Study on microbial corrosion inhibition of carbon steel in circulating cooling water system

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Abstract. Although the industrial circulating cooling water system can save a lot of water resources, there will be serious scaling and corrosion during operation. Based on the environmental friendliness of microbial corrosion inhibition technology, this work evaluated the influence of microbial environmental indicators on the corrosion rate of carbon steel in circulating cooling water system by full factor experimental design. The results showed that under 10-50 mg/L ammonia nitrogen, 1-3 L/min aeration fluxes, the corrosion rate getting lower with the increase of ammonia nitrogen concentration and the decrease of aeration rate, while the microbial content had little effect on the corrosion rate.

Keywords: Microbiological method; Corrosion inhibition; Cooling water system.

1. Introduction

With the development of social economy, the industrial water consumption is increasing, and the cooling water consumption accounts for 70% of the water consumption. Generally, the application of circulating cooling water system can save about 95% of the cooling water consumption [1-2]. However, scaling and corrosion occurred in the circulating cooling water system under the increasing of various ions in the water during the operation of the system, which could reduce the heat exchange efficiency, and even lead to corrosion and perforation of equipment and pipelines, resulting in accidents [3-4]. Therefore, how to control these drawbacks in the circulating cooling water system effectively has become an urgent problem to be solved.

At present, the most widely used treatment is to add corrosion and scale inhibitor to the circulating cooling water to maintain the normal operation of the system. He et al. [5] studied the corrosion inhibition properties of a combination of polyaspartic acid, polyepoxy succinic acid, polyamine polyether methylene phosphonate, and sodium gluconate for carbon steel in recirculating cooling water, the results show that the composite efficiently inhibited corrosion on carbon steel at relatively low dosages in severely corrosive soft water media. Khani and Arefinia [6] studied the corrosion inhibition mechanism of sodium nitrite on carbon steel has been carefully studied in different simulated cooling water solutions, they found that the corrosion inhibition increases by increasing the nitrite concentration.
up to 9mM in 5mM chloride solution at 25°C. In general, almost corrosion and scale inhibitors contain phosphorus. When a large amount of wastewater containing toxic substances and rich in phosphorus enters the external environment, it will increase the phosphate load of natural water, causing eutrophication of water and harm aquatic animals eventually.

Compared with chemical corrosion and scale inhibitor, biological method has obvious advantages. Its production cost is low, and it will not cause secondary pollution to the environment, which could greatly reduce the phosphorus content in the circulating cooling water. Microbial technology is to treat circulating cooling water by using biological enzymes and degradable microorganisms to solve the problems of scaling, corrosion and microbial growth, so as to achieve the effects of corrosion and scale inhibition and inhibition of bacteria and algae [7].

In this paper, the circulating cooling water is treated by microbial technology, and full factorial design was used to evaluate the importance of concentration of ammonia nitrogen; microbial content; aeration fluxes of corrosion Inhibition on steel, which can be foundation for further research.

2. Materials and methods

2.1. Materials.
20# carbon steel (48*23*0.4mm³, 21.33g), Analytical grade hydrochloric acid (HCl, 37%), ammonium sulfate ((NH₄)₂SO₄, AR), sodium hydroxide (NaOH, AR), glucose (C₆H₁₂O₆, AR), Sucrose (C₁₂H₂₂O₁₁, AR) were used in this work.

2.2. Experimental set-up and Operation.
In order to investigate the interactive effects of parameters on the corrosion inhibition of carbon steel, full factorial design was employed for the optimization the effects of concentration of ammonia nitrogen, microbial content and aeration fluxes on corrosion rate of carbon steel. The factorial design matrix and Vc (corrosion rate) measured in each factorial experiment was shown in Table 1. The low and high levels for the factors were selected according to some preliminary experiments. Vc was determined as average of three parallel experiments. The order in which the experiments were made was randomized to avoid systematic errors. The results were analyzed with the Minitab17 software, and the main effects and interactions between factors were determined.

| number | A concentration of ammonia nitrogen (mg/L) | B microbial content (%) | C aeration fluxes (L/min) | Result Vc (mm/a) |
|--------|------------------------------------------|------------------------|--------------------------|------------------|
| 1      | 10                                       | 0.005                  | 3                        | 0.03327          |
| 2      | 10                                       | 0                       | 3                        | 0.03589          |
| 3      | 30                                       | 0.0025                  | 2                        | 0.02890          |
| 4      | 10                                       | 0.005                   | 1                        | 0.03102          |
| 5      | 50                                       | 0.005                   | 1                        | 0.01552          |
| 6      | 10                                       | 0                       | 1                        | 0.03278          |
| 7      | 30                                       | 0.0025                  | 2                        | 0.02983          |
| 8      | 50                                       | 0                       | 3                        | 0.02665          |
| 9      | 50                                       | 0.005                   | 3                        | 0.02238          |
| 10     | 50                                       | 0                       | 1                        | 0.01760          |

3. Results and Discussion
Factors that influence the corrosion rate of carbon steel were evaluated by using factorial plots: main effect, interaction effect, the Pareto chart plot, normal probability plots, and the surface plot. ANOVA, F-value, P-value significant levels were used to check the significance of the effect on Vc. The results indicated that the corrosion rate of carbon steel varied obviously under different reaction conditions,
which were from 0.01552 to 0.03589 mm/a, indicating that the processing parameters need to be optimized to achieve the minimum corrosion rate.

3.1. Analysis of variance.

The regression analysis was implemented using all the independent variables and interactions. In order to ensure an appropriate model, the test for the significance of regression was performed by applying a variance analysis (ANOVA).

Table 2. ANOVA for the experimental design before optimization

| Resource                  | DF  | AdjSS   | AdjMS   | F       | P     |
|---------------------------|-----|---------|---------|---------|-------|
| Model                     | 6   | 0.000409| 0.000068| 19.55   | 0.017 |
| Linear                    | 3   | 0.000394| 0.000131| 37.62   | 0.007 |
| A                         | 1   | 0.000323| 0.000323| 92.52   | 0.002 |
| B                         | 1   | 0.000014| 0.000014| 4.13    | 0.135 |
| C                         | 1   | 0.00057 | 0.00057 | 16.21   | 0.028 |
| Two-factor interaction    | 3   | 0.000016| 0.000005| 1.49    | 0.376 |
| AB                        | 1   | 0       | 0       | 0.14    | 0.734 |
| AC                        | 1   | 0.000014| 0.000014| 3.99    | 0.14  |
| BC                        | 1   | 0.000001| 0.000001| 0.33    | 0.604 |
| Error                     | 3   | 0.00001 | 0.000003|         |       |
| Camber                    | 1   | 0.00001 | 0.00001 | 30.02   | 0.032 |
| Lack of fit               | 1   | 0       | 0       | 0.51    | 0.605 |
| Pure error                | 1   | 0       | 0       |         |       |
| Total                     | 9   | 0.00042 |         |         |       |

As shown in Tab. 2, F value 19.55 and P value 0.015 (<0.05) indicated that quadratic model about the factor A, B, C to corrosion rate of carbon steel was significant. The concentration of ammonia nitrogen (A) had the greatest effect on corrosion rate, followed by aeration fluxes (C), microbial content(B), concentration of ammonia nitrogen- aeration fluxes (AC), microbial content - aeration fluxes (BC), and concentration of ammonia nitrogen - microbial content (AB). F value for the lack of fit was not significant when F value was 0.51 and p-value was only 0.605, which mean that the regression model can explain the functional relationship between test factors and response variables fully.

Table 3. Effect coefficient table before optimization

| item        | Effect  | Coef   | SE Coef | T     | Variance expansion factor |
|-------------|---------|--------|---------|-------|--------------------------|
| Constant    | 0.027384| 0.000591| 46.37  | 0     |                          |
| A           | -0.0127 | -0.00635| 0.00066| -9.62 | 1                        |
| B           | -0.00268| -0.00134| 0.00066| -2.03 | 1                        |
| C           | 0.005318| 0.002659| 0.00066| 4.03  | 1                        |
| AB          | -0.00049| -0.00025| 0.00066| -0.37 | 1                        |
| AC          | 0.002637| 0.001319| 0.00066| 2     | 1                        |
| BC          | -0.00076| -0.00038| 0.00066| -0.58 | 1                        |

The positive values of these effects revealed that the increase of these parameters increased Vc. Conversely, negative values of the effects decreased the response (Vc). So it can be seen from Tab. 3 that the linear factors of A, B, the interaction AB and BC had a negative influence on the Vc while increasing the linear levels for C had a active influence on the response as the AC interactions showed[8]. The quadratic polynomial equation for corrosion rate was developed in terms of codes factors as shown in equation (1). This equation describes how the experimental variables and their interactions influence the corrosion rate:
Vc = 0.03576 - 0.000437A - 0.084B + 0.00106C - 0.0049AB + 0.000066AC - 0.152BC (1)

The Eq. (1) enabled the prediction of the corrosion rate of carbon steel (Vc) as a function of the initial concentration of ammonia nitrogen, microbial content and aeration fluxes. Not only are the main effects modeled, but also their interactions, which is the main advantage of the full factorial design compared to the traditional approach. This model was found to be adequate for prediction within the range of the chosen variables [9-10]

Fig. 1 showed the standardized effect between the parameters (A, B, C, AB, AC, and BC). All the interactions of the factor were statistically significant in determining Vc. These plots clearly indicated that concentration of ammonia nitrogen (A) was strongest in all factors, for the standardized effect of went over 3.18. The aeration fluxes (C) was statistically significant but much smaller. And the effect of other factors are not noticeable to Vc for the standardized effects were under 3.18.

Residual distribution plot (Fig.2) was used to test and verify the accuracy of results in full factorial design. The points in the graph were randomly scattered up and down around the line with residual equal to 0, which showed that the regression line fit the original observation well. It was not clear whether these results are “real” or “chance”. To identify the “real” effects, a normal probability plot of standardized residuals was used in Fig.3. One point on the plot was assigned to each effect [11]. We came to the conclusion that there is spatial instability between independent variables, and the data reliability of regression equation is relatively low for the points far away from the straight line in Fig.3.
The S value of Vc in Tab.4 was small, indicated that the observed value was closer to the fitting line, and the fitting effect of the regression model was good. The R² value for Vc was 0.9751, which was a desirable figure. An adjusted coefficient of determination is given along with the coefficient of determination. And it is obvious that the adjusted R² was fewer than the predicted R² value, as we have fewer observations per independent variable and the adjusted R² makes allowances for the degrees of freedom for each model. The adjusted R² was 0.74, which mean the regression of equation was not bad.

**Table 4. Regression analysis of the experimental design**

| S  | 0.0018677 |
|----|-----------|
| R-sq | 97.51% |
| R-sq (pre) | 92.52% |
| R-sq (adj) | 74.44% |

4. Optimization of model.

According to the analysis of the above results, the adjusted R² of the regression equation is a little low, so a more suitable model was obtained by optimizing the model, and the concentration of ammonia nitrogen (A), aeration fluxes (C), microbial content (B), and concentration of ammonia nitrogen-aeration fluxes (AC) were retained.

**Table 5. ANOVA for the experimental design after optimization**

(A: concentration of ammonia nitrogen; B: microbial content; C: aeration fluxes)

| Resource          | DF | AdjSS  | AdjMS  | F     | P  |
|-------------------|----|--------|--------|-------|----|
| Model             | 4  | 0.000408 | 0.000102 | 42.06 | 0  |
| Linear            | 3  | 0.000394 | 0.000131 | 54.17 | 0  |
| A                 | 1  | 0.000323 | 0.000323 | 133.21 | 0 |
| B                 | 1  | 0.000014 | 0.000014 | 5.94  | 0.059 |
| C                 | 1  | 0.000057 | 0.000057 | 23.34 | 0.005 |
| Two-factor interaction | 1 | 0.000014 | 0.000014 | 5.74  | 0.062 |
| AC                | 1  | 0.000014 | 0.000014 | 5.74  | 0.062 |
| Error             | 5  | 0.000012 | 0.000002 | F     | P  |
| Camber            | 1  | 0.000014 | 0.000001 | 17.05 | 0.015 |
| Lack of fit       | 3  | 0.000002 | 0.000001 | 1.44  | 0.534 |
| Pure error        | 1  | 0     | 0     | F     | P  |
| Total             | 9  | 0.00042 |        |       |    |

As shown in Tab. 5, the optimized regression equation was more significant than unoptimized regression equation for the F value 42.06 and P value 0 (<0.05). After optimizing the experimental design, both the concentration of ammonia nitrogen (A) and aeration fluxes (C) had the great effect on corrosion rate of carbon steel(Vc). The effects of microbial content(B) and concentration of ammonia nitrogen-aeration fluxes (AC) on Vc were similar. F value for the lack of fit was not significant when F value was 1.44 and p-value was only 0.534, and the pure error basically did not exist.

**Table 6. Regression analysis of the experimental design after optimization**

| S  | 0.0015564 |
|----|-----------|
| R-sq | 97.11% |
| R-sq (pre) | 94.80% |
| R-sq (adj) | 91.86% |

In addition, the regression analysis indicated that the selected model adequately described the observed data, explaining approximately 97.11% (due to R²=0.9711) of the variability of Vc. And the model presented an adjusted square correlation coefficient R² (adj) of 91.86%, fitting the statistical
model quite well. In this way, the dye uptake by sepiolite could be expressed using the following equation:

\[ V_c = 0.03689 - 0.000449A - 0.536B + 0.000681C + 0.000066AC \] (2)

5. Conclusions
The statistical design of the experiments combined with techniques of regression was applied in optimizing the conditions of corrosion inhibition for carbon steel. The concentration of ammonia nitrogen and aeration fluxes exerted the great influence on the corrosion rate (\(V_c\)). With the condition of 10-50 mg/L ammonia nitrogen and 1-3 L/min aeration fluxes, the corrosion rate getting lower with the increase of ammonia nitrogen concentration and the decrease of aeration rate, and the minimum corrosion rate is 0.01552 mm/a. The factorial experiments demonstrated significant antagonistic interaction between the concentration of ammonia nitrogen and aeration fluxes. This interaction had more influence on \(V_c\) than did the other interactions (microbial content - aeration fluxes, and concentration of ammonia nitrogen - microbial content). The concentration of ammonia nitrogen, microbial content had a negative influence on \(V_c\) while increasing the linear levels for aeration fluxes had a active influence on the \(V_c\).

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References
[1] J Yao, Ge H, Y Zhang, X Wang, Y Zhao. Influence of pH on corrosion behavior of carbon steel in simulated cooling water containing scale and corrosion inhibitors [J]. Materials and Corrosion, 2020, 71(8).
[2] A Koulou, M Chahboune, H Larhzil, R Touir, YE Kacimi. Eco-Friendly Tri-Sodium Citrate as Corrosion Inhibitor for Mild Steel in Synthetic Cooling Water System [J]. Journal of Basic & Applied Sciences, 2020, 16.
[3] G.R. Mettam, L.B. Adams. How to prepare an electronic version of your article, in: B.S. Jones, R.Z. Smith (Eds.), Introduction to the Electronic Age, E-Publishing Inc., New York, 1999, pp. 281-304.
[4] R Touir, M Cenoui, M E Bakri, M E Touhami. Sodium gluconate as corrosion and scale inhibitor of ordinal steel in simulated cooling water [J]. Corrosion Science, 2008, 50(6):1530-1537.
[5] C He, Z Tian, B Zhang, Y Lin, X Chen, M Wang, F Li. Inhibition Effect of Environment-Friendly Inhibitors on the Corrosion of Carbon Steel in Recirculating Cooling Water[J]. Industrial & Engineering Chemistry Research, 2015, 54(7).
[6] H Khani, R Arefinia. Inhibition mechanism of nitrite on the corrosion of carbon steel in simulated cooling water systems [J]. Materials and Corrosion, 2017, 69(3).
[7] Yi Zhe. Study on biological corrosion and scale inhibitor in the treatment of circulating cooling water [D].2017.
[8] L Torbjorn, S Elisabeth, A Lisbeth, T Bernt, B Rolf. Experimental design and optimization [J]. Chemometrics and Intelligent Laboratory Systems, 1998, 42:3-40.
[9] G Annadurai, Y L Lai, J F Lee. Statistical optimization of medium components and growth conditions by response surface methodology to enhance phenol degradation by Pseudomonas putida [J]. Journal of Hazardous Materials, 2008, 151(1):171-178.
[10] A. Hrinbernik, M Bauman, A Lobnik. Application of 2 k factorial design in wastewater decolorization research. XIXIMEKO World Congress Fundamental and Applied Metrology, 2009, pp. 2225-2229
[11] K Palanikumar, J P Davim. Assessment of some factors influencing tool wear on the machining of glass fibre-reinforced plastics by coated cemented carbide tools [J]. Journal of Materials Processing Tech, 2009, 209(1):511-519.