Performance Study of Environmentally Friendly Water Treatment Agents

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Abstract. In this paper, an environmentally friendly ternary water treatment agent was synthesized with three green raw materials, maleic acid, itaconic acid and sodium allylsulfonate. The static scale inhibition test was used to study the inhibitory properties of the product on the three main scales of calcium carbonate, calcium phosphate and calcium sulfate, as well as its dispersing properties on iron oxide and the biodegradability of the agent itself. As a result, the scale inhibition performance of the product on the three kinds of scale can reach 100%, and its dispersion performance is very excellent, and the ternary agent can be degraded by 67% in 28 days, which proves that this product is a biodegradable and environmentally friendly water treatment agent for use in recycled water.

Keywords: ternary chemicals; scale inhibition; dispersion; biodegradation

1 Introduction

In circulating cooling water system, adding chemicals is the most effective way to slow down scale precipitation[1-4]. Therefore, the research of scale inhibitors has become a hot spot in the field of circulating water treatment at home and abroad, and the types of copolymers are becoming more and more diversified[5-6]. At present, most of the water treatment chemicals widely used in the market are still phosphorus-containing chemicals[7], which have good scale inhibition effect, but the phosphorus emission will pollute the water environment and lead to eutrophication of water bodies. Environmentally friendly water treatment polymers synthesized from green raw materials are the research direction of water treatment chemicals[8,9].

In this paper, a ternary water treatment agent with excellent performance was obtained by free radical polymerization of maleic acid, itaconic acid and sodium allylsulfonate as raw materials in aqueous solution, and its synthesis conditions, scale inhibition and dispersing meter biodegradation properties were studied.

IDEE 2023, November 24-26, Zhengzhou, People's Republic of China

DOI 10.4108/eai.24-11-2023.2343440

2 Experimental part

2.1 Primary reagents

Maleic Acid, Itaconic Acid, Sodium Allyl Sulfonate, Sodium Bicarbonate, Anhydrous Calcium Chloride, Sodium Tetraborate, Ammonium Persulfate, Sodium Bisulfite, etc., all of the above drugs are analytically pure.

2.2 Main instruments

The main instruments include constant temperature water bath, magnetic stirrer, vacuum drying oven, spectrophotometer and so on.

2.3 Synthesis of copolymers

A certain mass of maleic acid, itaconic acid and sodium allylsulfonate were weighed and added to a four-necked flask along with distilled water, and all the solids were dissolved under stirring. After heating to a certain temperature in a water or oil bath, a catalyst (ammonium persulfate) and a chain transfer agent (isopropanol) were added, and the polymer solution was obtained by stirring the system for a period of time at a constant temperature.

2.4 Research on scale inhibition performance of copolymer on calcium carbonate

The experimental method refers to the national standard GB/T16632-2008, add the aqueous solution containing scale inhibitor in 500 mL conical flask (the concentration of calcium ion is 600 mg/L, the concentration of bicarbonate is 1200 mg/L, and the concentration of ions is in terms of calcium carbonate), and place the solution in a water bath at 80°C. The solution was cooled and titrated with EDTA solution to calculate the scale inhibition rate. The solution was placed in a water bath at 80°C for 10 hours at a constant temperature, and after cooling, the calcium ions in the supernatant were titrated with EDTA solution to calculate the scale inhibition rate, which was calculated by the following formula:

$$\eta_1 = \frac{V_1 - V_0}{V_2 - V_0} * 100\% \qquad (1)$$

Where V_0 (mL): the volume of EDTA required for titration of the solution after heating when no agent is added;

V_1 (mL): add the agent solution after heating the titration of the required volume of EDTA;

V_2 (mL): the volume of EDTA required for titration of raw water at room temperature.

2.5 Research on scale inhibition performance of copolymer on calcium sulfate

The experimental method refers to the national standard SY/T5673-93, in the conical flask add scale inhibitor and prepared water (the concentration of calcium ions is 5000 mg/L, the concentration of sulfate ions is 7500 mg/L, and the concentration of here ions is calcium sulfate), the solution is cooled after 25 hours of constant temperature in a 70°C water bath, and the supernatant is titrated with EDTA solution. in terms of calcium sulfate), the solution was cooled after 25 hours of constant temperature in a water bath at 70°C, and the calcium ions in the supernatant were titrated with EDTA solution to calculate the scale inhibition rate, which was calculated by the following formula:

$$\eta_2 = \frac{X_1 - X_0}{X_2 - X_0} * 100\% \qquad (2)$$

Where X_0 (mL): the volume of EDTA required to titrate the solution after heating when no copolymer is added;

X_1 (mL): the volume of EDTA required for titration after heating the solution with copolymer added;

X_2 (mL): the volume of EDTA required for titration of raw water at room temperature.

2.6 Research on scale inhibition performance of copolymer on calcium phosphate

With reference to the standard GB/T22626-2008, the solution containing scale inhibitor and prepared water (Ca^{2+} concentration of 250mg/L, PO_4^{3-}concentration of 1200mg/L) was thermostated at 80°C for 10 hours, and the phosphate content in the supernatant was measured after cooling. The phosphate content in the supernatant was measured after cooling for 10 hours, and the formula for calculating the scale inhibition rate of calcium phosphate was as follows:

$$\eta_3 = \frac{C_1 - C_0}{C_2 - C_0} * 100\% \qquad (3)$$

Where C_0: PO_4^{3-}concentration of the solution after heating when no copolymer is added;

C_1: PO_4^{3-}concentration of heated solution with copolymer added;

C_2: PO_4^{3-}concentration of raw water at room temperature.

The above units are mg/L.

2.7 Determination of dispersing properties of ferric oxide by pharmaceutical agents

The different concentrations of the agent and the preparation of water (at this time the concentration of calcium ions in terms of calcium carbonate, 150 mg/L, the concentration of ferrous ions 10 mg/L) mixed with strong stirring, placed in a water bath after a constant temperature of 5 hours. After the solution was cooled down, the transmittance of the upper layer of the clear liquid was determined, at this time, distilled water was used as a comparison, and the transmittance of distilled water was 100%, the smaller the transmittance of the sample, the more excellent the dispersing effect of the agent.

2.8 Determination of biodegradability

To determine the biodegradability of the copolymer, the solution containing the copolymer and the inoculum was firstly added to the sample bottle and then the bottle was sealed, and then the sample bottle was placed in a constant temperature shaker at 25°C with constant shaking, and the COD was measured on days 1, 7, 14, 21 and 28, respectively.The biodegradation rate of the copolymer was calculated using the measured COD data using the following formula:

$$\text{Bioderdationrate} = \left(1 - \frac{C_t - C_{bt}}{C_0 - C_{b0}}\right) * 100\% \qquad (4)$$

Where C_t: the content of COD in the solution containing the agent at the moment t;

C_{bt}: the content of COD in the blank solution at the moment t;

C_0: the content of COD in the blank solution at the initial moment.

The above units are mg/L.

3 Determination of the performance of copolymers

3.1 Scale inhibition properties of copolymers against calcium carbonate

The scale inhibition performance of the synthesized copolymer was determined, and the experimental results are shown in Figure 1. With the increasing dosage, the scale inhibition rate of copolymer on calcium carbonate is higher and higher, in the dosage of 40mg/L, the scale inhibition rate is 98%, and the dosage of 50mg/L, its scale inhibition rate reaches 100%.

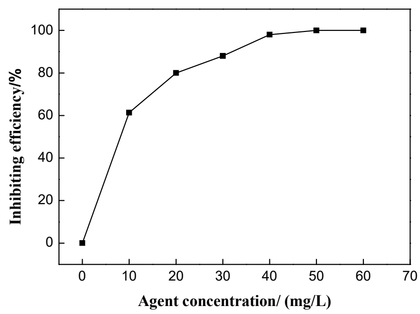

Fig.1. Scale inhibition of calcium carbonate

3.2 Scale inhibition performance of copolymer on calcium sulfate

The scale inhibition performance of copolymers on calcium sulfate was shown in the figure 2 below. From the figure, it can be concluded that the scale inhibition rate of copolymers on calcium sulfate reaches 100% at the dosage of 10 mg/L.

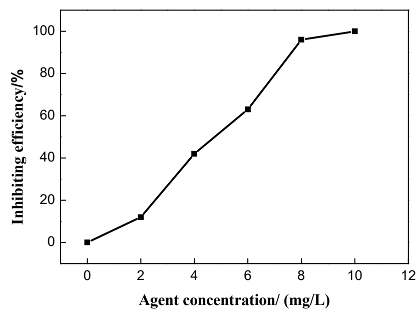

Fig.2. Scale inhibition of calcium sulfate

3.3 Scale inhibition properties of copolymers against calcium phosphate

Figure 3 shows the scale inhibition performance of the products on calcium phosphate. When the dosage of copolymer is low, it has almost no scale inhibition effect on calcium phosphate, and after increasing the dosage, the scale inhibition rate increases with the increase of dosage, and the scale inhibition rate reaches 100% when the dosage is 120 mg/L.

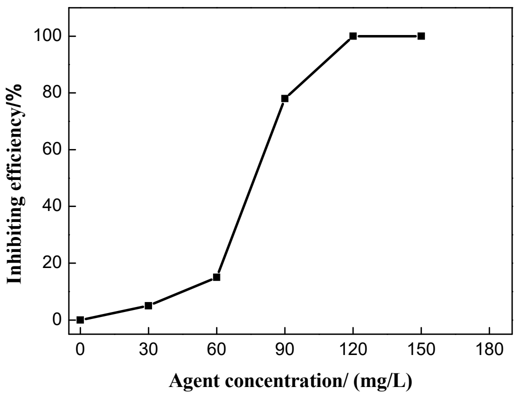

Fig.3. Scale inhibition of calcium phosphate

3.4 Dispersing performance of copolymerization

As shown in Figure 4 for the copolymerization product dispersion effect of the results obtained after the study, the three raw materials polymerization of the product dispersion effect is good, in the dosage of 120mg/L, dispersed iron oxide after the upper layer of the clear liquid transmittance of 32%, the dispersion effect is excellent.

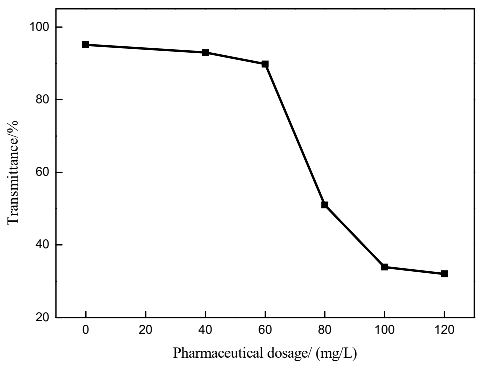

Fig.4. Dispersing properties of the copolymer

3.5 Copolymer degradability study

The biodegradability of the product was investigated using bioculture method and the results in figure 5 showed that the degradation rate was 67% in 28 days, which indicates that the copolymer is an easily biodegradable substance suitable for a wide range of applications in water bodies.

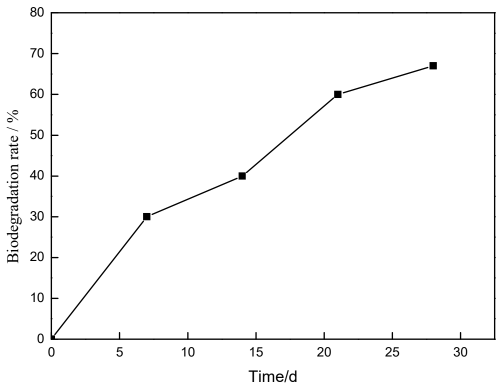

Fig.5. Biodegradability of the polymer.

4 Conclusions

A terpolymer water treatment agent was synthesized using maleic acid, itaconic acid and sodium allylsulfonate as raw materials. The performance of the product was measured, and the experiment showed that it has excellent scale inhibition and dispersion performance and good biodegradability, and it is an excellent scale inhibitor and dispersant for circulating water.

Acknowledgements: This project was supported by the Science and Technology Program of Hebei Academy of Sciences (No. 23701) and the High-level Talent Cultivation Grant Program of Hebei Academy of Sciences (2023G09).

References

[1] Liu Yu. Application and development direction of water treatment chemicals in waste leachate [J]. Popular Standardization, 2023, 386(02):120-122.

[2] Xia Ting, Fan Dayong, Zhang Jianmei. Research progress of compound modification of water treatment agent in China [J]. Fine and Specialty Chemicals, 2022, 30 (12):17-20.

[3] Yang Haiyan. Screening and Evaluation of Circulating Cooling Water Treatment Agents for Water Reuse [J]. Petrochemical Corrosion and Protection, 2020, 37(04): 20-24.

[4] Geng Cunzhen, Tang Meiru. Research progress of green water treatment agent polyaspartic acid and its derivatives [J]. Applied Chemical Engineering, 2015, 44 (07):1350-1353.

[5] Cheng Yushan, Xing Naihao, Zhang Lei, et al. Research on the formulation of environmentally friendly polyaspartic acid water treatment agent [J]. Cleaning World, 2018, 34(01):20-24.
[6] Li Hong, Chen Jianchang, Yuan Guoguang et al. Research on energy saving and emission reduction of modern industrial circulating water system [J]. China High-Tech, 2023 (09):102-104.
[7] BEAULIEU J J, DELSONTRO T, DOWNING J A. Eutrophication will increase methane emissions from lakes and impoundments during the 21st century[J]. Nature Communications, 2019, 10(1): 1375.
[8] MPELWA M, TANG S F. State of the art of synthetic threshold scale inhibitors for mineral scaling in the petroleum industry: A review[J]. Petroleum Science, 2019, 4: 830-849.
[9] POPOV K, RUDAKOVA G, LARCHENKO V, et al. A comparative performance evaluation of some novel “green” and traditional antiscalants in calcium sulfate scaling[J]. Advances in Materials Science and Engineering, 2016, 2016: 1-10