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# *In situ* gelation treatment of desulfurization wastewater using alginate

Yongtong Li[a,b], Yuan Zhuang[a,b,*], Dawei Ma[c], Baoyou Shi[a,b,d], Haotian Hao[a,b], Delin Li[e], Jian Chen[c], Jianmian Deng[f]

[a]*National Engineering Laboratory for Industrial Wastewater Treatment, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China, emails: yuanzhuang@rcees.ac.cn (Y. Zhuang), ytlimail@163.com (Y.T. Li), byshi@rcees.ac.cn (B.Y. Shi), tienhh@qq.com (H.T. Hao)*
[b]*State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*
[c]*Power Science Research Institute of State Grid Anhui Electric Power Co. Ltd., Hefei 230601, China, emails: dwma@mail.ustc.edu.cn (D.W. Ma), 82563579@qq.com (J. Chen)*
[d]*University of Chinese Academy of Sciences, Beijing 100049, China*
[e]*Anhui Xinli Electric Technology Consulting Co. Ltd., Hefei 230601, China, email: hflidelin@163.com*
[f]*School of Environmental and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450046, China, email: dengjianmian@ncwu.edu.cn*

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## ABSTRACT

To overcome the limitations of traditional desulfurization wastewater treatment in coal-fired power plants that entail complicated processes and high chemical consumption, we propose a novel *in situ* gelation treatment combining flocculation and adsorption using alginate without additional cross-linking agents. Metal ion pollutants in desulfurization wastewater were employed as cross-linkers to gelate biomacromolecules of alginate resulting in the simultaneous formation of hydrogels and the removal of pollutants. The results show that alginate can effectively utilize the metal ions in desulfurization wastewater, which are instantaneously gelated into hydrogels, resulting in flocculation and adsorption. An alginate dosage of 12 g/L and a reaction time of 3 h were identified as the optimum reaction conditions. Alginate was modified using 1,3,5-triazine-2,4,6-trithiol trisodium salt, ethylenediamine and thiosemicarbazide to enhance its contact with metal ions. The results demonstrate that the optimum treatment effect was obtained using ethylenediamine at 0.02 g/L, with removal rates of 71.1%, 70.8%, 64.1% and 65.0% for Ca, Cr, Cd and As, respectively. The method proposed here is easy to operate and with low cost, suggesting broad prospects for application in industrial wastewater treatment.

*Keywords:* Desulfurization wastewater; Alginate; *In situ* gelation; Ethylenediamine

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## 1. Introduction

Industrial wastewater is becoming a major problem in urban regions. In addition to heavy metals, industrial wastewater also contains a considerable amount of inorganic substances, organic compounds, surfactants, salts, etc, which affect the physical and chemical properties of water and toxicity to living organisms. The changes in natural water caused by industrial wastewater indirectly have deleterious effects on humans. Because they can cause heritable disorders that may pass to future generations [1–3].

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* Corresponding author.

Coal is considered one of the biggest sources of energy worldwide. But the presence of sulfur in coal causes significant environmental hazards and serious problems in its utilization [4–6]. The wet limestone–gypsum flue gas desulfurization process has been adopted for most Chinese coal-fired power plants for the removal of $SO_2$. To ensure desulfurization efficiency, prevent corrosion of desulfurization equipment and ensure the quality of gypsum, some wastewater must be discharged from the system [7–9]. The quality of coal will cause the water quality of desulfurization wastewater to be different [10].

The desulfurization wastewater produced by the flue gas desulfurization process is characterized by a high salt content, high hardness and a complex composition including multiple ions with significant toxicity and environmental risk [11,12]. Indicators of water quality in desulfurization wastewater are as follows [13]: (1) it has high suspended solids and soluble components including gypsum particles and multifarious ions; (2) it contains a variety of heavy metals such as Cd, Pb, Cr, As and Hg; (3) it is weakly acidic with a pH value of approximately 4.5–6.5; (4) the total dissolved solids of desulfurization wastewater are high with $Cl^-$, $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$.

The traditional desulfurization wastewater treatment method is a chemical precipitation coagulation process [14]. In China, most coal-fired power plants have adopted a triplet tank process (neutralization, flocculation and precipitation) to treat desulfurization wastewater, but there are problems with this process such as its complexity, variation in dosage, high consumption of chemicals and unreliable effluent water quality. In 2015, the State Council of China issued the "Water Pollution Control Action Plan" to emphasize the management of various types of water pollution. As the terminal wastewater produced by power plants, desulfurization wastewater has complex components and poor water quality. The goal of zero liquid discharge of desulfurization wastewater has been widely pursued [15,16]. Approaches to improvement in traditional industrial wastewater treatment methods have included extending the technological process or increasing reactor volumes and chemical doses, but this pathway to improvement is problematic for its high cost and high energy consumption, hindering the methods' commercial application [17]. The technologies of single pollutant removal and membrane purification are problematic because of their high cost, complexity and high risk of recycling [18,19]. Therefore, it is necessary to develop a new desulfurization wastewater treatment technology with a short process flow and low reagent use for commercial application.

The use of low-cost, highly effective and environmentally friendly materials for pollutant remediation is a hotspot in the environmental area [20,21]. The adsorbent is regarding as one of the promising techniques used for wastewater treatment, and the modification of adsorbents attracted much attention due to their enhanced adsorption capacities [22,23]. As an environmentally friendly green material, hydrogels are porous and have excellent adsorption properties for pollutants in wastewater [24–26]. Guan et al. [27] found that during desulfurization wastewater treatment, chitosan–metal complexes had better separating performance compared with the settling of metal hydroxides, suggesting that the use of hydrogels to remove heavy metals renders these metals easily separable from sediments in desulfurization wastewater. Alginate is an important family of natural polysaccharides extractable from seaweeds [28]. Gelation is an important feature of alginate, and alginate can form hydrogels through chelation with divalent cations via G-blocks [29]. Alginate has a number of free hydroxyl and carboxyl groups distributed along its chemical backbone that make it capable of functionalization to improve properties such as solubility and hydrophobicity. In recent years, alginate hydrogel has been widely used in wastewater treatment [30,31]. Zhuang et al. [32] formulated an alginate-based hydrogel with excellent removal effects for heavy metal ions in water, with a maximum adsorption capacity for $Cu^{2+}$ of 169.5 mg/g and for $Cr_2O_7^{2-}$ of 72.5 mg/g. Alginate hydrogel has great application potential for the removal of heavy metals from water and has definite research potential in the field of industrial wastewater treatment. Moreover, alginate is easily functionalized to further enhance its adsorption capacity [33]. Based on adsorption capacity, stability and recycling, number of studies have found that modified materials have better performance than native biomasses [34,35].

In this study, sodium alginate was used to treat desulfurization wastewater by *in situ* gelation. The heavy metals in desulfurization wastewater acted as crosslinkers to make sodium alginate gelatinize instantly, greatly reducing the reaction time. Heavy metals and suspended matter were removed during *in situ* crosslinking through flocculation, and the remaining heavy metals were further removed by adsorption on the hydrogel, resulting in in-depth treatment of desulfurization wastewater. Since desulfurization wastewater contains a variety of metal ions, sodium alginate can produce a polymetallic cross-linking state without the addition of other agents, improving the stability of alginate gel while efficiently treating the wastewater.

To further improve their treatment effects, sodium alginate materials were modified with 1,3,5-triazine-2,4,6-trithiol trisodium salt, ethylenediamine and thiosemicarbazide (TSC) [36–38]. The effects of sodium alginate dosage, reaction time and material modification on the removal of pollutants from desulfurization wastewater were investigated. Analysis of the treated wastewater materials was carried out to further characterize the mechanism. In this study, the effects and mechanisms for the deep treatment of desulfurization wastewater by a *in situ* gelation method are discussed and can be expected to provide a theoretical and practical basis for realizing the treatment of industrial wastewater with a short process flow and low quantities of reagents.

## 2. Materials and methods

### 2.1. Materials

The reagents used in this study mainly include sodium alginate, 1,3,5-triazine-2,4,6-trithiol trisodium salt, ethylenediamine and TSC. All chemical reagents used in this study were analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China) and used without further purification. All solutions were prepared using deionized water.

### 2.2. Characterization

The structure and morphology of the test materials were characterized using field-emission scanning electron microscopy (SEM, Hitachi S-4800, Japan). The pH was determined using a pH meter. Ca and Mg were determined by inductively coupled plasma spectroscopy (Optima 8300, USA). Ni, Zn, As, Cd, Pb and Cr were determined by inductively coupled plasma (Thermo Fisher ICP-MS, Thermo Fisher Scientific Co., Ltd., USA). After the reaction, the water sample was analyzed using an excitation–emission matrix (EEM) fluorescence spectrophotometer (F-4500, Hitachi, USA). Every sample had three replicates and a blank control, and the resulting equilibrium concentrations were calculated on average.

### 2.3. *In situ treatment using alginate*

This technology is compared with the traditional triplet tank in Fig. 1. It can be seen that the triplet tank is not only a complicated technological process but also involves many agents, high labor costs and a low degree of automation, while the addition of modified sodium alginate materials greatly shortens the technological process and reduces the necessary agents. The removal rate for most heavy metals when adding modified sodium alginate materials is obviously higher than the rate attained by the triplet tank process. Therefore, the one-step *in situ* gelation treatment has great prospects for commercial application.

The target wastewater in this study was desulfurized wastewater from unit 1 and unit 2 of a power generation plant prior to its entry into a triplet tank. Units 1 and 2 are separate generating sets of the power plant. These two parts will produce desulphurization wastewater under different working conditions. The water quality of the target wastewater is presented in Table 1. The total suspended solids of treated wastewater are 823 mg/L. The conductivity of desulphurization wastewater is 40 mS/cm. The concentration of chlorides is 19,858 mg/L, sulfates 3,427 mg/L and sulfides 0.365 mg/L. The hardness of the target wastewater is high, so the primary challenge is to remove heavy metal pollutants from water under conditions of high hardness and to judge the resulting performance by the removal rate of heavy metal pollutants.

Firstly, large particles suspended in the target wastewater were removed with quantitative filter paper and a suction

Table 1
Quality of target wastewater

| | |
|---|---|
| Ca (mg/L) | 1,214.75 |
| Mg (mg/L) | 1,085.5 |
| Ni (mg/L) | 0.061 |
| Zn (mg/L) | 0.352 |
| Hg (μg/L) | 0.35 |
| As (mg/L) | 0.023 |
| Cd (mg/L) | 0.169 |
| Pb (mg/L) | 0.189 |
| Cr (mg/L) | 0.005 |
| pH | 6.09 |

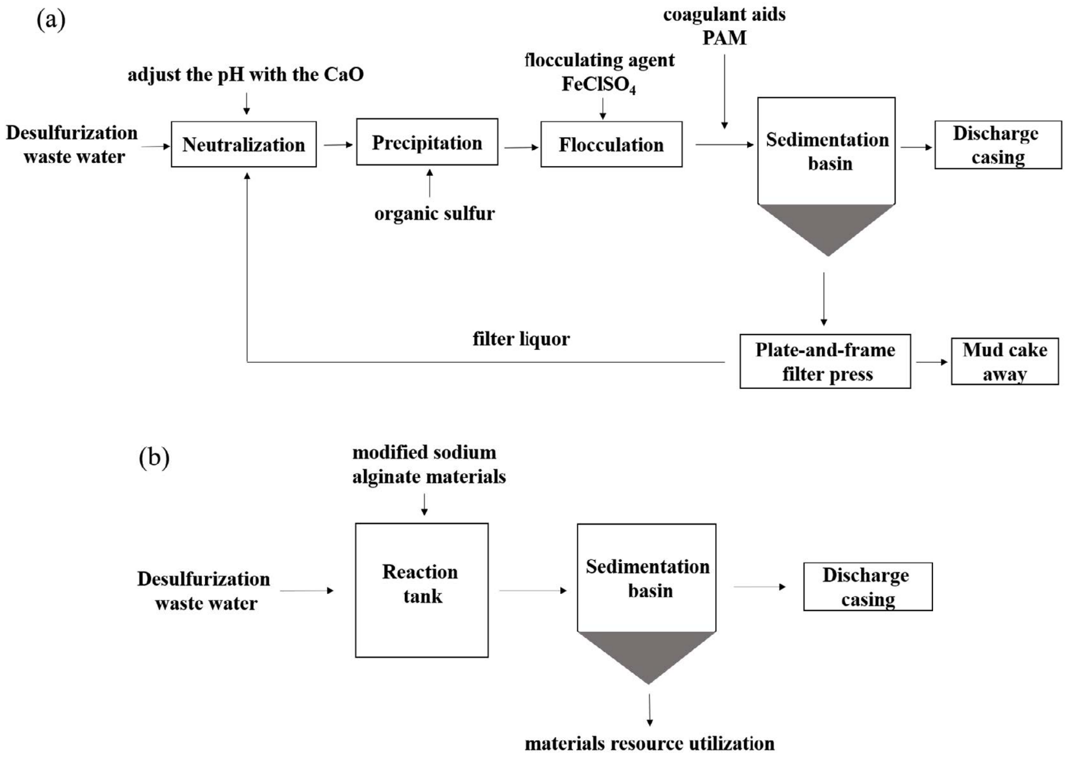

Fig. 1. (a) Technical diagram of the existing three-box process and (b) technical process diagram for the addition of modified materials.

filter device. The test material was then dripped into 500 mL of target wastewater using a peristaltic pump. To ensure that the material contacts well with the wastewater, the material was pumped into target wastewater containing a uniform filament of approximately 0.5 mm thickness.

As the amount of sodium alginate added and its reaction time was the most direct factors affecting the treatment effect, these effects were evaluated by batch experiments. Referencing the operating constraints of power plants such as the volume of water treatment facilities, the actual treatment times for desulfurization wastewater are generally not more than 3 h. On this basis, we set up four groups of experiments for comparison: (a) untreated wastewater; (b) sodium alginate at 6 g/L and a reaction time of 2 h; (c) sodium alginate at 6 g/L and a reaction time of 3 h; (d) sodium alginate at 12 g/L and a reaction time of 3 h. In these four groups of experiments, we compared the concentrations of heavy metals and the pH of water samples. After the reaction, the hydrogel was separated with a sieve and then the metal ion concentration in the treated wastewater was tested. Optimum conditions were determined by comparing the four treatments in preparation for the next step using modified sodium alginate materials.

### 2.4. *In situ treatment using modified alginate*

In this process, sodium alginate was mixed with 1,3,5-triazine-2,4,6-trithiol trisodium salt, ethylenediamine and TSC. The mixtures were added to the target wastewater according to the above method while keeping the volume of target wastewater at 500 mL, the reaction time at 3 h and the sodium alginate at a concentration of 12 g/L. The dosage of modifier was divided into five concentrations: 0.01, 0.02, 0.05, 0.1 and 0.15 g/L. After 3 h, the hydrogel was separated from the water, and the heavy metals and pH in the water were measured. The dosage for the modifier ethylenediamine and TSC was determined according to the optimal dosage for 1,3,5-triazine-2,4,6-trithiol trisodium salt.

## 3. Results and discussion

The formation process of the hydrogel is illustrated in Fig. 2. When the sodium alginate materials were introduced into the desulfurization wastewater the hydrogel formed quickly by complexing with heavy metal ions in the water, simplifying the separation of hydrogel from wastewater. Compared with traditional flocculation, this process avoids the disadvantage of sludge generation.

The data on the treatment of target wastewater with sodium alginate materials are presented in Fig. 3. It can be seen that increasing sodium alginate dosages and reaction times are conducive to the removal of metal ions. The pH of the wastewater decreases when the sodium alginate material is added. However, with increases in dosage, the pH gradually increases from 6.09 to 7.54, further promoting the adsorption and removal of metal ions. But the application of organic compounds to desulfurized wastewater resulted in a slight increase in total organic carbon (TOC). The TOC of desulphurization wastewater is 116 mg/L, and the TOC of wastewater treated with modified sodium alginate material is 152 mg/L. This shows that sodium alginate will leak slightly during the experiment.

In group D, the concentration of metal ions is lowest, with a sodium alginate concentration of 12 g/L and a reaction time of 3 h. The treated wastewater meets the discharge requirements for heavy metal pollutants as specified in the "Water quality control index for desulphurization wastewater by limestone-gypsum dehumidification in thermal power plant" DL/T997-2006, so the amount of reagent is not further increased; however, it can be seen from Fig. 3 that the removal effect of the addition of sodium alginate alone is not great, so the study proceeds to treatment with the modified sodium alginate material.

The data for sodium alginate materials modified by the addition of 1,3,5-triazine-2,4,6-trithiol trisodium salt is presented in Fig. 4. The concentrations of heavy metal ions (Ca, Mg, Ni, As and Cd) in treated wastewater are lowest when the dosage of 1,3,5-triazine-2,4,6-trithiol trisodium salt is 0.02 g/L. Other indicators such as Zn and Pb are consistent with this trend. The treatment effects on target wastewater for the three modified materials, compared with a modifier dosage of 0.02 g/L and a reaction time of 3 h, are presented in Fig. 5. The figure shows that all three modified materials have good removal effect on heavy metal ions in the target wastewater, but for some metal ions (As, Cd, Cr, Ni and Zn), sodium alginate is modified by ethylenediamine is more effective than the other two modifiers. It can be inferred that the treatment effect is greatest when ethylenediamine is used to modify sodium alginate and when the dosage of the modifier is 0.02 g/L. The amino group of ethylenediamine is helpful to enhance the chelation of heavy metals with the material.

EEM fluorescence spectroscopy tests of the target wastewater before and after treatment are shown in Figs. 6a–e. As shown in Figs. 6a–c, raw water without treatment contains more organic matter such as humic

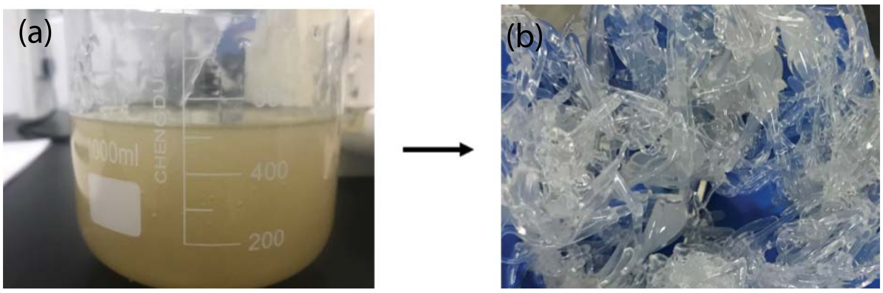

Fig. 2. Photograph of the *in-situ* treatment wastewater (a) and alginate hydrogel after treatment (b).

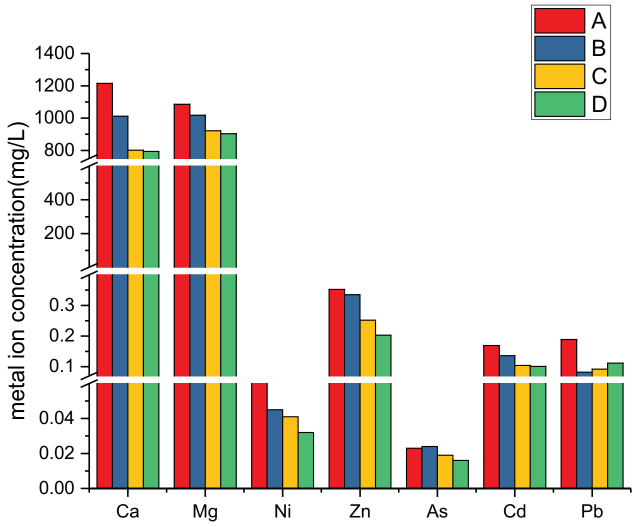

Fig. 3. Metal ion removal efficiency under different dosages and reaction times.

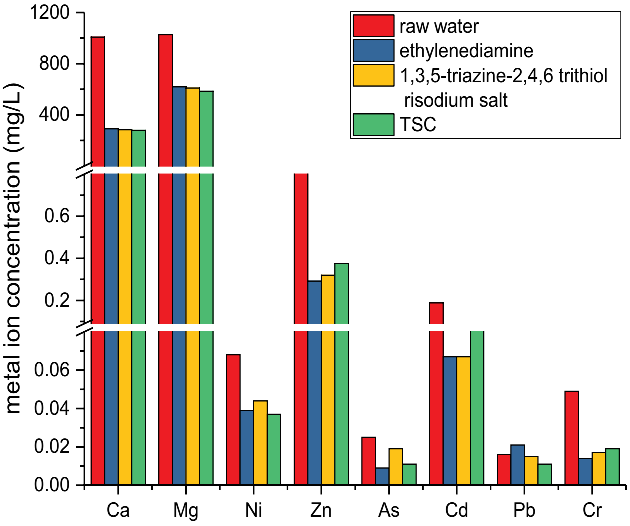

Fig. 5. Metal ion removal efficiency with different modifiers.

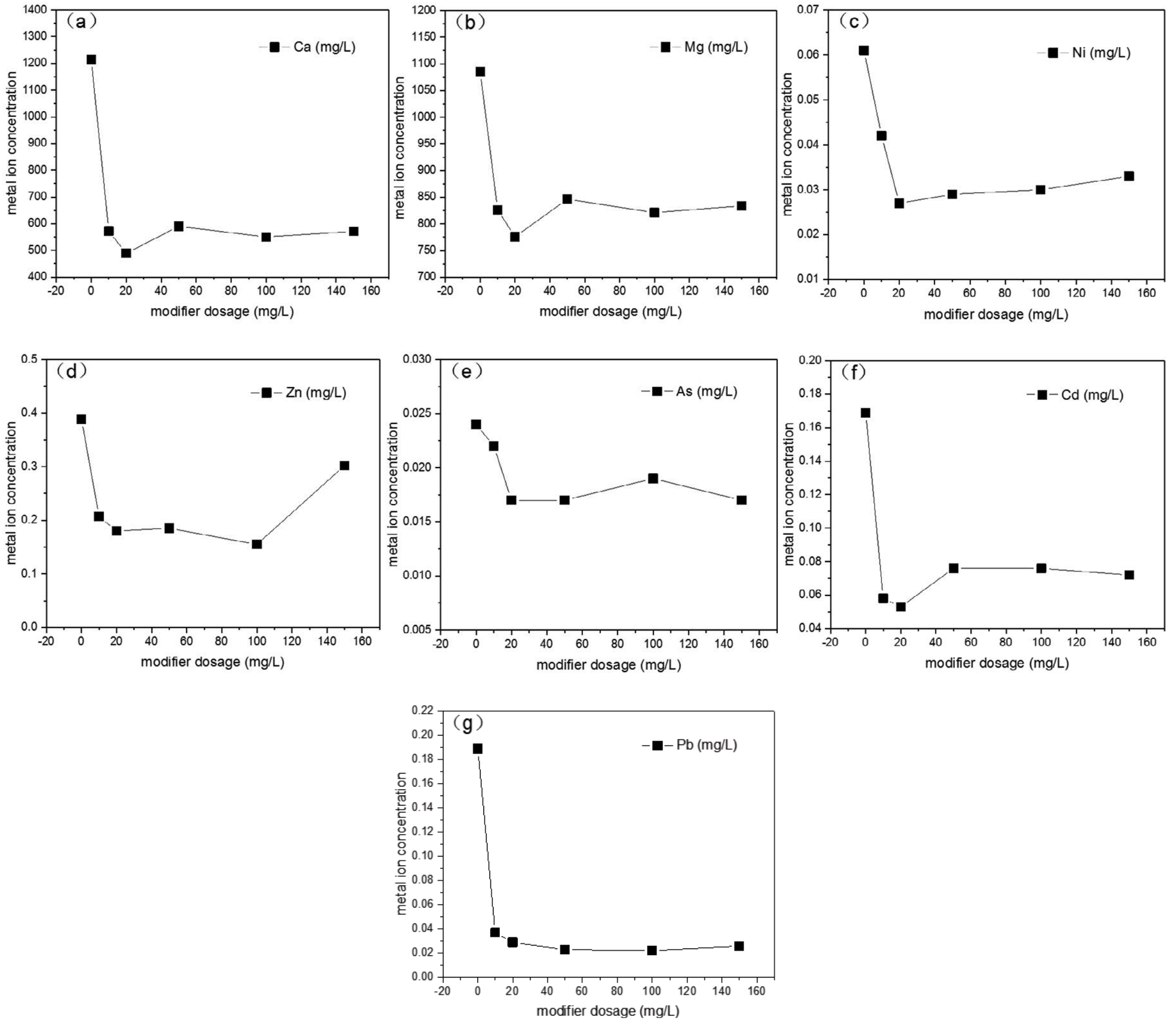

Fig. 4. Influence on metal ion removal efficiency under different modifier dosages. (a) Ca, (b) Mg, (c) Ni, (d) Zn, (e) As, (f) Cd, and (g) Pb.

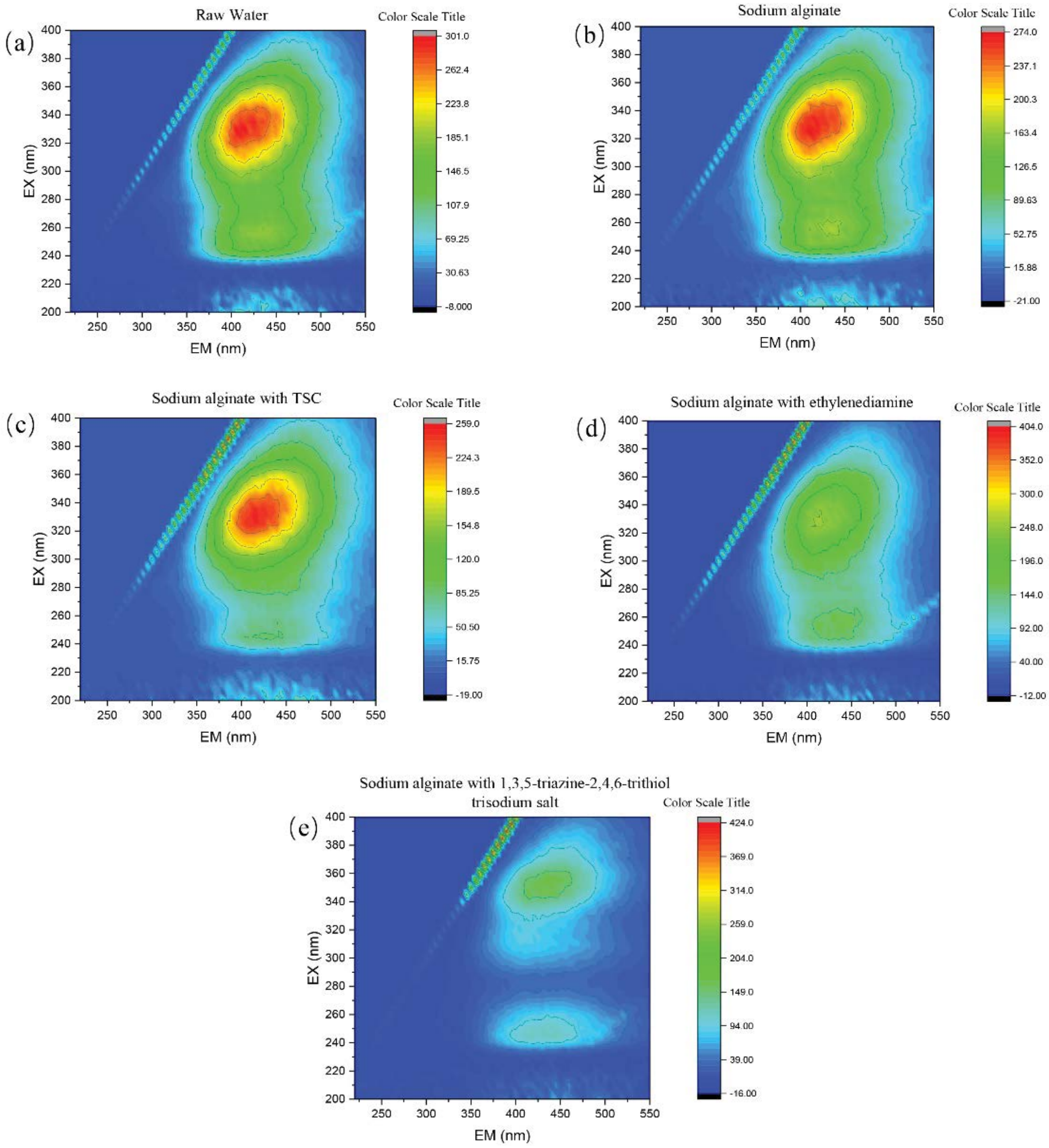

Fig. 6. (a) EEM of raw water, (b) EEM of raw water after treatment with sodium alginate, (c) EEM of raw water after treatment with sodium alginate and TSC, (d) EEM of raw water after treatment with sodium alginate and ethylenediamine, and (e) EEM of raw water after treatment with sodium alginate and 1,3,5-triazine-2,4,6-trithiol trisodium salt.

acid-like and fulvic acid-like. Sodium alginate material and TSC-modified sodium alginate material have no measurable effect on the removal of organic matter. In comparison, as seen in (d) and (e), the organic matter content of raw water significantly decreased after treatment with ethylenediamine-modified sodium alginate and 1,3,5-triazine-2,4,6-trithiol trisodium salt-modified sodium alginate. Among them, the most significant treatment effect is the use of 1,3,5-triazine-2,4,6-trithiol trisodium salt-modified sodium alginate to treat desulfurization wastewater, and the content of fulvic acid and humic acid are significantly reduced.

Then we compared the treatment effects of sodium alginate and modified sodium alginate on target wastewater. The modified materials have clearly better treatment effects than the unmodified materials for such pollutants as Ca, Mg, Ni, Zn, As, Cd and Pb. Among these, the removal rate for Ca by modified materials can reach 71.1%, Cr 70.8%, As 65.0%, Cd 64.1%, Ni 43.0%, Hg 40.0% and Zn 64.5%. This shows in the complex environment of desulfurization wastewater, the ability of modified sodium alginate material to chelate heavy metals is greater than that of sodium alginate. In this study, the best treatment effect of ethylenediamine-modified sodium alginate on target wastewater can be explained by the covalent cross-linking reaction between carboxyl of sodium alginate and amino of ethylenediamine, which makes the gel structure tend to be tight. It is more conducive to the formation of stable flocs and the fixation of heavy metals on the surface of the hydrogel. The removal rate for Ca by traditional triplet

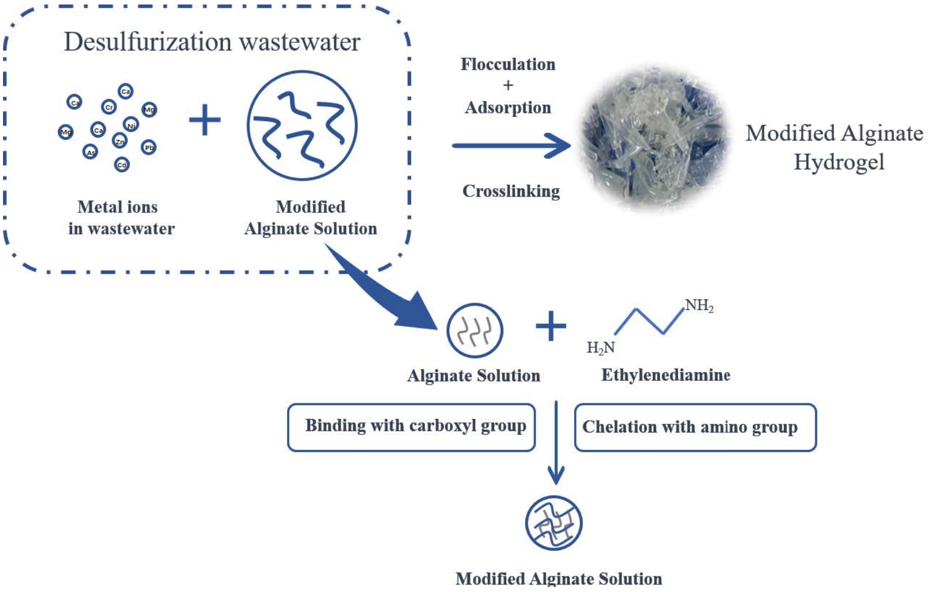

Fig. 7. Action mechanism of modified sodium alginate material.

tank process is 10%, As 27.6%, Hg 56.4%, Ni 8.5%and Zn 32.7%. Compared with the traditional triplet tank process, the *in situ* gelation treatment adopted in this research has significantly improved the removal effect of metal pollutants in desulfurization wastewater, especially for Ca, Zn, As and Ni. At the same time, the *in situ* gelation treatment can greatly reduce the dosage of chemicals and the process of desulfurization wastewater treatment.

The action mechanism of sodium alginate modified by ethylenediamine in the treatment desulfurized wastewater is presented in Fig. 7. The covalent cross-linking reaction between the carboxyl group of sodium alginate and the amino group of ethylenediamine can make the gel structure tend to be tight, which greatly improving the ability of the gel to chelate metal ions [39,40]. With the help of heavy metal pollutants in desulfurization wastewater, the modified alginate solution can quickly form modified alginate hydrogel in the complex water environment to achieve flocculation and adsorption.

## 4. Conclusions

This study developed a *in situ* gelation method for the treatment of desulfurization wastewater using the metal ions present in wastewater as crosslinkers to gelate alginate. The different batch exploratory results indicated that with increases in the sodium alginate dosage and reaction times the treatment effects were progressively improved. The effects of different modified sodium alginate materials are compared. Ethylenediamine is selected as the most effective at modifying sodium alginate, and the optimal treatment effect is a modifier dosage of 0.02 g/L, a concentration of sodium alginate of 12 g/L and a reaction time of 3 h. The removal rate for Ca from target wastewater using modified materials can reach 71.1%, Cr 70.8%, As 65.0%, Cd 64.1%, Ni 43.0% and Zn 64.5%. Comparing the process flows and removal rates, the *in situ* gelation method achieves a standard discharge of desulfurization wastewater with short process flows and a low use of reagents, placing the method in the foreground for industrial applications.

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