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A study on the removal of highly concentrated organic matters in saline lake water and the mechanism of magnesium ion loss in water treatment

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ABSTRACT

Nafine Chemical Industry Group Co. Ltd. extracted inorganic salts from the saline lake of Shanxi Yuncheng, China. Because of the complexity of component and the high content of organic matters in the saline lake water, the purity of the inorganic salts was influenced directly. As a result, the organic matters in the saline lake water were needed to be removed. In order to solve this problem, different water treatment processes were utilized to remove the organic matters in saline lake water, but some valuable metal ions would lose, especially the magnesium ion in water treatment processes. The purpose of this paper is to study the treatability of high concentrated organic matters in saline water by O_3/H_2O_2 oxidation, O_3/H_2O_2 oxidation followed coagulation and activated carbon adsorption respectively, and the mechanisms of magnesium ion loss were analyzed. The results showed that O_3/H_2O_2 oxidation can change the structure of organic matter and increase the content of carboxylic groups in organic matters which resulted in the complexation with magnesium ion. So that magnesium ion would be lost along with the removal of organic matters by coagulation or activated carbon adsorption following oxidation. However, it indicated that the magnesium ion loss could be decreased effectively through pH adjusting after oxidation.

Keywords: Saline lake water; Organic matter removal; Magnesium ion loss; Advanced oxidation process; Coagulation; Complexation

1. Introduction

The Saline Lake of Yuncheng, which is located in the southwest of the Shanxi Province, China, is the third biggest inland saline lake of sulfate-sodium type. The lake is 132 km^2 and it came into being before 500 million years. As sea level went down, the mountains emerged, a great amount of saliferous minerals converged in the lake and it became a natural saline lake after a long term precipitation and evaporation. Both the Saline Lake of Yuncheng Shanxi and the famous Israel Dead Sea belong to inland saline lake now.

The Saline Lake of Yuncheng was famous for producing various kinds of salt over 4000 y old. Nafine Chemical Industry Group Co. Ltd. (Nafine Co. Ltd) is one of the earliest and biggest enterprises in producing

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magnesium hydroxide and barium sulfate from saline lake water. However, the saline lake is badly polluted as the result of wastewater discharge. Therefore, if the saline lake water was used as the raw material to produce the most valuable products, magnesium hydroxide and barium sulfate, the quality of the products are often inferior and the purities are low. As a result, the removal of organic matters in saline lake water is of great significance for increasing the product purity of Nafine Co. Ltd. In order to solve this problem, different processes were utilized to remove the organic matters in saline lake water, but some valuable metal ions would lose in water treatment processes, especially the magnesium ion. According to the requirements of salt manufacturing of Nafine Co. Ltd, if the removal rate of organic matters is greater than 70% and the loss of magnesium ion is within 10%, the product purity can be improved and reach the requirements. Aiming at this goal, based on the previous study [1,2], the characteristics of O_3/H_2O_2, coagulation and activated carbon adsorption following O_3/H_2O_2 oxidation hybid processes for organic matters removal was analyzed in this paper respectively. By comparing the variation of the structures of the organic matters after oxidation, the mechanism of magnesium ion loss in water treatment was discussed. According to the pathway of magnesium ion loss, an effective process for organic matter removal with low magnesium ion loss was proposed.

2. Materials and methods

2.1. Raw water quality

The raw water is from the Saline Lake of Yuncheng Shanxi. The salinity in the raw water is close to the saturated salt water. Table 1 is the basic characteristics of raw water for the experiment.

Table 1
Characteristics of raw water (Unit: g l^{-1})

Item	pH	COD_{Cr}	TOC	TDS	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-
Value	6.8	5.0	3.0	700	0.03	120	100	300

2.2. Experiment units

O_3/H_2O_2 experiment adopted static test and the raw water volume for oxidation was 2000 ml. The ozone reactor utilized titanium alloy porous diffusion plate.

Jar tests were adopted for coagulation. The coagulant was aluminum sulfate ($Al_2(SO_4)_3$ $18H_2O$). The volume of water sample was 1000 ml. In the present work, the coagulation procedure was 1 min of rapid mix at 200 r min^{-1}, 30 min of slow stirring at 20 r min^{-1} and 30 min settling time.

GAC adsorption was conducted by a filter bed with an effective depth of 100 cm at a rate of 10 m h^{-1}.

2.3. Analytical method

1. Analysis of organic matters concentration
   Potassium chromate method was used to measure the organic matters in water expressed by COD_{Cr}.
2. Analysis of magnesium ion content
   As is shown in Table 1, the content of magnesium ion is very high in raw water. The calcium ions, which will contribute the hardness, can be neglectable by contrast. Therefore, using the EDTA method to measure the total hardness can reflect the content of the magnesium ion approximately.
3. Analysis of organic matters structure
   Raw water and oxidized water were concentrated with nonpolar column and anionic polar column and extracted by polar organic solvent methanol and nonpolar organic ethyl acetate respectively. Extracted samples were detected by Trace2000 GC-MS (Finnigan, US). The analysis condition is as following: Quadrupole mass spectrometer detection of electron impact source by using the DB-5MS capillary column of J&W company (30 m × 0.25 mm, i.d.: 0.25 μm); Applying splitless injection and the temperature of injector is 240°C; The helium carrier flow is 0.50 ml min^{-1}; The temperature program initiated at 50°C, then raised at 3°C min^{-1} to 220°C and held for 30 min.
4. Analysis of organic matters molecular weight
   Size Exclusion Chromatography (SEC) method of High performance liquid chromatograph (HPLC) was used to determine the molecular weight of the organic matters. HPLC analysis was conducted using a LC-2000 liquid chromatographic analyzer (Shimadzu, Japan) with W520 gel column (Dia 15 mm, length 350 mm, Cutoff molecular weight 6000, Void volume 12 ml), the detector is UV detector at 254 nm. According to the chromatographic diagram, it can deduce the molecular weight distribution before and after oxidation [3]. The mobile phase was 0.02 M Na_2HPO_4 and 0.02 M KH_2PO_4 and the velocity was 0.4 ml min^{-1}.
5. Analysis of organic matters fluorescence
   Measurements of fluorescence intensity were obtained with FP-6500 fluorescence spectrophotometer (JASCO, Japan). The excitation wavelength was set at 220 nm, and the emission wavelength was scanned from 250 to 650 nm.

3. Results and discussion

3.1. Effect of O_3/H_2O_2 treatment on organic removal and magnesium ion loss

Raw water was oxidized by O_3/H_2O_2 at the dosage of 0.25 mg O_3 mg^{-1} COD for 30 min with different H_2O_2 dose. As shown in Fig. 1, the relationship between organic matters removal and ozone dosage was built through analyzing the COD_{Cr} and Mg^{2+} of the treated water. It can be seen that the rate of organic matters removal by O_3/H_2O_2 increases with the increasing of H_2O_2 dosage. However, when the dosage of H_2O_2 is 3 g l^{-1}, the rate of COD removal remains unchanged about 20%. Meanwhile, the magnesium ion loss is steadily kept at about 2%.

3.2. Effect of O_3/H_2O_2 preoxidation on coagulation

In order to improve the organic matter removal, O_3/H_2O_2 and coagulation hybrid process was conducted, and the effect of O_3/H_2O_2 preoxidation on coagulation was shown in Fig. 2. The oxidation condition is the same as Fig. 1, and the coagulant dosage was 300 mg Al l^{-1}. As shown in Fig. 2, O_3/H_2O_2 and coagulation hybrid process can improve the COD removal. It can be seen that the rate of organic matter removal and magnesium ion loss increase till 3 g l^{-1} is reached and the maximum COD removal rate and magnesium ion loss are both about 35%. However, when the dosage of H_2O_2 was higher than 3 g l^{-1}, the organic matter removal decreased with the increasing of H_2O_2 dosage. Meanwhile, the loss of magnesium ion also decreased.

The molecular weight distribution was analyzed before and after O_3/H_2O_2 oxidation (H_2O_2 dosage is 3 g l^{-1}). The result was shown in Fig. 3. As shown in Fig. 3, the molecular weight of organic matters in raw water was mainly about 3000. After O_3/H_2O_2 oxidation, the content of organic matters with high molecular weight decreased, but the organic matters with low molecular weight increased in the treated water, which was mainly below 1000. It indicated that the organic matters with high molecular weight were decomposed into those with low molecular weight by O_3/H_2O_2 oxidation, which is the main function of advanced oxidation as well as O_3/H_2O_2 process [4]. In general, organic matter with low molecular weight is difficult to be removed by coagulation [5]. With the increasing of H_2O_2 dose, the amount of organic matters with low molecular weight could be much higher, and resulted in the low COD removal.

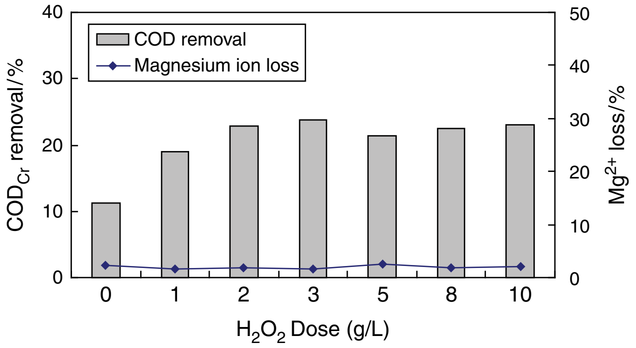

Fig. 1. Relationship between organic matter removal, magnesium ion loss by O_3/H_2O_2.

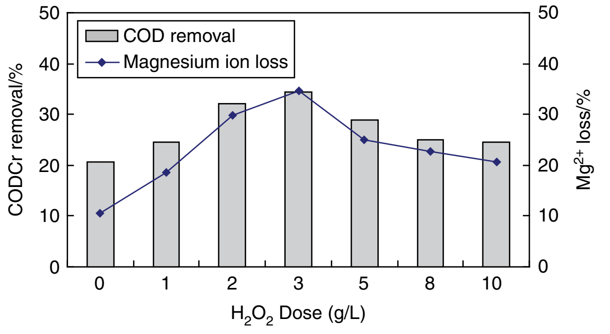

Fig. 2. Effect of O_3/H_2O_2 on coagulation.

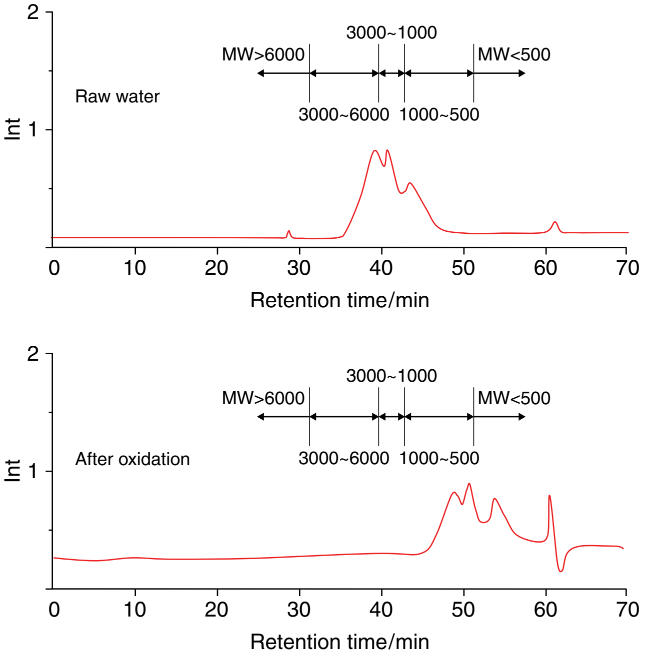

Fig. 3. MW distribution before and after O_3/H_2O_2 oxidation.

3.3. Effect of O_3/H_2O_2 preoxidation on GAC adsorption

Similarly, GAC adsorption following O_3/H_2O_2 preoxidation was also conducted as shown in Fig. 4. It can be seen form Fig. 4, O_3/H_2O_2 and GAC adsorption hybrid process can dramatically improve organic matter removal efficiency, which could reach up to 88%. However, the magnesium ion loss increased correspondingly, which is about 60% at most.

3.4. Mechanisms of magnesium ion loss

In order to ascertain the mechanisms of the magnesium ion loss along with the removal of organic matters

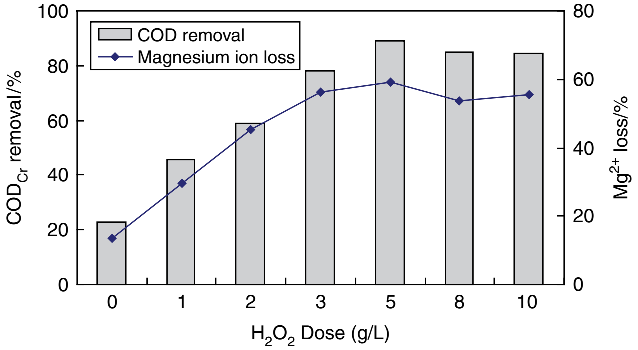

Fig. 4. Effect of O_3/H_2O_2 on GAC adsorption.

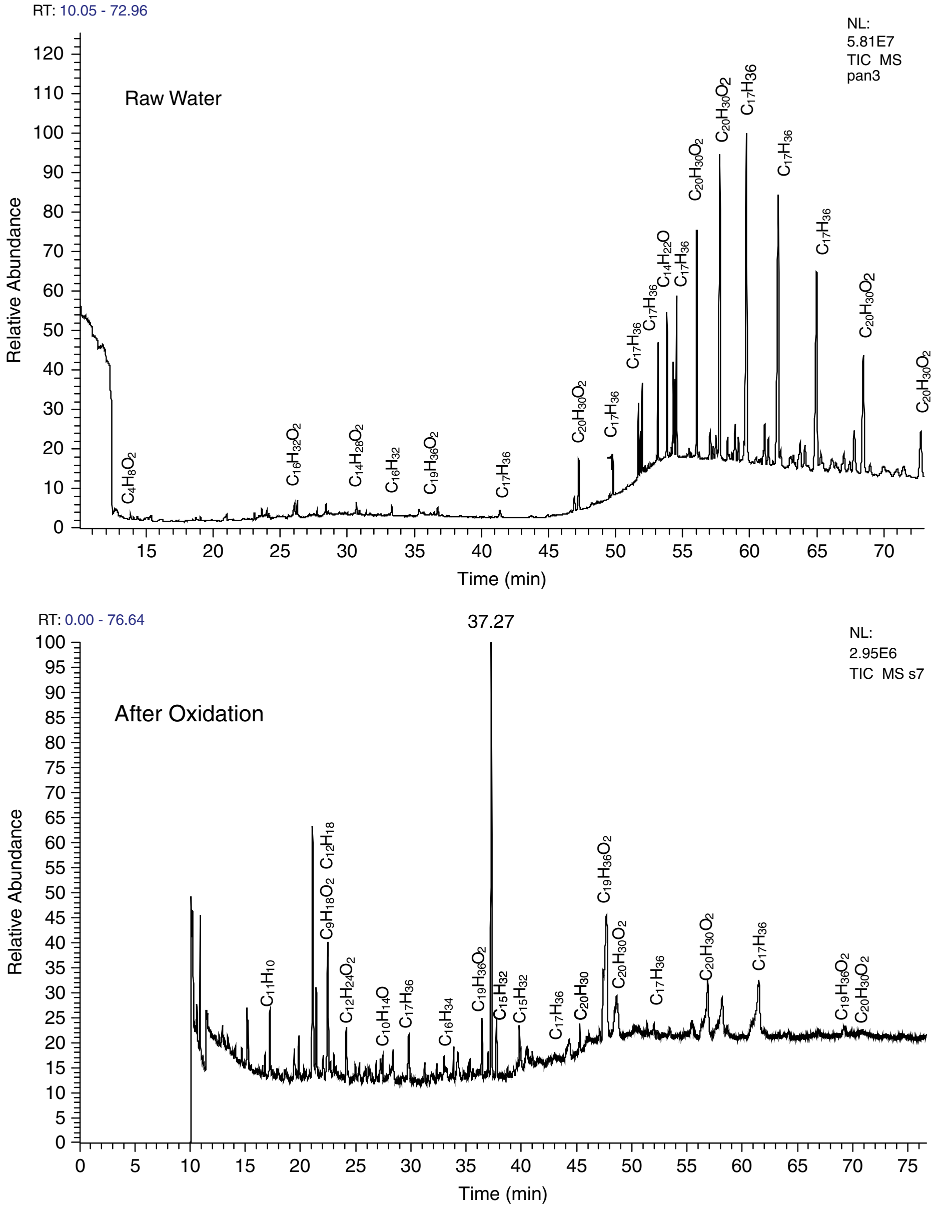

Fig. 5. GC-MS analysis result of raw water and treated water by O_3/H_2O_2 for nonpolarity organic matters.

by O_3/H_2O_2 and coagulation, O_3/H_2O_2 and GAC adsorption hybrid processes, the structures of organic matters before and after O_3/H_2O_2 oxidation were analyzed by GC-MS and fluorescence detection. Figs. 5 and 6 were the variation of the structures of nonpolar and polar organic matters before and after O_3/H_2O_2 oxidation (ozone dosage was 0.25 mg O_3 mg^{-1} COD and H_2O_2 dosage was 3 g l^{-1}).

As shown in Figs. 5 and 6, the organic matters with unsaturated structures transformed into organic matters with saturated structures after ozone and H_2O_2 catalyzed oxidation. After ozone and H_2O_2 catalyzed oxidation, the content of carboxyl groups and hydroxyl groups increased observably. It indicated that the organic matters containing carboxyl groups and hydroxyl groups could complex with polyvalent cations, such as aluminum coagulant and magnesium ion, and then be removed from water [6,7]. As for the activated carbon adsorption, the organic matters with smaller molecular weight and saturated structures can be easily removed by activated carbon adsorption [8].

Generally speaking, the organic matters with carboxyl groups and hydroxyl groups have the ability of

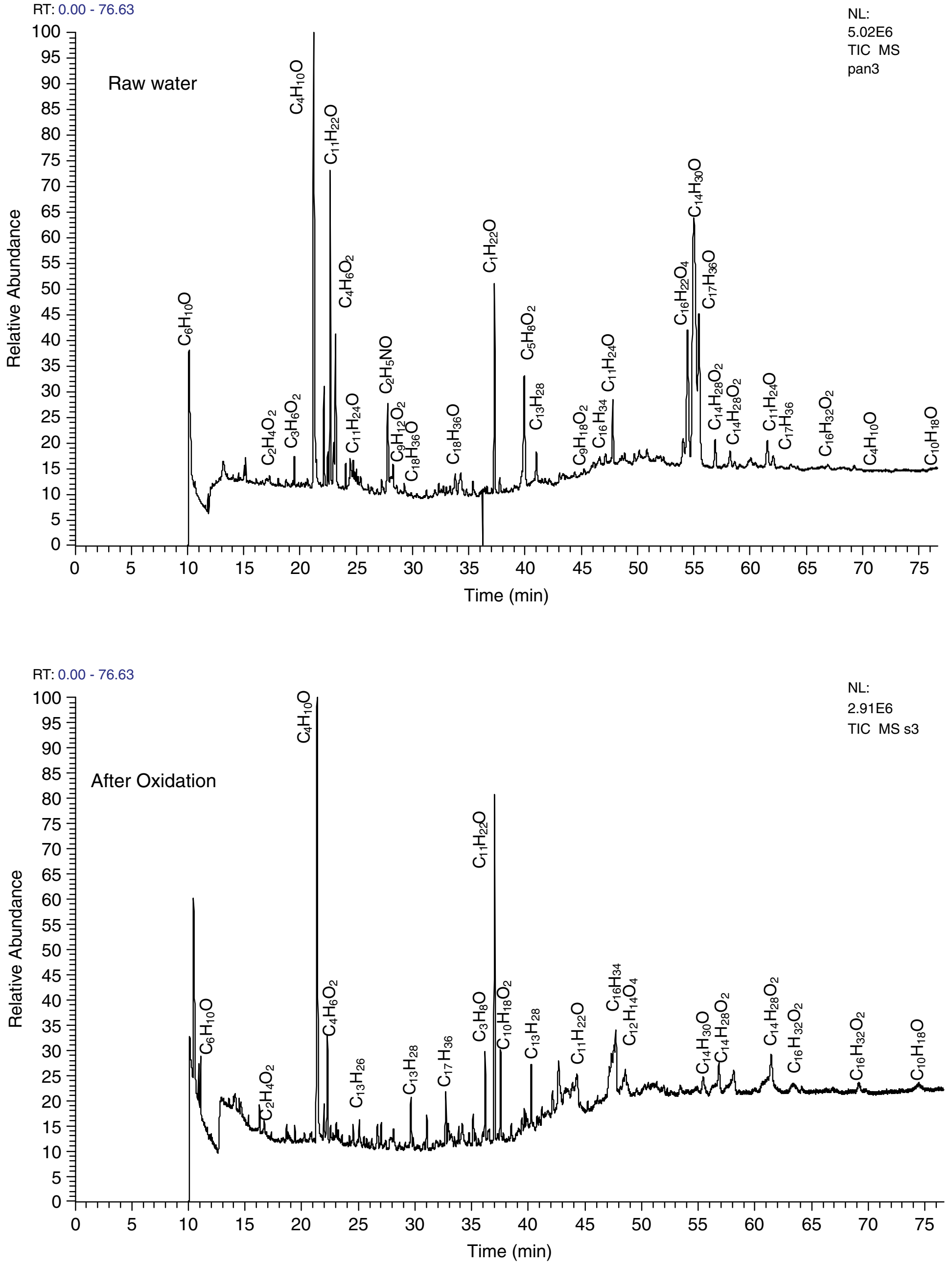

Fig. 6. GC-MS analysis result of raw water and treated water by O_3/H_2O_2 for polarity organic matter.

deprotonation or the ability of protonation. The groups with deprotonation or protonation ability can usually coordinate with metal ions in water [9,10]. When the organic matters coordinate with the magnesium ion, the fluorescent characteristic will be weaken. Fig. 7 showed the variation of fluorescence intensity before and after oxidation. As shown in Fig. 7, the fluorescence intensity of raw water was much stronger than that after ozone catalyzed oxidation which indicated that the organic matters binded magnesium ion in water.

According to the analysis above, as the structures of organic matters changed by oxidation, the increasing of the content of carboxylic acid resulted in the coordination complex between organic matters and magnesium ion. The magnesium ion coordinated with organic matters would be lost in the water when the organic matters were removed by the following processes such as coagulation, GAC adsorption.

3.5. Effect of pH adjusting on magnesium ion loss and organic matters removal

Based on the analysis above, it can make a conclusion that the magnesium ion loss along with the removal of organic matters is attributed to the complexation of the increasing carboxylic groups by oxidation with magnesium ion. Usually, organic matters containing carboxylic groups complexed with cationic ions are pH dependent, and protonation is dominant at low pH value [11,12]. Fig. 8 showed the relationship between organic matter removal and magnesium ion loss by GAC adsorption by pH adjusting after preoxidation at raw water pH value.

As shown in Fig. 8, when the pH value was adjusted to pH 2.0 after oxidation, the loss of magnesium ion remains at about 5%. In addition, the COD removal could reach about 90%, which was higher than before. It may be of help to improve adsorption at acidic pH value. Therefore, the effective process for controlling the magnesium ion loss and improvement of organic matters removal was O_3/H_2O_2 following GAC adsorption at pH 2.0. And in this way, the purity of magnesium hydroxide produced by Nafine Co. Ltd could be guaranteed effectively.

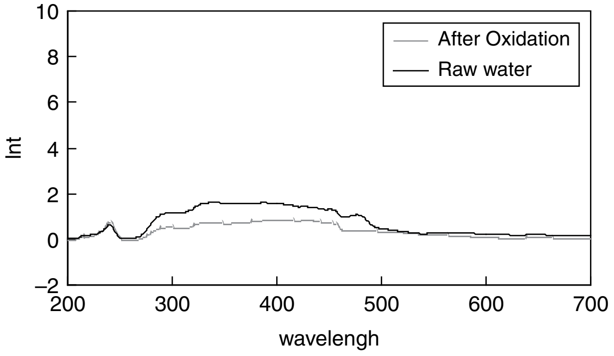

Fig. 7. Comparison of fluorescence intensity of raw water and treated water at different ozone dose.

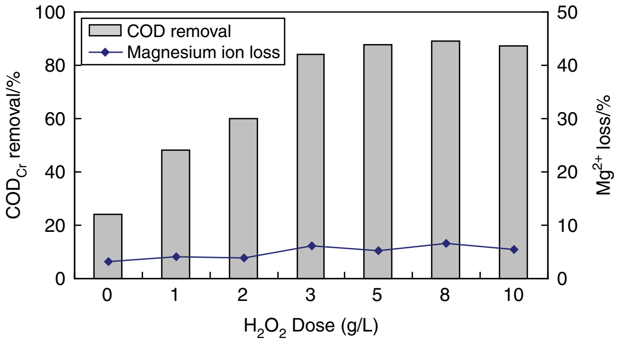

Fig. 8. Relationship between organic matter removal, magnesium ion loss by GAC adsorption after O_3/H_2O_2 at pH 2.

4. Conclusions

From the experimental results explained in the former sections, conclusions can be drawn as follows:

1. By GC-MS and fluorescence detection analysis, it found that O_3/H_2O_2 oxidation could increase the content of carboxylic groups, which resulted in the coordination complex between organic matters and magnesium ion. And the magnesium ion coordinated with organic matters would be lost when the organic matters were removed by the following processes such as coagulation, GAC adsorption.
2. Adjusting pH to acid conditions after O_3/H_2O_2 oxidation, protonation is dominant at low pH value and the complexes between organic matters and magnesium ion could be restrained. In this way, the magnesium ion loss with the removal of organic matters can be effectively controlled.
3. According to the product purity requirements of Nafine Co. Ltd, the suitable treatment process is O_3/H_2O_2 oxidation following activated carbon adsorption at pH 2.0.

Acknowledgements

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