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Study on scale inhibition performances and interaction mechanism of modified collagen

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HIGHLIGHTS

- A scale inhibitor was prepared by modified chrome shavings hydrolyzing collagen.
- The scale inhibitor had good ability on calcium carbonate scale inhibition.
- The calcite crystal growth was inhibited by the scale inhibition.

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ABSTRACT

The modified collagens with rich carboxyls were prepared by chemically modifying collagen, which was firstly extracted by hydrolyzing chrome shavings, using the multi-aldehyde acid compounds (MACs) as the modifiers. Then those modified collagens and the blank collagen were used as scale inhibitors to implement scale inhibition tests. Scanning electron microscope (SEM) and XRD analyses were utilized to characterize morphology and crystal form of calcium carbonate scale. Results showed that the Ca^{2+} concentration and pH were the main influencing factors within the scale inhibition system, specifically the scale inhibition efficiency would be reduced with the increase of Ca^{2+} concentration and pH. Both the two types of scale inhibitors were more sensitive to the temperature, i.e., the scale inhibition rates were in a downward trend with augment of the temperature. The crystal form of calcium carbonate could be completely distorted to form a vaterite crystal through the action of modified collagens, thus the scale inhibition effect is achieved.

1. Introduction

Scale inhibitor is an important water treatment agent which is generally added into the industrial circulating cooling water. Its main function is to keep the circulating cooling water system efficiently transferring the heat and to ensure the normal operation of the industrial circulating cooling water. The common scale inhibitors mainly include inorganic phosphorus-containing polymer scale inhibitor, organic phosphate scale inhibitor, organic water-soluble polymer scale inhibitor, etc. [1]. Although the polymer scale inhibitor and phosphorus-containing scale inhibitor are highly efficient as a scale inhibitor, they have some fatal flaws such as difficult biodegradation in the water and eutrophication of the phosphorus-containing scale inhibitor. Therefore, the study that is to use natural products and their modified materials as biodegradable and eco-friendly scale inhibitors reaches great development [2,3].

In the traditional leather industry, 1 t of the raw leather can only be converted to 100 kg of finished leather while it generates more than 300 kg of solid wastes, most of which are chrome shaving. More importantly, 80% of the chrome shavings are collagen-like protein [4,5]. China is one of the largest countries in leather production and each year the wasted chrome shavings can be up to 1.4 million t [6]. So the resource utilization of collagen-like protein in the wasted chrome shavings has always been a hot topic among the leather and chemistry industry, and environmental protection researchers. It is well known that there are some carboxyls and amino groups in the molecular chains of the protein and the carboxyls have the complexation function to Ca^{2+}. However, the way to change the pendant amino groups into carboxyls via carboxylation modification will lead a certain amount of carboxyl groups into the protein molecular chains. In the present experiment, we have used the multi-aldehyde acid compounds (MACs) as the modifiers and modified the collagen that was extracted by hydrolyzing the chrome shavings, in which way we have obtained the modified collagens with rich carboxyls. To study the scale inhibition of the modified collagen is to explore a feasible and reasonable methodology for the resource utilization of collagen-containing solid wastes (chrome shavings) in leather production and the development of a new efficient scale inhibitor.

2. Experimental

2.1. Instruments and agents

The instruments used in the present research included a precision force-increasing electric mixer, an RE-2000B rotary evaporator, a precisive pHs-3C, an S-4800 filed emission scanning electron microscope

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(SEM), and an D/max2200PC X-ray diffractomer (XRD). The chemicals used included analytical grade glyoxal and melamine as well as technical grade collagen powder extracted by hydrolyzing cowhide chrome shavings and glyoxalic acid (50%). Deionized water was used throughout the whole experiment.

2.2. Methods

2.2.1. Preparation of chemicals

2.2.1.1. Preparation of multi-aldehyde acid compounds (MACs). Multi-aldehyde acid compounds (MACs) used in the present experiment were synthesized according to the literature [7] and the specific procedures are described as follows in detail. First, add the melamine and an appropriate amount of deionized water into a three-neck flask equipped with an electric mixer, a reflux condensing tube and a thermometer. Then heat the materials until the temperature reaches 50–60 °C. At this time add the sodium glyoxylate solution into the flask according to the ratio of a:1 (a = 5, 4, 3, 2) between n (sodium glyoxylate) and n (melamine). Next heat the reaction system up to 70 °C and let it continue reacting for 90 min. After a while, reduce the temperature to 40–50 °C and add the glyoxal aqueous solution based on the ratio of (6-a):1 between n (glyoxal):n (melamine). Warm the flask to 50 °C to react for 90 min. In the end, adjust the solid content to 40%.

2.2.1.2. Preparation of modified collagens. Weigh 600 g of the prepared MAC solution and put it into the three-neck flask equipped with an electric mixer, a reflux condensing tube and a thermometer. Then add in 15–25 g of collagen powders, adjust the pH to 7.5–8, and rise the temperature to 70 °C and keep the temperature for 4 h. At last, a condense yellow sticky solid is formed. Meanwhile, control the water amounting to be 30%.

2.2.2. Test of scale inhibition performance

Taking the modified collagen as a scale inhibitor, we have implemented the scale inhibition experiment referring to the national standard (GB/T16632-2008) [8] of the People's Republic of China. The process is as follows: add 250 mL of deionized water into a 500 mL volumetric flask, and 20 mL of standard calcium chloride solution with a mass concentration of 16.7 g/L was added through a burette. A solution of scale inhibitor sample of 0.5 g/L was added through a pipette and subsequently shaken well. Then, a borax buffer solution with a mass concentration of 3.8 g/L was added and shaken well. 40 mL of standard sodium bicarbonate solution (shaken while adding) with a mass concentration of 25.2 g/L was slowly added through a burette, and then diluted to the scale with deionized water and shaken.

The test and blank solutions were placed in conical flasks, respectively, and then the two conical flasks were immersed in a thermostatic water bath (the level of the test solution should not be higher than that of the water batch) of 80 ± 1 °C to stay for 10 h at constant temperature. The solutions were filtered with medium-speed quantitative filter papers after cooling to room temperature. The Ca^{2+} concentration within the filtrate was titrated using titration, and the scale inhibition rate of the scale inhibitor was calculated according to the following formula. The impacts of those conditions on the scale inhibition rate were considered by different Ca^{2+} concentrations, experimental temperatures and pH values.

The scale inhibition performance η of a water treatment agent expressed as a percentage was calculated according to formula (1):

$$\eta = \frac{\rho_1 - \rho_2}{\rho_3 - \rho_2} \times 100 \quad (1)$$

where ρ_1, ρ_2, ρ_3 are the mass concentrations of calcium ion in the test solution after the test using a water treatment agent and without use of a water treatment agent as well as before the test, respectively, and their units are all mg/mL.

2.2.3. Sample collection of $CaCO_3$ scale

Add 120 mL of the 0.1 mol/L $CaCl_2$ solution into a 500 mL beaker, then 4 mL of 1 g/L scale inhibitor solution, and slowly pour 240 mL of the 0.1 mol/L $NaHCO_3$ solution into the beaker to make the concentration of Ca^{2+} and HCO_3^- in the solution to be 12 mmol/L and 24 mmol/L, respectively. After fully and evenly mixing the solution, place it into thermostatic water of 30 °C for 10 h. Finally, take out the scale and dry it in order to get the analyses subject of SEM and XRD.

3. Results and discussion

3.1. Structure of MACs and scale inhibition effect of modified collagens by MACs

According to the document [7], the conclusion is that the structure of MACs is related to the molar ratios among the melamine, sodium glyoxylate and glyoxal. Namely, we can obtain four types of MACs by controlling those molar ratios during the experiment. The structure diagrams for the four kinds of MACs are shown in Fig. 1 as follows. In Fig. 1, "a" means the molar ratios between the sodium glyoxylate and melamine.

The chemical modification to the collagen was carried out through the reactions between the aldehyde groups in MACs and the amino groups in collagen. Thus, the collagen molecular chain acquired a large number of carboxyl groups. The schematic diagram for the chemical modification principle of the collagen is shown in Scheme 1 as follows:

The modified collagens by four MACs and the blank collagen were used as scale inhibitors to carry out scale inhibition tests and the results are displayed in Table 1. From Table 1, it could be seen that the scale inhibition rates of the modified collagens were obviously higher than that of the unmodified collagens, which is caused by the addition of the carboxyls. It can chelate Ca^{2+} and reduce calcium carbonate scale accordingly. With the augment of carboxyls in MACs which were used to modify collagens, the scale inhibition rate of the modified collagen was gradually increased except the modified collagen by MAC 4. That is to say, scale inhibition rate of the modified collagen by MAC 3 was the highest and could reach 93%, but that of the modified collagen by MAC 4 lowered and reached 89%. This phenomenon can be explained that with the increase of carboxyls from MAC 1 to MAC 3, more and more carboxyls are grafted onto the collagen chain and thus their scale inhibition rates gradually rise. However, as far as MAC 4 is concerned, there are up to 5 carboxyls but only one aldehyde group on the MAC structure which will reduce the reaction between MAC 4 and the collagen and the number of carboxyls grafted onto the collagen chain. Furthermore, due to steric hindrance among the molecules, formation of calcium scale with perforated mesh structure [9] is unfavorable (Fig. 2).

3.2. Effects of scale inhibitor dosage and temperature

The experiments were in order to study the patterns of how temperature and inhibitor dosage affect the scale inhibition performances under the condition of taking the unmodified collagen and the collagen modified by MAC 3 as the scale inhibitors, and setting the pH of the water sample to 6–6.5 and the concentration of Ca^{2+} to 250 mg/L. Results are separately shown in Figs. 3 and 4. It could be seen that both the scale inhibition effects of the two materials were gradually decreased with the increase of temperature. The scale inhibition rate of the unmodified collagen to the calcium carbonate in aqueous solution was relatively low, and the maximum scale inhibition rate was not more than 35%. It is well known that there is only 22.6% of the carboxyl-containing amino acids per 100 amino acid residues within