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A comprehensive experimental of degradation of pollutants in oil fields by sodium persulfate

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Abstract. A comprehensive experiment of Fenton-like method was designed to degrade oilfield pollutants. The effects of sodium persulfate on viscosity reduction of oilfield pollutants under different reaction conditions were investigated. The emphasis was put on the determination of viscosity, and the method of data processing should be learned to optimize the best viscosity reduction scheme. The experimental content can be closely combined with the basic theoretical knowledge of Applied Chemistry in oilfields, and can be applied to field practice. It helps students to understand the role of viscosity reducers and improve their functional ability of applying chemical knowledge. At the same time, the degradation and treatment methods of oilfield pollutants meet the requirements of green chemistry and enable students to establish environmental protection concept.

Keywords: Comprehensive experiment, Sodium persulfate, Oilfield Pollutants, degradation.

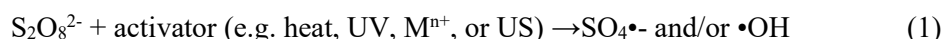
1. Introduction

In the oil exploitation and oilfield development process, the ternary composite flooding oil recovery technology is widely used. In the ternary composite flooding oil recovery process, oilfield contaminants containing residual surfactants, alkalis and polymers are produced, and polymers are used in the later stage of mining [1]. Oil displacement produces many oilfield contaminants containing refractory polymers, such as hydroxypropyl guar, polyacrylamide (PAM), carboxymethyl cellulose (CMC) and other oilfield polymers, which are complex in structure and difficult to degrade, chemical oxygen demand (COD) is high [2], direct emissions will cause environmental pollution, and does not meet national emission standards, so it needs to be treated and discharged [3]. These high polymers can not achieve good results by physical methods such as oil-water separation, so biodegradation means or chemical degradation means can be carried out. Among them, for polymers with low biochemical degradation rate such as PAM, we can choose to use chemical means for processing [4-5].



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Traditional methods for treating wastewater include physical methods, chemical methods, and biological methods. However, their existence is difficult to completely mineralize pollutants into small molecules or ions, have a long reaction period, and are susceptible to secondary pollution [6]. Advanced Oxidation Technology (AOPs) is a new technology that uses different methods to generate free radicals to degrade polymeric contaminants. Hydroxyl radical ($\bullet\text{OH}$), as one of the most effective oxidants, generated from the Fenton or Fenton-like process, the supreme oxidation potential of ($\bullet\text{OH}$) makes it a strong oxidant for water treatment, soil remediation, biological sensors, and material synthesis. Considering the more active of sulfate radicals ($\text{SO}_4\bullet^-$) for oxidation with the higher reduction potential of 2.5-3.1V compared to ($\bullet\text{OH}$) (1.8-2.7V) persulfate has been recently studied as an oxidant alternative for treating organic contaminants in contaminated soil and groundwater [7-8]. Normally, heat, ultraviolet light, transition metals ions (Mn^{2+}), electrochemical, ultrasound (US) or other methods can activate PS to generate ($\text{SO}_4\bullet^-$). The ($\text{SO}_4\bullet^-$) can then induce the generation of ($\bullet\text{OH}$), another powerful and nonselective oxidant. Based on this, a persulfate was designed as a comprehensive experiment for the degradation of oilfield pollutants. This experimental design is beneficial to improve the experimental skills of undergraduates in the field of applied chemistry, and also follows the environmental protection concept advocated by various petrochemical industries [9-10].



The comprehensive chemistry experiment of applied chemistry combines multiple experiments in series, which changes the traditional mode in which the experiments are self-contained and disconnected from each other. It has played a positive role in enhancing students' comprehensive experimental skills, cultivating innovative and scientific thinking skills, and developing good scientific research habits. The reform of comprehensive experimental skills training mode is comprehensive, economical and modern for professional knowledge and skills. The undergraduate students of the professional development of enterprise development have important guiding significance [11].

2. Design of the experiment

2.1. Objective

(1) Learn about the reaction mechanism of sodium persulfate degradation by consulting the literature or related books.

(2) Master the use method of the kinematic viscosity automatic measuring instrument for petroleum products;

(3) Mastering the preparation and treatment methods of the fracturing fluid base slurry;

(4) Learn to process experimental data, according to the best experimental solution and find relevant literature analysis to reduce the viscosity of the fracturing fluid.

2.2. Principle

In the experiment, guar gum was used to simulate oilfield wastewater. Guar gum is a galactomannan extracted from the seeds of *Cyamopsis tetragonoloba*, a native plant of India [12]. It is a non-ionic, water-soluble and because of its low cost and excellent viscosifying properties, it and its derivatives are extensively used in industrial applications including food, oil recovery, personal care, etc. Structurally it has a biodegradable and biocompatible heteropolysaccharide composed of a β -(1-4) mannopyranose backbone linked with α -(1-6) D-galactopyranose units. The structure is shown in Figure 1. [13]. The main important industrial use of guar gum is as a hydraulic fracturing fluid in oil and gas recovery. Now, a guar gum derivative containing hydroxyl group, hydroxypropyl guar gum (HPG), has been widely used as oilfield fracturing additive because of its high viscosity of aqueous solutions even at low concentrations. Therefore, there is a large amount of hydroxypropyl guar gum in the produced water after fracturing which needs to be treated due to its high viscosity. Hence, it is urgent to develop effective methods to remove hydroxypropyl guar gum from the contaminated environment.

Persulfate oxidation technology is a new advanced oxidation technology, which can activate persulfate and promote the production of sulfate radical ($\text{SO}_4^{\bullet-}$) to remove many refractory polymer pollutants from sewage. The properties of persulfate remain relatively stable, and it dissolves in water and ionizes persulfate ion ($\text{S}_2\text{O}_8^{2-}$). At room temperature, the reaction rate of this ion is slower and the effect of oxidative degradation of polymer is not obvious. However, under the conditions of heating, illumination or transition metal catalyst, the O-O bond in persulfate ion ($\text{S}_2\text{O}_8^{2-}$) is broken and stimulated to form sulfate radical negative ion ($\text{SO}_4^{\bullet-}$). The free radical has strong oxidation ability, its oxidation ability is stronger than persulfate itself, the ability of oxidizing and degrading polymer is greatly improved, and it has strong oxidation ability in acidic, neutral and alkaline systems, effectively expanding the application scope of pH. Advanced oxidation technology of persulfate has the advantages of non-selectivity and less influence by pH in the treatment of polymers contained in wastewater. It avoids the defects of traditional wastewater treatment methods and has more advantages. Therefore, it is more and more favored by scientific researchers. In order to make the advanced oxidation technology of persulfate effective, the key is to promote the production of sulfate radical ($\text{SO}_4^{\bullet-}$) by activation technology, and use the strong oxidation ability of free radical to achieve the purpose of efficient and rapid degradation of polymers contained in sewage. The commonly used methods of activating persulfate to produce free radicals are thermal activation, photoactivation and transition metal catalyst activation [14-15].

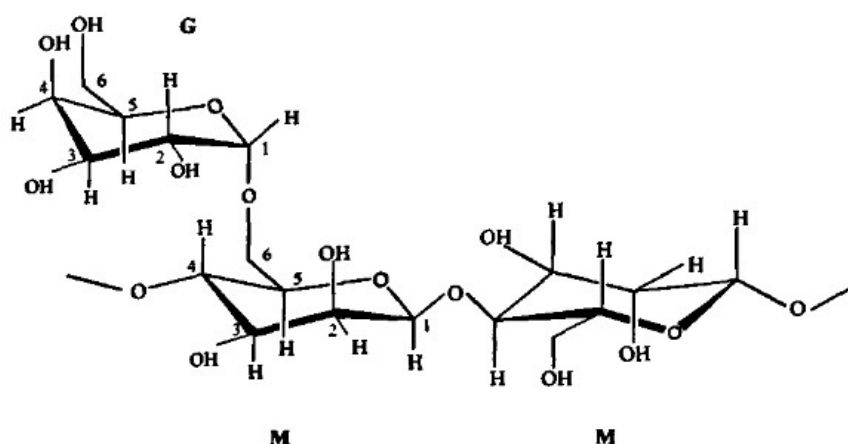


Fig.1 The basic structural unit of guar gum.

2.3. Materials

SYD-265H Petroleum Products Kinematic Viscosity Automatic Measuring Instrument, Shanghai Benshan Instrument Equipment Co., Ltd; CP214 Analytical Balance, Ahaus Instrument (Changzhou) Co., Ltd;

2.4. Methods

1. Check the power supply voltage, frequency and grounding is reliable. Then connect the three-core power cord of the chassis to the AC220V/50Hz power supply.

2. According to the test temperature used, the liquid is poured into the bathtub.

3. Choose appropriate capillary viscometer according to test temperature.

4. Open the power switch on the left side of the instrument. At this time, the LCD screen of the thermostat has a digital display, the PV display position shows the current bath temperature value, and the SV display position shows the set temperature value.

5. Set the SV value according to the test requirements: press the "function" key on the panel of the thermostat by hand, press the mobile key and the add and subtract key, select the temperature that needs to be set, and then press the "function" key. SV Display Position Displays Settings.

6. When the temperature in the bathtub is correct and stable, the test can be carried out. 5 mL hydroxypropyl guar gum solution is taken from the pipette and added to the Ukrainian viscometer which has been operated at constant temperature. A certain amount of sodium persulfate is added to make the amount of peroxide 10% of hydroxypropyl guar gum mass, and distilled water is added to make the total volume of the solution 10 mL and stir evenly. The kinematic viscosity of hydroxypropyl guar gum was measured within 40 minutes from the second of mixing sodium persulfate with hydroxypropyl guar gum. The catalytic effect of the catalyst was preliminarily evaluated by the effect of viscosity reduction.

2.5. Attention

Before the experiment, the safety problems should be emphasized for the students. We should monitor any accidents at any time during the process. After experiment, the waste liquid should be poured into the assigned waste liquid barrel, and a special one should be treated harmlessly, and no water should be poured into the sink and the sewer.

3. Questions and exercises

(1) How does persulfate catalyze the degradation of hydroxypropyl guar gum? What are the free radicals that react?

(2) According to the catalytic degradation ability of persulfate in the experiment, the literature was searched. What oxidants could catalyze the degradation of hydroxypropyl guar gum?

4. Conclusions

Combining with the actual situation of field treatment of oilfield pollutants, this paper designs a comprehensive experiment of oilfield pollutant treatment with simple operation and low energy consumption, requiring students to master the use method of automatic measuring instrument for kinematic viscosity of petroleum products, master the preparation and processing method of fracturing fluid-based slurry, and learn to process experimental data, and obtain the actual results. Check the best scheme and find the relevant literature to analyze the method of reducing the fracturing fluid viscosity. In the process of consulting literature and designing experiments, students must have the ability to analyze and solve problems, which is conducive to broadening their horizons and improving their research potential. At the same time, because the experiment involves a wide range of content, there are many factors reflecting the conditions of the investigation, which need more people to cooperate to complete, improve the students' team cooperation ability, and be good at analyzing and processing data, so as to determine the best experimental scheme. The comprehensiveness of the experiment is embodied in the use of the instrument, the processing of the data and the discussion of the results.

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