Experimental Study on the Treatment of Organic Wastewater Containing Iron with High Efficiency Flocculant

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Abstract. The treatment of industrial wastewater containing Fe3+ by the new high efficiency compound flocculant MD-816 was discussed. The effects of flocculant dosage, pH value and stirring rate on the removal of COD, ammonia nitrogen and Fe3+ were discussed. The results show that when the dosage of flocculant is 200 mg.L⁻¹, the pH of waste-water is 5, and the stirring rate is 250 r/min, the removal efficiency of Fe3+ in industrial iron containing waste-water is better, the removal rate of Fe3+ is 99.99%, the mass concentration of Fe3+ is 0.043 mg.L⁻¹, the removal rate of COD is 76.27%, the lowest is 51.16 mg.L⁻¹, the removal rate of ammonia nitrogen is 93.28%, the lowest is 7.92 mg.L⁻¹. The treatment effect meets the requirements of the maximum allowable discharge mass concentration (Fe3+ ≤ 0.1 mg.L⁻¹, COD ≤ 100 mg.L⁻¹, ammonia nitrogen ≤ 10 mg.L⁻¹) in the integrated waste-water discharge standard (GB 8978-1996).

1. Introduction

Heavy metal pollutants are widely concerned by the global scientific community because of their persistence and non-degradability [1, 2]. Industrial process will produce a large number of wastewater containing high concentrations of different heavy metals (such as chromium, nickel, copper, cadmium and platinum) [3]. The pollution of organic iron in water mainly comes from smelting, industrial electroplating and beneficiation. Too high Fe³⁺ concentration in the water is easy to cause the water quality to turn yellow. In serious cases, it will cause the water to turn red and black, giving off a fishy smell of iron [4]. Iron is an essential physiological trace element for human body, but excessive intake of iron will lead to chronic poisoning [5]. There will be cirrhosis, osteoporosis, cartilage calcification, diabetes and so on. Therefore, it is necessary to treat the iron wastewater.

At present, chemical neutralization precipitation, sulfide precipitation, oxidation-reduction reaction, ion exchange, adsorption and flocculation have been applied to the treatment of wastewater containing heavy metals [6, 7]. Among these methods, adsorption and flocculation are the most important because of their high efficiency, simplicity and cost-effectiveness.

Inorganic flocculant is widely used in industrial wastewater treatment. It has the advantages of low dosage, wider range of use, biodegradability, innocuity and lower price. In recent years, inorganic flocculants, especially inorganic high molecular silicic acid flocculants, have attracted extensive attention in the field of wastewater treatment due to their high molecular weight and charge neutralization ability.
Therefore, this paper takes the new high-efficiency flocculant MD-816 developed by our research group as the research object, through changing the dosage of flocculant, the pH of wastewater and the stirring rate to investigate the effect of iron removal efficiency, and also to investigate the effect of the flocculant on the removal of COD and ammonia nitrogen from industrial iron wastewater, using the integrated wastewater discharge standard (GB8978-1996) as the index to determine the ability of new flocculant to treat wastewater containing iron.

2. Materials and methods

2.1. Materials and reagents
All commercial grade chemicals, sodium silicate (Na$_2$SiO$_3$.9H$_2$O), iron sulfate (Fe$_2$(SO$_4$)$_3$), zinc sulfate (ZnSO$_4$.7H$_2$O) and sodium tetraborate decahydrate (Na$_2$B$_4$O$_7$.10H$_2$O), are purchased from Beijing Guoyao Chemical Co.Ltd. All of these chemicals are used without any additional purification steps. Prepare all solutions with deionized water. The iron wastewater from a coking plant in Shanxi Province is taken as the research object, and the indicators are shown in Table 1 below.

| Water                        | pH  | Fe$^{3+}$/mg.L$^{-1}$ | COD/mg.L$^{-1}$ | NH$_3$-N/mg.L$^{-1}$ |
|------------------------------|-----|----------------------|----------------|-----------------------|
| Iron containing wastewater   | 5.42| 693.2                | 215.63         | 116.63                |
| National standard            | 6-9 | 0.1                  | 100            | 15                    |

2.2. Test method

2.2.1. MD-816 flocculant preparation and characterization. The polysilicic acid solution was prepared by preparing sodium silicate solution of certain concentration and activating it under certain conditions. In the prepared polysilicic acid solution, add zinc sulfate, sodium tetraborate decahydrate and other agents in turn according to the calculated dosage, continue to quickly stir to make it polymerize, place it at room temperature for aging for a period of time after full reaction, and then obtain flocculant MD-816.

The aged MD-816 liquid sample was dried at 50°C, and characterized by FT-IR with KBr as the background. The aged MD-816 liquid sample and the coagulated sludge were dried and milled at 70°C, and characterized by SEM.

2.2.2. Coagulatitiones. Transfer 250ml of organic wastewater containing iron into a 500ml glass beaker with a measuring cylinder, add 10% (mass fraction) of MD-816 solution, adjust the pH with NaOH solution, place the beaker on a six connected digital display electric mixer, and stir for 10min at room temperature with 300r/min. To ensure the mixing of the mixture and the waste water. After coagulation, floc growth was observed by stirring at a slow mixing rate (100r/min) for 5min, and then settling for 20min. The supernatant was taken to determine the concentration of COD, ammonia nitrogen and ferric ion in the wastewater after reaction. Three parallel experiments.

2.3. Analysis method
The instrument of Lianhua Technology Co., Ltd. was used to measure the COD and ammonia nitrogen of wastewater (the principle is spectrophotometry), the pH was measured by pH meter, the concentration of Fe$^{3+}$ was measured by inductively coupled plasma method, and the concentration of iron ion in three samples of three times of occurrence test was measured within 98% confidence interval.

3. Organization of the Text

3.1. FT-IR characterization of MD-816
The FT-IR characterization results of MD-816 are shown in Fig 1.
It can be seen from Fig. 1 that there is a stretching vibration peak of poly-o-h at 620 cm\(^{-1}\), a stretching vibration peak of Ti-O-Ti at 989 cm\(^{-1}\), and a weak ion peak at 1104 and 1200 cm\(^{-1}\) is the stretching vibration peak of Ti-O-Ti contained in the tetravalent complex \([Ti\,(OH)\,(H_2O)_{6-n}]_4\times N\) produced by titanium hydrolysis. At 1382 cm\(^{-1}\), there is an OH stretching vibration peak connected with Ti, and at 1626 cm\(^{-1}\), there is a bending vibration peak of crystal water in the sample. The results of infrared spectrum analysis show that Ti atom is more involved in the synthesis of flocculant than in the form of titanium sulfate.

3.2. **SEM characterization of MD-816**

The dried MD-816 was scanned by electron microscope and magnified to 1000 and 3000 respectively to obtain Fig. 2 (a) and Fig. 2 (b). The dried sludge was scanned by electron microscope and magnified to 1000 and 5000 respectively to obtain Fig. 2 (c) and Fig. 2 (d).

It can be seen from Fig. 2 (a) and Fig. 2 (b) that the surface of MD-816 is a huge stem like structure, forming a three-dimensional network macromolecular polymer with a variety of valence bond structures, which is easier to capture the fine colloidal particles in wastewater. It can be seen from Fig. 2 (c) and Fig. 2 (d) that the surface morphology of MD-816 has changed greatly after coagulation, and the sludge structure after coagulation is compact and agglomerated. It is preliminarily shown that MD-816 may coagulate more Fe\(^{3+}\).
Figure 3. EDS characterization results

3.3. Flocculation reaction results

3.3.1. Effect of flocculant dosage on wastewater treatment. Change the dosage of flocculant (take 100 200 400 600 800 1000 mg. L\(^{-1}\) respectively), at the stirring rate and settling time of 300r/min and 10min respectively. Under other conditions, take COD, ammonia nitrogen and residual Fe\(^{3+}\) concentration as indicators to determine the dosage of flocculant, as shown in Fig 4.

Figure 4. Effect of MD-816 dosage on wastewater treatment

It can be seen from the above figure that with the increase of flocculant dosage, the concentration of iron ion in the treated water first decreases and then increases, and then decreases when it reaches 1000mg. L\(^{-1}\), but it reaches the lowest when the dosage is 200mg. L\(^{-1}\), because the polymer flocculant has a long molecular chain, which can be adsorbed on more than two particles at the same time to form a bridging structure, so that particles can aggregate. In other words, flocculation occurs, and the amount
of flocculant is too much. At the beginning, the suspended particles will be surrounded by a number of polymer chains, and there is no blank part to adsorb other polymer chains, resulting in oversaturation of the surface of the particles and re stabilization. The flocculation effect is worse.

3.3.2. Effect of pH on wastewater treatment. Under the condition of changing pH (4.0, 5.0, 6.0, 7.0, 8.0, 9.0, respectively) and other conditions unchanged, taking cod, ammonia nitrogen and residual Fe$_{3}^{+}$ concentration as indicators, the optimal pH of flocculation conditions is determined. The results are shown in Fig 5.

![Figure 5](image)

**Figure 5.** Effect of pH on wastewater treatment effect

It can be seen from the above figure that in a certain pH range, with the increase of pH, the Fe$_{3}^{+}$ content decreases with the decrease of pH. When pH is 5, the Fe$_{3}^{+}$ content suddenly decreases, and then the iron content does not fluctuate with the increase of pH. This is because when pH is large, although Fe (OH)$_3$ precipitates are produced in the solution, it keeps hydrolysis balance in a certain pH range, so the Fe$_{3}^{+}$ removal rate almost remains unchanged with the increase of pH.

3.3.3. Effect of mixing speed on wastewater treatment effect. Take the best conditions (the dosage of flocculant is 200mg. L$^{-1}$ and pH is 5) determined in sections 3.3.1 and 3.3.2, control other conditions unchanged, adjust the mixing rate to 200 250 300 350 400 450r / min, after settling, go to the supernatant to determine the concentration of COD, ammonia nitrogen and residual Fe$_{3}^{+}$, and determine the best mixing rate of flocculation conditions, as shown in Fig 6.

![Figure 6](image)

**Figure 6.** Effect of mixing rate on wastewater treatment effect
It can be seen from the above figure that when the stirring rate reaches 250-350 r/min, the Fe$^{3+}$ content, COD and ammonia nitrogen values in the wastewater gradually decrease, and when the stirring rate is greater than 350 r/min, the Fe$^{3+}$ content, COD and ammonia nitrogen slightly increase, because when the stirring rate is too high, the floc that has been flocculated will be broken, resulting in poor flocculation effect. Therefore, the optimal stirring rate is 250 r/min. Under the optimal conditions, the ammonia nitrogen in the wastewater can be reduced to below 10 mg L$^{-1}$, COD to below 90 mg L$^{-1}$, and chroma to 0. The specific effect is shown in Fig 7 below.

![Figure 7. Comparison of wastewater before and after reaction](image)

4. Conclusion
To sum up, the new flocculant MD-816 shows a very significant effect in the treatment of industrial iron containing wastewater, which can remove a large number of Fe$^{3+}$ at a lower dosage, and also can greatly reduce the COD and ammonia nitrogen of wastewater, reaching the comprehensive wastewater discharge standard - GB 8978-1996. The best flocculation conditions are as follows: the dosage of flocculant is 200 mg L$^{-1}$, the pH of wastewater is 5, and the stirring rate is 250 r/min. It provides a more efficient method for the treatment of industrial organic iron wastewater, and also shows that the flocculant has a promising application in the treatment of industrial organic iron wastewater.

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