Environmental Engineering Education—An Example of a Comprehensive Experiment of Treating Oilfield Sewage Containing Polyacrylamide Using Electrochemical Oxidation Methods

Bo YANG1,2,* Gang CHEN1,a Tao YU2,b and Cheng-Tun QU1,2,c

1College of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Environmental Pollution Control and Reservoir Protection in Oil and Gas Field, Xi'an Shiyou University, Xi'an, Shaanxi 710065;

2State Key Laboratory of Petroleum Pollution Control, CNPC Research Institute of Safety and Environmental Technology, Beijing, 102206

*yangbo@xsyu.edu.cn, agangchen@xsyu.edu.cn, b180708@xsyu.edu.cn, cjianqct@xsyu.edu.cn

Keywords: Comprehensive experiment; Electrochemical oxidation; Polyacrylamide.

Abstract. In order to enhance the comprehensive experimental ability and provide environmental engineering education, an applied environmental engineering comprehensive experiment of treating oilfield sewage containing polyacrylamide (PAM) using electrochemical oxidation was designed in this paper. This experiment combines the basic oilfield environmental protection theory, test skills and polymer flooding practice, which can improve students' professional experimental skills, skills of analysis and problem solving. Using sewage containing PAM as experimental material can improve students' environmental awareness and help to put the environmental engineering ideas into oil recovery in the future.

Introduction

Polymer flooding technology is an important technology to improve oil recovery. PAM as a displacement agent can improve the mobility ratio, displacement efficiency and sweep area of oil recovery displacement fluid, which could improve oil recovery. [1] As the oil displacement used PAM, with high molecular weight, high viscosity, high oil-water interface film strength, long oil beads gathering time and float slowly during the treatment process, will lead to a certain impact on the efficiency and effect of treating sewage containing PAM. Because of these properties the treated sewage can not meet the discharge or reinjection standard. [2] At the same time, due to the inclusion of acrylamide in industrial PAM, it has obvious toxicity to human body. If the sewage after oil removal is discharged or injected directly, will lead to the accumulation of PAM in the environment and pollute the surrounding water, soil and groundwater. [3,4]

This runs counter to the green, circular and harmonious development, which advocated by China. Therefore, the degradation of PAM in oilfield sewage can help reduce the difficulty of treatment of oilfield sewage and save costs; on the other hand, the treated sewage can be used for reinjection after treatment, and can also save water resources. And saving water is of great significance.

For environmental engineering students, Analytical Chemistry, Electronic and Electrical Technology, and Water Pollution Control Engineering are essential core courses. The above courses require students to understand the theory, combine practice and field experience, and develop students' ability to comprehensively analyze and solve problems and collaborate ability. In order to enable students to acquire more knowledge and skills in the field within a limited experimental time, it is necessary to skillfully design a comprehensive experiment.

Environmental engineering education is a process of social practice carried out by means of education. It is based on the relationship between human beings and the environment, with the aim of solving environmental problems, achieving sustainable development; and with the mission of cultivating environmental protection talents by improving people's environmental awareness, effective participation ability, popularizing environmental protection knowledge and skills. This
teaching and research section combined with scientific research results to design a series of comprehensive experiments with environmental engineering education characteristics. The comprehensive steps in the experiment in terms of preparation of simulated sewage, determination of PAM concentration in solutions, establishing and using of standard curve, calculation of polymer removal rate and characterization of treatment effect, operation of electrochemical oxidation reactor and optimizing parameters.

Environmental protection and resource conservation of this experiment are reflected in the reduction of the treatment difficult of poly-sewage effectively, the improvement of re-use rate, the recycling of water resources, and the secondary utilization of poly-containing sewage, which avoid the environmental pollution caused by the discharge and re-injection of poly-sewage, has important environmental significance. This experimental design not only enables students to learn about the knowledge of PAM and polymer flooding, the theory and operation of electrochemical oxidation, but the basic principles of UV-visible spectrophotometer and standard curve. At the same time, it also cultivates students' awareness of environmental protection, and reflects the environmental protection concept advocated by environmental engineering.

**Experimental Purpose**

1. Master the basic method for preparing an aqueous solution of PAM;
2. Understand the mechanism of electrochemical oxidation, the principle of standard curve and the method of drawing;
3. Master the use of major instruments such as UV-Vis spectrophotometer, acidity meter, analytical balance, digital thermostat magnetic stirrer, and electrochemical reactor;
4. Learn to analyze the causes of changes in the main parameters of PAM-containing sewage through data analysis and literature query.

**Experimental Principle**

The PAM-containing sewage has high molecular weight, high viscosity, and high oil-water interface film strength, resulting in high concentration of polymer and oil in the treated sewage, causing the treated wastewater cannot meet the discharge or reinjection standard. The electrochemical oxidation method is used to oxidize the PAM in sewage, which can effectively reduce the concentration of polymer harmful substances in the sewage, improve the oil-water separation efficiency, reduce the oil concentration, and effectively solve the poly-containing sewage harmless treatment task. The experiment uses a small electrochemical reactor to achieve the purpose of degrading organic matter in the solution by redox reaction. In the reaction, the oxidant H$_2$O$_2$ is extra added to occur a hydroxyl radical (•OH) under the catalysis of Fe$^{2+}$. The •OH is a strong oxidizing substance, which can oxidize and break the polymer chain. During the electrochemical oxidation process, the pH of the simulated sewage is maintained at 3.5. The main reason is that under acidic conditions, the Fe$^{2+}$ catalyzes the high efficiency of H$_2$O$_2$ to generate hydroxyl radicals, but when the pH is less than 3, the Fe$^{2+}$ are easy to be combined with water and occur Fe[(H$_2$O)$_6$]$^{2+}$, reducing the catalytic efficiency; when the pH is higher than 4, generation of hydroxyl radicals will be inhibited, Fe$^{2+}$ easily precipitate with hydroxide ions. The electrode reaction formula is as follows:

Anode $\begin{align*}
Fe-2e^-$ & $\rightarrow Fe^{2+} \\
\text{Cathode} & \\
H^++2e^- & $\rightarrow H_2 \uparrow \\
O_2+2H^++2e^- & $\rightarrow H_2O_2 \text{ (when there is small amount of dissolved O}_2\text{)} \\
\text{In solution} & \\
Fe^{2+}+ H_2O_2 & $\rightarrow OH^-+Fe^{3+}+OH^- \\
Fe^{3+}+ OH^- & $\rightarrow Fe(OH)_3 \downarrow
\end{align*}$

(1) (2) (3) (4) (5)
Reagents and Instruments

Experimental Drugs

$\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$, $\text{CdI}_2$, Soluble starch, $\text{CH}_3\text{COOH}$, PAM (molecular weight: 5 million), $\text{Br}_2$, $\text{KBr}$, $\text{HCOONa}\cdot 2\text{H}_2\text{O}$, $\text{H}_2\text{O}_2(30\%)$, $\text{C}_2\text{H}_3\text{NaO}_2\cdot 3\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4(98\%)$, $\text{NaCl}$, $\text{Na}_2\text{SO}_4$, $\text{KCl}$.

Experimental Instruments

UV-visible spectrophotometer, precision electric mixer, acidity meter, analytical balance, digital thermostat magnetic stirrer, DC power supply, small electrochemical reactor.

Experimental Steps

Preparation of Base Solution

0.50 g of PAM with an average molecular weight of 5 million was weighed in analytical balance and placed in a 1500 mL beaker during stirring with a magnetic stirrer (180-200 rpm). The PAM were dissolved in 1000 mL of distilled water and stirred for 3.5 h to prepare a PAM solution with an initial concentration of $500\,\text{mg}\cdot\text{L}^{-1}$, and stored at room temperature for later use. The solution must be made at the same day with experiment.

Optimization of Electrochemical Oxidation Parameters

1. Using a measuring cylinder, take 2000 mL of pre-formed PAM solution (see 5.1), adjust the pH of the solution to 3.5 with dilute sulfuric acid, and pour into the electrochemical reactor for reaction use;
2. Under constant electrolysis time (10 min) and $\text{H}_2\text{O}_2$ addition amount ($20\,\text{mg}\cdot\text{L}^{-1}$), the current intensity was adjusted to 1.0, 1.5, 2.0, 2.5, 3.0 3.5, 4.0 A for electrochemical oxidation of PAM degradation experiment;
3. Under constant electrolysis time (5 min) and current intensity (2.0 A), the $\text{H}_2\text{O}_2$ addition amount was adjusted to 0, 10, 20, 30 mg•L$^{-1}$ to conduct electrochemical oxidation experiments of polyacrylamide degradation;
4. Under constant current intensity (2.0 A) and $\text{H}_2\text{O}_2$ addition amount($20\,\text{mg}\cdot\text{L}^{-1}$), the electrolysis time was adjusted to 5, 15 and 20 min respectively to carry out the electrochemical oxidation experiment of polyacrylamide degradation;
5. After the end of the experiment, the samples after electrolysis were allowed to stand for 40 min, the supernatant were taken, and the PAM content in the solutions after degrading under different current intensity, oxidant addition amount and reaction time was examined, and the optimal electrochemistry was discussed.

Determination of Residual Polymer Concentration and Calculation of Removal Rate

In this experiment, the concentration of PAM in solutions was determined by the starch- CdI$_2$ method.\[5\]

**Determination Principle.** The PAM concentration in the experiment is based on determining the concentration of the water-soluble polymer containing the primary amine side chain group, which is the concentration of the amide group. The conversion of the amide to the amine in the reaction is based on the first step of the Hofmann rearrangement. Adding a buffer solution into the polymer sample can be used to eliminate the influence from high-valent ions such as Fe$^{3+}$ and Bi$^{3+}$; maintaining the pH at 5 is beneficial to the production of N-bromoamide, and ensures that the bromoaomide does not react with HCOONa. Excess Br$_2$ is reduced with HCOONa, and the amide oxidation product can oxidize I$^-$ in the presence of linear starch to form a characteristic blue starch iodide complex. The complex has the strongest absorption peak at 574 nm and can be measured with spectrophotometer.
**Reagent Preparation.** 1. Buffer solution: dissolve 25 g of C$_2$H$_3$NaO$_2$$\cdot$3H$_2$O into 400 mL of distill water, add 0.75 g of H$_4$AlO$_5$S, and adjust the pH to 5.0 with HAC, and finally dilute the buffer in the volumetric flask to 1000 mL by distill water.

2. Starch-CdI$_2$ coloring agent: 5.5 g CdI$_2$ was dissolved into 200 mL of distill water, boiling for 10 minutes after stirred and dissolved, and then cooled down to room temperature. 2.5 g of soluble starch was added into 200 mL of boiling water, stirred and gently boiling for 5 min. The starch solution was added to the CdI$_2$ solution, filtered and dilute with distill water to 1000 mL.

3. Br$_2$/KBr solution: dissolve 6.0 g of KBr with a small amount of bromine water, and dilute with bromine water to 50 mL, and store it in the dark.

4. HCOONa (1 wt%): 1.000 g of HCOONa was weighed, stirred until dissolve, and dilute with distill water to 100 mL.

**Standard Curve Drawing.** 1. Take a certain amount of pre-formed PAM solution (see 4.1.1), adding distilled water during the stirring by use a magnetic stirrer at 100 rpm, to make a series standard concentration PAM solutions in terms of 25, 50, 100, 150, 200, 250, 300, 350 mL•L$^{-1}$ respectively.

2. Add 2 mL samples of different standard concentration PAM solutions to different colorimetric tubes and add 25 mL buffer solution.

3. Add 1 mL of Br$_2$/KBr solution to different colorimetric tubes and react accurately for 10 min.

4. Add 5 mL of HCOONa solution to different colorimetric tubes and react accurately for 5 min.

5. Add 5 mL of starch-CdI$_2$ solution to different colorimetric tubes, and measure the absorbance at 574 nm after 10 min by spectrophotometer.

6. The coordinate system was established by the absorbance value measured with different standard concentration PAM solutions and the standard PAM concentration values, and the standard curve of PAM solutions concentration was drawn by computer.

The examples of PAM solutions concentration and the corresponding absorbance values are shown in Table 1. The fitted PAM solutions concentration standard curve is shown in Fig. 1.

<table>
<thead>
<tr>
<th>PAM solution concentration [mg•L$^{-1}$]</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>250</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbance [Abs.]</td>
<td>0.01</td>
<td>0.024</td>
<td>0.059</td>
<td>0.097</td>
<td>0.173</td>
<td>0.241</td>
</tr>
</tbody>
</table>

![Figure 1. PAM Solution Concentration Standard Curve.](image)

**Calculation of PAM Removal Rate**

The PAM removal rate is shown in Equations 6:

\[
PAM\,\text{removal\,rate} = \left(\frac{\text{initial\,concentration}}{\text{residual\,concentration}}\right) \times 100\% \tag{6}\]

**Questions**
1. Why a magnetic stirrer is used for low-speed agitation during the preparation of PAM solution?

2. During the electrochemical reaction, floating phenomenon could be observed, try to explain the reason.

3. Why should we draw a standard curve of PAM solution concentration? What is the relationship of this curve to electrochemical oxidation experiments?

**Summary**

This experiment involves a wide range of knowledge. It is necessary to comprehensively investigate the different parameters of electrochemical oxidation of sewage containing PAM. In the experiment, the preparation of PAM solutions and its performance, as well as the composition of sewage containing PAM and its treatment methods can be understood. In the process of reviewing literature and designing experiments, students must have certain analytical and problem-solving abilities, which will help expand students' horizons and improve their research potential. At the same time, this experiment uses electrochemical oxidation to treat oilfield sewage containing PAM. It will not only solve the pollution of PAM-containing wastewater, but can improve students' environmental awareness. This experiment is carried out in groups, which is conducive to enhancing students' collaboration and teamwork ability.

**Acknowledgement**

This research was financially supported by the Key Laboratory Scientific Research Program of Shaanxi Provincial Education Department (No.14JS085) and Scientific Research and Technology Development External Collaboration Project of China Petroleum Safety and Environmental Protection Technology Research Institute (No.2016D-5006-08).

**References**


