Study on scale inhibition properties of chitosan derivatives

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Abstract—The chitosan derivatives scale inhibitor CTS-AMPS was synthesized by using chitosan and 2-acrylamido-2-methylpropane sulfonic acid as raw materials and ammonium persulphate as initiator, and the structure of the product was determined by ATR-FTIR. The scale inhibition performance of CTS-AMPS for municipal water was tested. The results showed that when the concentration factor of municipal wastewater is 2.5 times and the dosage is 30 mg/L, the scale inhibition reached 76.6%. The results of SEM show that the scale inhibition performance of CTS-AMPS is mainly due to lattice distortion.

1. Introduction

At present, the recharge water used in industrial circulating cooling water is still dominated by groundwater and surface water, while the municipal wastewater (MWW) was rarely used[1]. The scale and corrosion inhibitors used in the simultaneous treatment system mostly contain phosphorus, which not only easily lead to water eutrophication, but also difficult to biodegradation[2]. With the shortage of water resources and the requirements of sustainable development strategy, the discharge of phosphorus containing wastewater at home and abroad is becoming increasingly strict. Therefore, the development of environmentally friendly water treatment agents has become the focus of research at home and abroad[3]. Chitosan, with its unique biological structure, is a natural environmental recyclable and degradable point, which is in line with green. In recent years, many scholars at home and abroad have studied different kinds of chitosan derivatives used as scale inhibitors and corrosion inhibitors, but there are common shortcomings such as single performance and poor biodegradable[4,5]. Chitosan derivatives with both scale inhibition, dispersion and corrosion inhibition properties are rarely reported.

In this paper, CTS-AMPS was prepared from CTS and 2-acrylamido-2-methylpropane sulfonic acid (AMPS). The effects of the raw material ratio, initiator dosage on the scale resistance of municipal wastewater were studied. The optimal synthesis conditions are as follows: mass ratio of CTS: AA is 3.00: 1.93; the amount of initiator is 10%; the reaction temperature is 70 °C, and the reaction time is 4 h. The resistance of $CaCO_3$ in municipal wastewater could reach 76.6%, when the concentration factor of MWW is 2.5 times and the dosage is 30 mg/L.

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2. Materials and Methods

2.1. Regents

Chitosan, analytical pure, was purchased from Shanghai Aladdin Biochemical Technology Co., LTD; China. Ammonium persulphate, analytical purity, was got from Guangfu Fine Chemical Research Institute; China. AMPS, analytical pure, was purchased from Tianjin Fuchen chemical reagent factory, China. Acetic acid, analytical pure, was purchased from Shanghai Aladdin Biochemical Technology Co., LTD; China.

2.2. Regents Synthesis of CTS-AMPS

In a 250 mL four-mouth flask equipped with a thermometer, reflux condenser tube and drip funnel, 3.00 g of chitosan and 150 mL of glacial acetic acid aqueous solution with a volume fraction of 2% were added, and after N_2 was introduced, magnetic stirring made it completely dissolved, at this time, the aqueous solution had a certain viscosity and was colorless and transparent. At a stirring speed of 500 r/min, a certain amount of APS aqueous solution with a mass fraction of 1% was slowly added to the solution dropwise, the reaction temperature was controlled below 70 °C, the reaction was 0.5 h, and the solution gradually turned light yellow during the reaction. When the temperature rises to 70 °C, start to slowly add 3.84 g AMPS dropwise, after dropping, maintain the reaction temperature of 70 °C, and carry out grafting and copolymerization for 4 h to obtain the light-yellow product CTS-AMPS. The schematic diagram of the composition is shown in Figure 1.

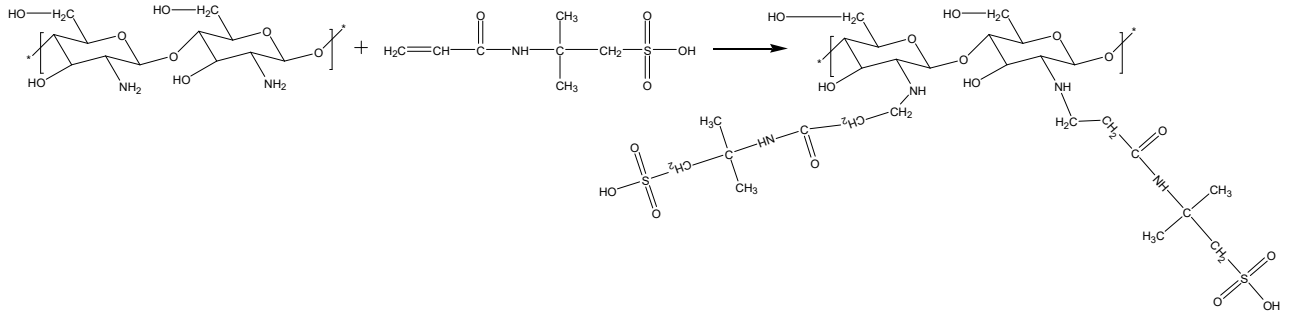

Figure 1. Schematic diagram of CTS-AMPS synthesis

2.3. Characterization of CTS-AMPS

Infrared spectrum of CTS-AMPS was measured via a Frontier Fourier-transform infrared (FTIR) spectrometer (PerkinElmer, USA.) with the attenuated total reflection (ATR) attachment. The wave number range was 4000-650 cm^{-1}.

2.4. Methods for analysis of scale inhibition mechanism

SEM images were observed on an Inspect S50 scanning microscope (FEI, USA). The acceleration voltage was 10 kV and the magnification was 2000 times. The appearances of the CaCO3 crystals with and without CTS-AA-PSI were observed by SEM (FEI Inspect S50).

2.5. Scale inhibition experiment

The experimental water was municipal wastewater (Shijiazhuang city). The parameters are as follows: pH=8.30, The electrical conductivity is 1149 μS/cm^2, the total alkalinity is 160.13 mg/L($CaCO_3$), The calcium hardness is 342.97 mg/L($CaCO_3$), TP=7.57 mg/L, Cl^- = 40.12 mg/L.

Add 500 mL of municipal reclaimed water to a 1 L beaker, add a certain amount of agent to be tested (the dosage of the agent is calculated according to the solid content of the agent to be tested), stir well, put the beaker into a water bath with a temperature of (80±1 °C) for evaporation concentration, and start timing when the temperature reaches the set temperature. When the solution has evaporated to 200 mL, remove and cool to room temperature before transferring to a 200 mL volumetric flask. If the experimental solution is less than 200 mL, deionized water can be replenished to the scale and shaken well (note: the replenishment water should not exceed 10 mL), then cover and continue to place in the (80±1 °C) water bath and continue to time for 10 h. After the timing is over, remove the volumetric flask and cool to room temperature, then pipette 25 mL of the supernatant, add 20 mL of deionized water, and sequentially add 1 mL of sodium hydroxide solution with a mass fraction of 20% and an appropriate amount of calcium carboxylate indicator, titrated with EDTA standard solution. In the experiment, the blank experiment without adding the agent was used for comparison, and the rest of the experimental steps were the same as above except without the agent to be tested. The scale inhibition rate ($\eta\%$) was calculated by the following formulas[6].

$$\eta\% = \frac{\rho_1 - \rho_0}{1.5\rho_2 - \rho_0} \quad (1)$$

In the formulas, ρ_0 is the mass concentration of Ca^{2+} in the supernatant after blank heating and concentration, mg/L; ρ_1 is the mass concentration of Ca^{2+} in the supernatant after heating and concentration with scale inhibitor, mg/L; ρ_2 is the mass concentration of Ca^{2+} in municipal water, mg/L.

3. Results and discussion

3.1. Characterization of CTS-AMPS ATR-FTIR analysis.

By comparing Figure2 (a) and (b), it can be found that the skeleton vibration peak of CTS appears at 890 cm^{-1}, while in CTS-AMPS, the skeleton vibration peak strength weakens and the position red shift is at 896 cm^{-1}. Moreover, the peak of N-H stretching vibration appeared at 3320 cm^{-1}, which was corresponded to the I band of amide group, while the peak at 1540 cm^{-1} (Figure 2 a) and 1591 cm^{-1} (Figure 2 b) was that of C=O vibration corresponding to the II band of amide group. There was a sharp absorption peak at 1659 cm^{-1}, which was caused by the –COOH[7]. The peak at 1060 cm^{-1} was the stretching vibration absorption peak of sulfonic group[8]. The appearance of these new peaks indicates that amide and sulfonic groups are introduced into the structure of CTS-AMPS.

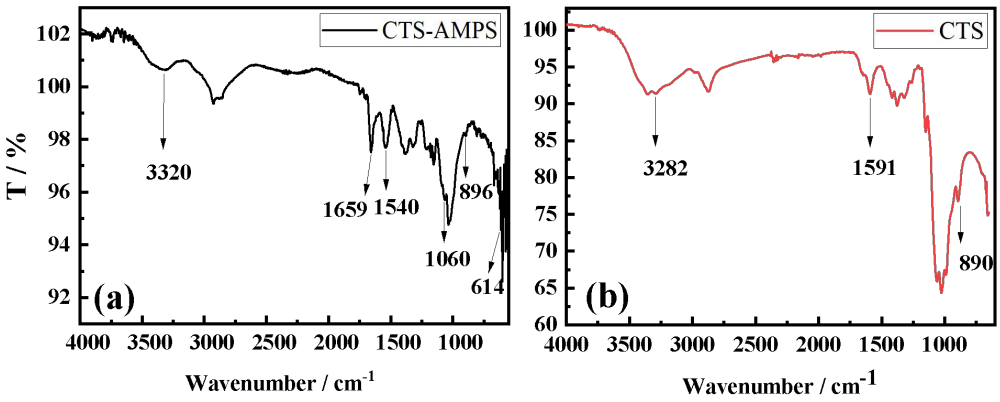

Figure 2. (a) Infrared spectrum of CTS-AMPS (b) CTS

3.2. Scale inhibition performance and mechanism

The scale inhibition rate of CTS-AMPS under different dosage is shown in Figure 3. With the dosage increases, the scale inhibition rate gradually increases, reaching 76.6% when the dosage is 30 mg/L, and 78.2% when the dosage is 40 mg/L. Considering the cost increase caused by excessive dosage, the optimal dosage is determined to be 30 mg/L. Because the composition of municipal water is complex, it is difficult to study its scale inhibition mechanism, so we use the calcium carbonate deposition method to prepare scale samples. Before the scale inhibition experiment began, a slide with the size of 0.5cm2 was placed at the bottom of the conical bottle.

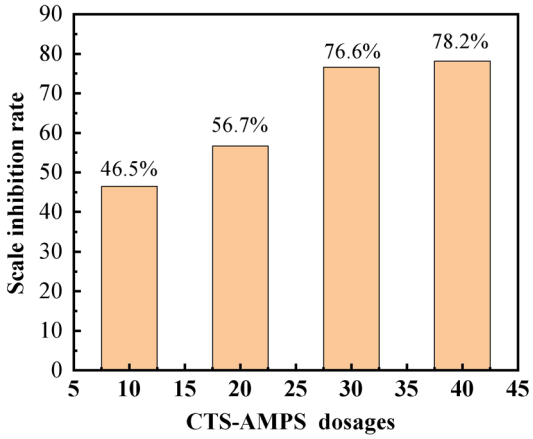

Figure 3. Scale inhibition rate of CTS-AMPS with different dosages

After the experiment, the slide with scale was taken out after drying, the slides were glued to the conductive adhesive and sprayed with gold, and then observed by scanning electron microscope and XRD. Then the corresponding contents of calcite and vaterite are calculated using the following formula, the results are shown in Figure 4[9].

$$I_V^{110}/I_C^{104}=7.690\times X_C/X_V \quad (2)$$

$$X_C + X_V = 1 \quad (3)$$

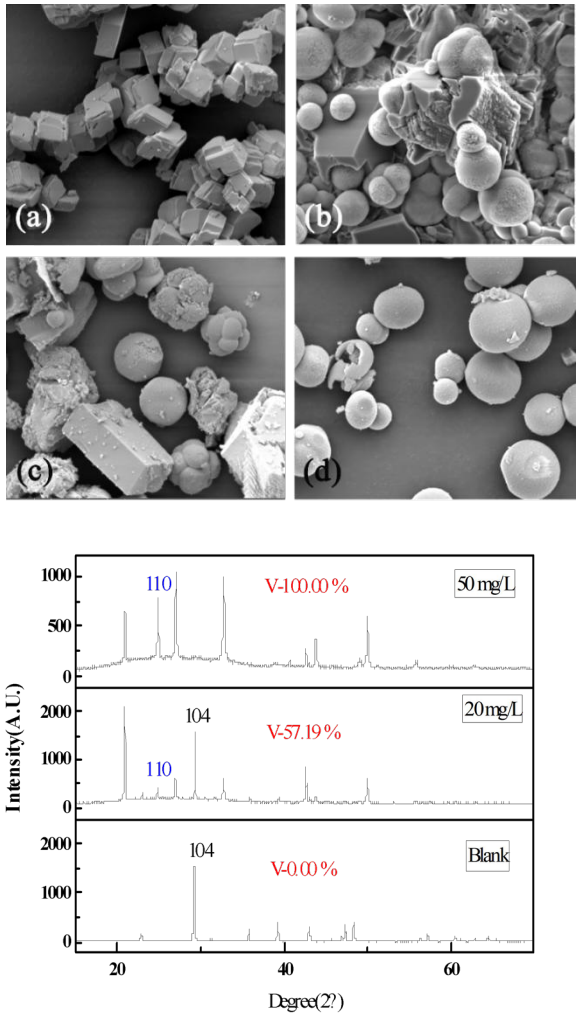

Figure 4. SEM and XRD of $CaCO_3$ samples with CTS-AMPS at different dosages (a,0 b,10 c,20 and d,30 mg/L)

It can be seen from Figure 4 that all the blank samples are angular calcite blocks and the percentage of vaterite is 0%. With the gradual increase of the amount of CTS-AMPS, irregular spheroids begin to appear on the crystal surface of calcite. [10] At a dosage of 20 mg/L, the vaterite content was 57.19%, and the surface becomes rough and irregular until the amount of CTS-AMPS is 30 mg/L, and all the square blocks become

spherical (V-100%), which proves that the scale inhibition performance of CTS-AMPS is due to lattice distortion.

4. Conclusions

The chitosan derivatives scale inhibitor CTS-AMPS was synthesized by using chitosan and 2-acrylamido-2-methylpropane sulfonic acid as raw materials and ammonium persulphate as initiator. The scale inhibition performance of CTS-AMPS for municipal water was tested. The results showed that when the concentration factor of municipal wastewater is 2.5 times and the dosage is 30 mg/L, the scale inhibition reached 76.6%. The results of SEM show that the scale inhibition performance of CTS-AMPS is mainly due to lattice distortion.The results show that the chemically modified chitosan derivatives have excellent scale inhibition properties on municipal wastewater, and more kinds of chitosan derivatives can be developed for scale inhibition in the future

Acknowledgments

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References

1. Pramanik B K, Shu L, Jegatheesan V, et al. (2019) Effect of the coagulation/persulfate pre-treatment to mitigate organic fouling in the forward osmosis of municipal wastewater treatment[J]. Journal of environmental management, 249: 109394. https://doi.org/10.1016/j. jenvman.2019.109394.
2. Zhai J, Ren D, Xiao Y, et al. (2023) Synthesis of phosphorus-free terpolymer and its inhibitory performance on scale formation[J]. Journal of Polymer Research, 30(6): 232. https://link.springer.com/article/10.1007/s10965-023-03610-z.
3. Xiao Y, Ren D, Zhai J, et al. (2023) Synthesis and properties of a new polycarboxylic acid multi-polymer scale inhibitor suitable for industrial circulating water[J]. Journal of Applied Polymer Science, e54270. https://doi.org/10.1002/app.54270.
4. Ma W, Yang L, Wu Y, et al. (2023) Synthesis, characterization and properties of a novel environmentally friendly ternary hydrophilic copolymer[J]. RSC advances, 13(17): 11685-11696. https://doi.org/10.1002/jccs.201200441.
5. Mady M F, Abdel-Azeim S, Kelland M A. (2021) Investigation of the antiscaling performance of phosphonated chitosan for upstream petroleum industry application[J]. ACS Sustainable Chemistry & Engineering, 9(48): 16494-16505. https://doi.org/10.1021/acssusc hemeng.1c06786.
6. Sinopec Group. Cooling water analysis and test methods[M]. (1989) Beijing: Petroleum Press, 71-374.
7. Zhou M, Gu Y, Yi R, et al. Synthesis and property study of ter-copolymer P (MA-AMPS-HPA) scale inhibitor[J]. (2020) Journal of Polymer Research, 27: 1-12. https://link.springer. com/article /10.1007/s10965-020-02270-7.
8. Cui C, Zhang S. (2019) Synthesis, characterization and performance evaluation of an environmentally benign scale inhibitor IA/AMPS co-polymer[J]. New Journal of Chemistry, 43(24): 9472-9482. https://doi.org/ 10.1039/C9NJ01355E.
9. Zheng Y, Gao Y, Li H, et al. (2021) Chitosan-acrylic acid-polysuccinimide terpolymer as environmentally friendly scale and corrosion inhibitor in artificial seawater[J]. Desalination, 520: 115367.https://doi.org/10.1016/j.desal.2021.115367.
10. Ji Y, Chen Y, Le J, et al. (2017) Highly effective scale inhibition performance of amino trimethylenephosphonic acid on calcium carbonate[J]. Desalination, 422: 165-173. https://doi.org/10.1016/j.desal.2017.08.027