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Study on the Performance of Polyaspartic Acid Water Treatment Agent

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Abstract

In the industrial circulating water system, water treatment agents are usually added to control the corrosion and scaling of the equipment. Polyaspartic acid (PASP) has the characteristics of high efficiency of scale inhibition and corrosion inhibition, non-toxic, biodegradable as a new type of green and environmental water treatment agent. Therefore, more and more people are studying the PASP. In this work, the optimum formula of the PASP was obtained by using the orthogonal test method, which was composed of 10 mg/LPASP, 0.5 mg/L benzotriazole (BTA), 20 mg/Lsodium tungstate (Tun) and 10 mg/Lsodium gluconate (Glu). The methods of scanning electron microscope (SEM) analysis, small dynamic simulation experiment, electrochemical test and biodegradation test were employed to study the optimum formula performance. It is especially emphasized that the copper scale inhibition rate and corrosion inhibition rate reached 99.22% and 0.0006mm/a, respectively, the biodegradation rate can reach up to 75.1% in 28 days. The experimental results show that the optimum formula solution has excellent effect of scale and corrosion inhibition, and has a strong characteristic of biodegradation, which belongs to a new type of green and environmental water treatment agent.

1. Introduction

Scale deposition is not a simple accumulation, unlike other types of deposition. In fact, it is a complex crystallization process that eventually forms a kind of hard scaling [1]. Scale inhibitors are thought to have a significant effect on scale and can reduce or even terminate the growth rate of crystals deposited in a scaling environment. Corrosion phenomena are very common in the circulating water system, endangering equipment safety and even causing replacement of equipment. Therefore, corrosion inhibitors are often used to add in water control equipment corrosion in the system. In order to control the circulating water system, the scale inhibitor and corrosion inhibitor should be added to control the scaling and corrosion of the equipment. Therefore, the development of water treatment agent with dual functions of corrosion inhibition and scale inhibition has become a hot topic in today's research. With the enhancement of people's consciousness in environmental protection, it becomes more and more important to study the environment-friendly water treatment agent [2-4]. PASP has been widely used in water treatment and other fields, because it has very good biodegradability and higher scale and corrosion inhibition capacity, especially under the condition of high Ca^{2+} concentration [5-7]. PASP has a linear polyamide structure, similar to the amide bond structure of protein, therefore, it can be degraded completely and has no effect on the environment [8].

At present, more and more people are beginning to think that PASP is a substitute for green water treatment, and a lot of experimental studies on the scale and corrosion inhibition of PASP were carried out [9].

The main purpose of this paper is to use PASP as the research object, using orthogonal test method to find the best formula. The performance of the optimum formula was studied by SEM analysis, small dynamic simulation experiment, electrochemical test and biodegradation test. It is especially emphasized that the biodegradation rate can reach up to 75.1% in 28 days. The results obtained here show the formula belongs to the category of environmental friendly green water treatment agent. It provides a reliable reference for workers engaged in water treatment technology and service.

2. Experimental Part

2.1. Study on Synergistic Effect of Compound Formula

PASP is regarded as a kind of environmentally friendly and multifunctional polymer material, which possesses the property of high efficiency of scale inhibition, biodegradation, non-toxic and dispersion. BTA is a highly effective copper corrosion inhibitor, which can form a protective film on the copper surface by chemical adsorption to achieve the inhibition effect, and the dosage is low. The inhibition effect of Tun on copper is mainly due to Tun and copper weak oxidizing action, protective film of cuprous oxide or copper oxide was formed on the surface of copper, the corrosion inhibition effect is very obvious. Glu has the advantages of low cost and has good synergistic effect on chemical compound corrosion inhibitor [10].

The orthogonal test method (four factors and two levels) was employed to study the synergistic effect of PASP, BTA, Tun and Glu.

2.2. Morphology Studying by SEM

The corrosion behavior of carbon steel was analyzed by JSM-6510 SEM. The carbon steel sample is attached to the sample stage with conductive adhesive, and then observed at an accelerating voltage of 15 kV and a magnification of 1000 times.

2.3. Small Dynamic Simulation Experiment

The scale inhibition efficiencies of the water treatment agent were investigated by scale analysis instrument which made in Dalian. The experimental conditions were as follows: 658mg/L total hardness, 343mg/L total alkalinity (as CaCO₃), 482 mg/L calcium ions (as CaCO₃), the volume of test solution was 65 L; the circulating liquid temperature was 40°C; the flow rate of circulating water was 200L/h. Take water samples regularly and test the concentration of calcium and chloride ions. The scale inhibition efficiency is calculated according to the concentration ratio of calcium and chloride ion [10].

2.4. Electrochemical Experiment

The classical three-electrode system, which auxiliary electrode, reference electrode and working electrode were platinum electrode, saturated calomel electrode and A₃ carbon steel (the total surface area was 1.0 cm²), respectively, was used to measure polarization curves by potentiodynamic scanning at room temperature. The polarized scanning range and scanning rate were $E_{corr} = \pm 0.3$ V and 0.5 mV/s, and test water was running water. Before testing, working electrode was polished by 800#~1200# abrasive paper, the cleaning sequence is distilled water, anhydrous ethanol and acetone, then dry naturally and immersed in the electrolyte 0.5 h.

2.5. Experimental Study on Biodegradation of Water Treatment Agent

The biological degradation of water treatment agent was determined by the method of carbon dioxide production, referring to the national standard GB/T20778-2006, the experiment time was 28 days.

3. Results and Discussion

3.1. Study on Synergistic Effect of Compound Formula

The orthogonal test method (four factors and two levels) was used to study the synergistic effect of four compounds. The results were listed in table 1.

Table 1. The results of orthogonal test.

Test scheme	PASP (mg/L)	BTA (mg/L)	Tun (mg/L)	Glu (mg/L)	Corrosion rate (mm/a)	Inhibition rate (%)
1	10	0.5	10	10	0.0023	94.56
2	10	0.5	10	20	0.0031	91.87
3	10	1	20	10	0.0015	98.02
4	10	1	20	20	0.0019	96.13
5	20	0.5	20	10	0.0024	94.47
6	20	0.5	20	20	0.0016	97.14
7	20	1	10	10	0.0035	91.98
8	20	1	10	20	0.0039	91.25
9	—	—	—	—	0.0523	
Average 1	95.145	94.510	92.415	94.757		
Average 2	93.710	94.345	96.440	94.097		
Range	1.435	0.165	4.025	0.660		

As can be seen from table 1, in the eight test schemes, the copper corrosion rate are all less than 0.005mm/a, meeting the GB/T50050-2007 "industrial circulating cooling water treatment design specification" requirement. formula 3 is the best combination scheme in table 1, 10mg/LPASP + 1mg/LBTA + 20mg/L Tun + 10mg/L Glu, the corrosion rate was only 0.0015 mm/a and the inhibition rate reached 98.02%. Through the analysis of the average and range of each factor, we can get the formula which has best inhibition effect should be 10 mg/LPASP + 0.5 mg/LBTA + 20 mg/L Tun + 10 mg/L Glu. We carried out supplemented experiments to study this formula, the results indicated that the copper corrosion rate

was 0.0006 mm/a and inhibition rate reached 99.22%, consistent with the results of the orthogonal test. Therefore, we recognized complement the experimental formula as the optimal compound formula.

3.2. Using SEM to Compare and Analyze

Two A3 carbon steel specimens were placed in the blank solution and the optimized compound formula solution respectively. The rotating hanging-piece test was carried out and analyzed by scanning electron microscope. The results were shown in figure 1.

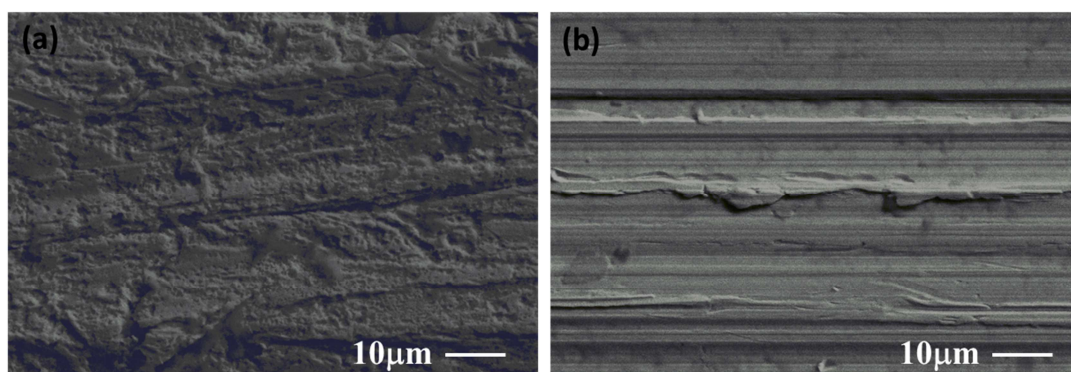


Figure 1. The test specimens were analyzed by SEM.

The image of surfaces in the absence of water treatment agent (Figure 1(a)) showed a heterogeneous layer comprised of loose scales shape, as well as some small globular granules. It indicated that the carbon steel specimens were corroded seriously. However, the images of surfaces exposed to water treatment agent (Figure 1(b)), showed a smooth and dense film on the carbon steel, basically free of corrosion, it was due to the formation of an inhibitor film retarded the diffusion of dissolved oxygen.

3.3. Small Dynamic Simulation Experiment

In industrial recycling water system, water treatment agents and circulating water always flow together. Therefore, the performance of water treatment agent can be studied more authentically by using small dynamic simulation experiment. We conducted a small dynamic simulation experiment to research the scale performance of four element composite formula. The test results were listed in table 2.

Table 2. The small dynamic simulation test data statistics.

Ca ²⁺ Concentration ratio	Cl ⁻ Concentration ratio	Scale inhibition rate (%)
1.0	1.0	100
1.5	1.5	100
2.0	2.09	95.7
2.5	2.71	92.3
3.0	3.32	90.4

Table 2 shows that circulating water hardness was 658mg/L and temperature was 40°C, four element compound formula scale inhibition efficiency was very excellent, the scale

inhibition rate reached up to 90% even under the high concentration ratio conditions. Therefore, the four element compound formula can be used in the circulating water which has high hardness and high concentration ratio.

3.4. Polarization Curves Determined by Electrochemical Workstations

Using the electrochemical workstations, the polarization curves of carbon steel in the blank solution (a) and the optimal compound formula solution (b) were shown in figure 2.

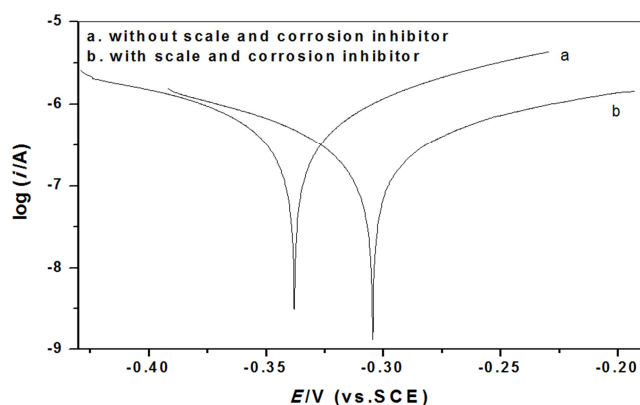


Figure 2. Polarization curves of carbon steel in two different solutions.

Under the condition of adding the optimal compound formula solution, the self-corrosion potential and current were $E_0 = -0.31$ V, $J_0 = 1.22 \times 10^{-8}$ Amp·cm⁻². However, without the addition of the optimal compound formulation solution, the

self-corrosion potential and current were $E_0 = -0.34$ V, $J_0 = 1.91 \times 10^{-8}$ Amp·cm⁻². After adding the optimal compound formula solution, with the increase of the self-corrosion potential, the polarization curve of the carbon steel is positively shifted. Moreover, the slope of the cathode polarization curve decreases obviously, and the slope of the anodic polarization curve increases slightly. According to the above discussion, it can be seen that the optimal compound formula solution is a mixed-type inhibitor based on cathode polarization.

3.5. Experimental Study on Biodegradation of the Optimal Compound Formula Solution

Glycine (Gly) is one of the most easily biodegradable amino acids. Under the same conditions, referring to the national standard GB/T 20778--2006, and its 28 d biodegradation rate is up to 85%. Biodegradability of water treatment agents evaluated with Gly as reference substance, the results as shown in figure 3.

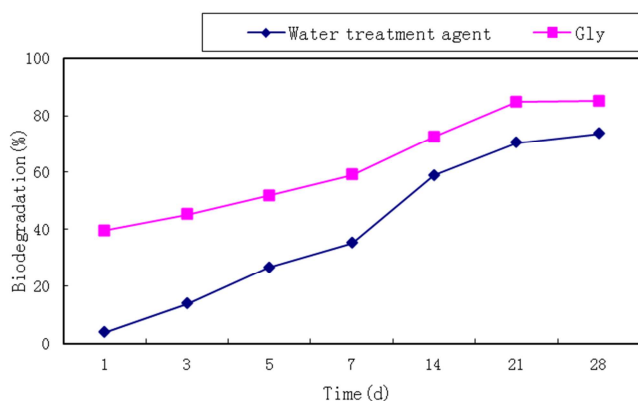


Figure 3. Relationship between degradation rate and time.

As can be seen from figure 3, at the beginning of the period, the biodegradation rate of water treatment agent was very low. However, with the change of time, the biodegradation rate was as high as 75.1% in 28 days. Therefore, the water treatment agent has a preminent biological degradation, and belongs to the category of environmental friendly green water treatment agent.

4. Conclusions

Being proved effective and feasible by the field experiment, the water treatment agent will play an important part in operating the circulating water systems. The following

conclusions were obtained.

The optimized composition of the water treatment agent was 10mg/L PASP, 0.5mg/L BTA, 20mg/L Tun, and 10mg/L Glu. The formula has excellent effect of scale and corrosion inhibition, and has a strong biological degradation. The SEM morphology analysis results showed that the optimized compound formula solution has excellent corrosion inhibition efficiencies. Small dynamic simulation experiment indicated that the optimal compound formula solution has excellent scale inhibition ability even in the circulating water with high hardness and high concentration ratio. Potentiodynamic polarization curves indicated that the optimal compound formula solution was a mixed inhibitor based on cathode polarization. Experimental study on biodegradation results showed that the optimal compound formula solution was biodegradable, and it belongs to the category of environment-friendly green water treatment agent. It provides a reliable reference for workers engaged in water treatment technology and service.

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