁻¹ to 0.15 g·L⁻¹, the COD concentration increased

rather than decreased. It can be seen that under an Fe powder dosage of 0.075 g·L⁻¹, the COD concentration was the lowest, with the highest removal rate of 41.0%. It was obvious that Fe powder dosage will affect the COD removal effect. As for the reason, when the Fe powder dosage was below 0.075 g·L⁻¹ and the Fe powder dosage was increased, more Fe²⁺ was produced, which contributes to catalytic decomposition of H₂O₂ and results in more ·OH [24–26], thus speeding up the reaction efficiency and increasing the COD removal rate. When the Fe powder dosage was above 0.075 g·L⁻¹, excessive Fe²⁺ was produced in a short period of time, and the excess Fe²⁺ reacted with ·OH to form Fe³⁺ (Equation (8)) [27]. The consumption of ·OH hinders the reaction, resulting in a decreased COD removal rate. Hence, the optimum Fe powder dosage was determined to be 0.075 g·L⁻¹. The Fe powder dosages were all determined to be 0.075 g·L⁻¹ in the subsequent experiments.

$$Fe^{2+} + \cdot OH \to Fe^{3+} + OH^{-}$$
(8)

3.4. Impact of pH on COD Removal

Both Fenton and Fenton-like processes can degrade pollutants by producing \cdot OH in the reaction process. The potential of \cdot OH increases with the decrease in pH, and the oxidation capacity is enhanced, so that the pollutants can be degraded more effectively. It can be seen that the pH affects the efficiency of the decomposition of H₂O₂ into \cdot OH, thus affecting the treatment efficiency of Fenton-like processes. Therefore, pH is one of the most important characteristics of natural waters that affects the rates of contaminants removal by ZVI, since pH greatly affects the rate of ZVI corrosion [28,29]. Usually, the pH of Fenton reaction is mostly between 3 and 5, but some scholars have found that intrinsic synergy of Fenton oxidation and in-situ coagulation is achieved in the tannic acid (TA)/Fe(III)/H₂O₂ process, demonstrating the simultaneous removal of multiple pollutants over a wide pH range. Under the optimal conditions (TA/Fe(III)/H₂O₂ = 25 mg/L/0.1 mM/0.5 mM), 95.4% of Sulfamethazine and 98.4% of turbidity were simultaneously removed at pH = 7 [27].

The experiment therefore adjusts and optimizes pH within a certain range to explore its change rule. In this study, the reaction pH was set to 2.5, 3.5, 4.5, 5.5, 6.5, 7.5, and 8.5 under Fe powder dosage $0.075 \text{ g}\cdot\text{L}^{-1}$, H_2O_2 dosage 33.3 mg·L⁻¹, reaction time 1 h, and reaction temperature 25 °C. The COD concentration in the aqueous solution was measured after the reaction, and the final COD removal rate was calculated, with results shown in Figure 5.



Figure 5. pH impact on the COD removal rate (reaction conditions: iron powder dosage is 0.1 g/L; H₂O₂ dosage is 33.3 mg/L; reaction temperature is $25 \degree C$; reaction time is 1 h).

Figure 5 shows that when the pH increases from 2.5 to 4.5, the COD concentration tends to increase; when the pH increases from 4.5 to 6.5, the COD concentration increases rapidly;

when the pH increases from 6.5 to 8.5, the COD concentration exhibits an unobvious increasing trend. It can be seen that COD concentration was lower under lower pH, i.e., the COD removal rate was higher. The low pH facilitates the oxidative degradation reaction. As for the reason, for inorganic contaminant removal, an enhancement in the performance of ZVI was observed with decreasing pH [30–32]. The good performance of ZVI at low pH should be mainly ascribed to the acceleration of iron corrosion and dissolution of the passivated oxide layers on the ZVI surface, while a high pH deteriorates the performance of ZVI due to more mineral precipitation, which inhibits the mass transfer [33]. As a result, the removal of pollutants in water under alkaline conditions was not as effective as that under acidic conditions. However, lowering solution pH to very acidic conditions (e.g., below 3.8) might also diminish the ZVI performance, as it could cause a fast loss of ZVI particles through Fe dissolution, and/or lead to an excessive accumulation of hydrogen bubbles at the ZVI interface, which may decrease the available reactive surface area for contaminants removal [14]. If the pH was too low, it was more demanding on the equipment. Considering the cost and the corrosion resistance of the equipment, there was no need to adjust the wastewater pH, since the pH of the desulfurization wastewater was generally 4.5~6.5 [2].

3.5. Impact of Reaction Temperature on COD Removal

Desulfurization wastewater has a general temperature of around 45 °C. It emits heat to the external environment in the form of thermal radiation when transported in the pipeline, leading to decreased temperature. In this study, comparison was carried out under the reaction temperatures of 35 °C and 25 °C, respectively. The reaction conditions, such as pH, reaction time, Fe powder dosage, and H₂O₂ dosage, were kept consistent, except for the reaction temperature. The COD concentration in the aqueous solution was measured after the reaction, with results shown in Figure 6.



Figure 6. Reaction temperature impact on the COD removal rate (reaction conditions: iron powder dosage is 0.1 g/L; H₂O₂ dosage is 33.3 mg/L; pH is 6.5).

Figure 6 shows that, under a reaction temperature of 25 °C, when the reaction time was consistent, the COD concentration in the aqueous solution was higher after the final reaction than that at the reaction temperature of 35 °C, and the removal rate was lower than that at 35 °C. Hence, COD removal rate increases with the increasing temperature, and high temperature contributes to the reaction process. The reason for the increased COD removal rate may be that with the increase in reaction temperature, the speed of \cdot OH generation by H₂O₂ was accelerated, and thermal motion of particles in solution was intensified, which accelerates the collision between particles and increases the degradation rate [34]. It should

be noted that elevating temperature means increasing energy consumption. The general temperature of desulfurization wastewater is about 45 $^{\circ}$ C. It emits part of its heat to the external environment in the form of thermal radiation when transported in the pipeline, leading to decreased temperature, but the temperature will not decrease substantially, so the desulfurization wastewater is not heated in the actual project in order to save energy and reduce the operating cost.

3.6. Mechnism of COD Removal by ZVI Fenton-like Process

From the experiments on the influencing factors, it can be seen that Fe^0 dosage, H_2O_2 dosage, pH, etc. have a greater effect on ZVI Fenton-like treatment of desulfurization wastewater. Combined with Equations (1)–(5), it can be seen that in the ZVI Fenton-like reagent system, OH with strong oxidation ability was mainly produced in two ways: one was the interaction of H_2O_2 catalyzed by Fe^{2+} , and the other was the interaction of zero-valent iron with H_2O_2 at its surface active site [35]. The reaction mechanism of ZVI Fenton-like degrading organic matter in wastewater can be shown by Figure 7. The three valence states of iron in the system are in a dynamic equilibrium with the intervention of H_2O_2 and H^+ . When any concentration of Fe^0 , H_2O_2 , and pH changes, the existing chemical equilibrium is broken, making the reaction Equations (1)–(5) proceed in the positive or negative direction, thus changing the concentration of Fe^{2+} , Fe^{3+} , OH, and OH^- in the ZVI Fenton-like system, and thus affecting the efficacy of wastewater treatment. This is the reason to explore the optimal dosage of iron powder and H_2O_2 , which not only achieves the best effect but also saves reagents [36]. As shown in Figure 7, the injected Fe^0 can remove a part of macromolecular organic matter, halides, and heavy metals from the water body due to its own absorption, reduction, and co-precipitation [37]. However, more due to the addition of Fe⁰, it can react with H_2O_2 and H^+ anti-generation to generate a large amount of Fe²⁺, and at the same time, it will also generate ·OH with strong oxidizing ability. Subsequently, Fe^{2+} continues to oxidize under the action of H_2O_2 and H^+ to generate Fe^{3+} , and this process will generate more ·OH, which can further oxidize the small molecules of organic matter into carbon dioxide and water in the water body [38]. The generated ·OH oxidizes and breaks the organic complexes, releasing free metal ions, which are then removed through chemical precipitation. It is worth noting that Fe²⁺ can also generate Fe³⁺ under the oxidation of \cdot OH. At this point, if there is an excess of Fe⁰ in the aqueous solution, Fe^{3+} will react with Fe^{0} to form Fe^{2+} [39,40]. The reaction system is H⁺-consuming, so there is a requirement for pH, which is consistent with the experimental results of pH-influencing factors. In summary, Fe^0 dosage, H_2O_2 dosage, and pH play crucial roles in the ZVI Fenton-like system for treating desulfurization wastewater, and it is necessary to explore the dynamic equilibrium requirements between them and the optimal operating dosage.



Figure 7. ZVI Fenton-like treatment of desulfurization wastewater reaction mechanism diagram.

4. Conclusions

In this study, the effect of reaction time, iron powder dosage, H_2O_2 dosage, pH, and reaction temperature on treatment performance was investigated for the ZVI Fenton-like oxidation method for treating desulfurization wastewater. The internal mechanism of ZVI Fenton-like treatment of desulfurization wastewater was investigated by combining the influencing factors and the analysis of Fe⁰, Fe²⁺, and Fe³⁺ in the presence of H₂O₂ and H⁺ in a dynamic equilibrium relationship. Taking a thermal power plant triple tank desulfurization wastewater as an example, its COD concentration was 170.6 mg·L⁻¹, and the COD concentration of the desulfurization wastewater was reduced to about 100 mg·L⁻¹ at pH 4.5~6.5, reaction time of 1 h, under the conditions of an iron powder dosage of 0.075 g·L⁻¹, an H₂O₂ dosage of 33.3 mg·L⁻¹, and a reaction temperature of 35 °C. It should be noted that this study was only completed in the laboratory, and if it is to be applied to practical projects, pilot scale tests must be carried out to further understand the operating parameters.

Author Contributions: Conceptualization and writing—original draft, Z.L.; Formal analysis, W.Z.; Funding acquisition, X.L., Investigation, X.Y. and W.Y.; Writing—review & editing, H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by The Foundation of Central Guidance on Local Science and Technology Development (2022BGE252).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All datasets are publicly available.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. de Gisi, S.; Molino, A.; Notarnicola, M. Enhancing the recovery of gypsum in limestone-based wet flue gas desulfurization with high energy ball milling process: A feasibility study. *Process Saf. Environ. Prot.* **2017**, *109*, 117–129. [CrossRef]
- Ma, S.; Chai, J.; Chen, G.; Yu, W.; Zhu, S. Research on desulfurization wastewater evaporation: Present and future perspectives. *Renew. Sustain. Energy Rev.* 2016, 58, 1143–1151. [CrossRef]
- Dong, Y.; Li, Y.; Zhang, L.; Cui, L.; Zhang, B.; Dong, Y. Novel Method of Ultralow SO₂ Emission for CFB Boilers: Combination of Limestone Injection and Activated Carbon Adsorption. *Energy Fuels* 2017, *31*, 11481–11488. [CrossRef]
- 4. Gude, V.G. Energy and water autarky of wastewater treatment and power generation systems. *Renew. Sustain. Energy Rev.* 2015, 45, 52–68. [CrossRef]
- Han, X.; Yuan, T.; Zhang, D.; Dai, Y.; Liu, J.; Yan, J. Waste heat utilization from boiler exhaust gases for zero liquid discharge of desulphurization wastewater in coal-fired power plants: Thermodynamic and economic analysis. J. Clean. Prod. 2021, 308, 127328. [CrossRef]
- Sun, Z.; Chen, H.; Zhao, N.; Feng, Y.; Liu, F.; Cai, C.; Che, G.; Yang, L. Experimental research and engineering application on the treatment of desulfurization wastewater from coal-fired power plants by spray evaporation. *J. Water Process Eng.* 2021, 40, 101960. [CrossRef]
- Ma, S.; Chai, J.; Chen, G.; Wu, K.; Xiang, Y.; Wan, Z.; Zhang, J.; Zhu, H. Partitioning characteristic of chlorine ion in gas and solid phases in process of desulfurization wastewater evaporation: Model development and calculation. *Environ. Sci. Pollut. Res.* 2019, 26, 8257–8265. [CrossRef]
- Azam, K.; Raza, R.; Shezad, N.; Shabir, M.; Yang, W.; Ahmad, N.; Shafiq, I.; Akhter, P.; Razzaq, A.; Hussain, M. Development of recoverable magnetic mesoporous carbon adsorbent for removal of methyl blue and methyl orange from wastewater. *J. Environ. Chem. Eng.* 2020, *8*, 104220. [CrossRef]
- Yan, J.; Yuan, W.; Liu, J.; Ye, W.; Lin, J.; Xie, J.; Huang, X.; Gao, S.; Xie, J.; Liu, S.; et al. An integrated process of chemical precipitation and sulfate reduction for treatment of flue gas desulphurization wastewater from coal-fired power plant. *J. Clean. Prod.* 2019, 228, 63–72. [CrossRef]
- 10. Koralegedara, N.H.; Pinto, P.X.; Dionysiou, D.D.; Al-Abed, S.R. Recent advances in flue gas desulfurization gypsum processes and applications—A review. *J. Environ. Manag.* **2019**, 251, 109572. [CrossRef]
- Han, X.; Zhang, D.; Yan, J.; Zhao, S.; Liu, J. Process development of flue gas desulphurization wastewater treatment in coal-fired power plants towards zero liquid discharge: Energetic, economic and environmental analyses. J. Clean. Prod. 2020, 261, 121144. [CrossRef]

- 12. An, W.; Zhao, J.; Lu, J.; Han, Y.; Li, D. Zero-liquid discharge technologies for desulfurization wastewater: A review. *J. Environ. Manag.* **2022**, *321*, 115953. [CrossRef]
- 13. Zhu, Y.; Fan, W.; Feng, W.; Wang, Y.; Liu, S.; Dong, Z.; Li, X. A critical review on metal complexes removal from water using methods based on Fenton-like reactions: Analysis and comparison of methods and mechanisms. *J. Hazard. Mater.* **2021**, 414, 125517. [CrossRef] [PubMed]
- 14. Sun, Y.; Li, J.; Huang, T.; Guan, X. The influences of iron characteristics, operating conditions and solution chemistry on contaminants removal by zero-valent iron: A review. *Water Res.* **2016**, *100*, 277–295. [CrossRef] [PubMed]
- Fu, F.; Xie, L.; Tang, B.; Wang, Q.; Jiang, S. Application of a novel strategy-Advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater. *Chem. Eng. J.* 2012, *189*, 283–287. [CrossRef]
- 16. Pliego, G.; Zazo, J.A.; Garcia-Munoz, P.; Munoz, M.; Casas, J.A.; Rodriguez, J.J. Trends in the Intensification of the Fenton Process for Wastewater Treatment: An Overview. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45*, 2611–2692. [CrossRef]
- 17. Peng, Y.; Xu, J.; Liu, T.; Mao, Y.-G. Controlled synthesis of one-dimensional BiOBr with exposed (110) facets and enhanced photocatalytic activity. *CrystEngComm* **2017**, *19*, 6473–6480. [CrossRef]
- 18. Zhang, N.; Zhang, G.; Huang, T.; Chong, S.; Liu, Y. Fe₃O₄ and Fe₃O₄/Fe₂+/Fe-0 catalyzed Fenton-like process for advanced treatment of pharmaceutical wastewater. *Desalination Water Treat.* **2017**, *93*, 100–108. [CrossRef]
- Quintana, G.O.; Fagnani, E.; Candello, F.P.; Guimaraes, J.R. The Dichromate Method versus the Photoelectrochemical Method: The Synergistic Influence of Turbidity and Chlorides on Chemical Oxygen Demand Analysis. J. Braz. Chem. Soc. 2018, 29, 490–498. [CrossRef]
- Guo, M.; Weng, X.; Wang, T.; Chen, Z. Biosynthesized iron-based nanoparticles used as a heterogeneous catalyst for the removal of 2,4-dichlorophenol. *Sep. Purif. Technol.* 2017, 175, 222–228. [CrossRef]
- Rezaei, F.; Vione, D. Effect of pH on Zero Valent Iron Performance in Heterogeneous Fenton and Fenton-like Processes: A Review. Molecules 2018, 23, 3127. [CrossRef]
- 22. Ramos, P.B.; Vitale, P.; Barreto, G.P.; Aparicio, F.; Dublan, M.Á.; Eylera, G.N. Treatment of real non-biodegradable wastewater: Feasibility analysis of a zero-valent iron/H₂O₂ process. *J. Environ. Chem. Eng.* **2020**, *8*, 103954. [CrossRef]
- Galdames, A.; Ruiz-Rubio, L.; Orueta, M.; Sanchez-Arzalluz, M.; Luis Vilas-Vilela, J. Zero-Valent Iron Nanoparticles for Soil and Groundwater Remediation. Int. J. Environ. Res. Public Health 2020, 17, 5817. [CrossRef]
- Zhang, W.; Gao, H.; He, J.; Yang, P.; Wang, D.; Ma, T.; Xia, H.; Xu, X. Removal of norfloxacin using coupled synthesized nanoscale zero-valent iron (nZVI) with H₂O₂ system: Optimization of operating conditions and degradation pathway. *Sep. Purif. Technol.* 2017, 172, 158–167. [CrossRef]
- Chang, M.-C.; Shu, H.-Y.; Yu, H.-H. An integrated technique using zero-valent iron and UV/H₂O₂ sequential process for complete decolorization and mineralization of C.I. Acid Black 24 wastewater. J. Hazard. Mater. 2006, 138, 574–581. [CrossRef] [PubMed]
- Cheng, R.; Cheng, C.; Liu, G.-h.; Zheng, X.; Li, G.; Li, J. Removing pentachlorophenol from water using a nanoscale zero-valent iron/H₂O₂ system. *Chemosphere* 2015, 141, 138–143. [CrossRef] [PubMed]
- Ali, J.; Shahzad, A.; Wang, J.; Ifthikar, J.; Lei, W.; Aregay, G.G.; Chen, Z.; Chen, Z. Modulating the redox cycles of homogenous Fe-(III)/PMS system through constructing electron rich thiomolybdate centres in confined layered double hydroxides. *Chem. Eng.* J. 2021, 408, 127242. [CrossRef]
- 28. Bae, S.; Hanna, K. Reactivity of Nanoscale Zero-Valent Iron in Unbuffered Systems: Effect of pH and Fe(II) Dissolution. *Environ. Sci. Technol.* **2015**, *49*, 10536–10543. [CrossRef]
- 29. O'Carroll, D.; Sleep, B.; Krol, M.; Boparai, H.; Kocur, C. Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. *Adv. Water Resour.* **2013**, *51*, 104–122. [CrossRef]
- Alowitz, M.J.; Scherer, M.M. Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal. Environ. Sci. Technol. 2002, 36, 299–306.
 [CrossRef]
- Guan, X.; Jiang, X.; Qiao, J.; Zhou, G. Decomplexation and subsequent reductive removal of EDTA-chelated Cu-II by zero-valent iron coupled with a weak magnetic field: Performances and mechanisms. *J. Hazard. Mater.* 2015, 300, 688–694. [CrossRef] [PubMed]
- 32. Jiang, X.; Qiao, J.; Lo, I.M.C.; Wang, L.; Guan, X.; Lu, Z.; Zhou, G.; Xu, C. Enhanced paramagnetic Cu²⁺ ions removal by coupling a weak magnetic field with zero valent iron. *J. Hazard. Mater.* **2015**, *283*, 880–887. [CrossRef] [PubMed]
- Bae, S.; Lee, W. Influence of Riboflavin on Nanoscale Zero-Valent Iron Reactivity during the Degradation of Carbon Tetrachloride. Environ. Sci. Technol. 2014, 48, 2368–2376. [CrossRef]
- 34. Gan, L.; Li, B.; Guo, M.; Weng, X.; Wang, T.; Chen, Z. Mechanism for removing 2,4-dichlorophenol via adsorption and Fenton-like oxidation using iron-based nanoparticles. *Chemosphere* **2018**, 206, 168–174. [CrossRef]
- Dulova, N.; Trapido, M.; Dulov, A. Catalytic degradation of picric acid by heterogeneous Fenton-based processes. *Environ. Technol.* 2011, 32, 439–446.
- Bogacki, J.; Marcinowski, P.; Zapalowska, E.; Maksymiec, J.; Naumczyk, J. Cosmetic wastewater treatment by the ZVI/H₂O₂ process. *Environ. Technol.* 2017, *38*, 2589–2600. [CrossRef]
- Guan, X.; Sun, Y.; Qin, H.; Li, J.; Lo, I.M.C.; He, D.; Dong, H. The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: The development in zero-valent iron technology in the last two decades (1994–2014). *Water Res.* 2015, 75, 224–248. [CrossRef] [PubMed]

- Zhou, T.; Li, Y.; Ji, J.; Wong, F.-S.; Lu, X. Oxidation of 4-chlorophenol in a heterogeneous zero valent iron/H₂O₂ Fenton-like system: Kinetic, pathway and effect factors. *Sep. Purif. Technol.* 2008, *62*, 551–558. [CrossRef]
- 39. Gu, K.; Li, H.; Zhang, J.; Li, J. Performances and Interactions of Contaminants Removal from Water by Sulfidated Zerovalent Iron. *Prog. Chem.* **2021**, *33*, 1812–1822. [CrossRef]
- Yang, S.; Ren, T.; Zhang, Y.; Zheng, D.; Xin, J. ZVI/Oxidant Systems Applied in Water Environment and Their Electron Transfer Mechanisms. Prog. Chem. 2017, 29, 388–399. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.