Screening and Evaluation of Two Dye Wastewaters as Additives for Carbon Steel Corrosion Inhibitors in Acidic Environments

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ABSTRACT: To reduce the cost of synthetic organic corrosion inhibitors in corrosion protection, dye wastewater exhibiting a synergistic effect is used with organic corrosion inhibitors to reduce the amount of high-cost molecules. The corrosion inhibition effects of the cationic dye methylene blue (MB) and the anionic dye methyl orange (MO) are tested. The test methods include electrochemical methods, weight-loss tests, and so on. MB exhibits better performance on the tested steel, with the anticorrosion efficiency reaching as high as 75.40%, which is chosen as an additive for organic corrosion inhibitors. After that, an organic inhibitor decamethylene bis-pyridinium dibromide (DBP) is selected for compounding with MB, and the corrosion inhibition effect under different ratios is tested. Similar effects of the compound inhibitor to the pristine sample are obtained at a ratio of MB/DBP = 6:4. In addition to experiments, theoretical calculations have also confirmed that the addition of dye molecules can inhibit corrosion. This research not only provides a way to reuse dye wastewater but also proposes measures to reduce the cost of organic corrosion inhibitors and, at the same time, provides new ideas for environmental protection and metal protection.

1. INTRODUCTION

As a common material, low-carbon steel is widely used in the oilfield industry, chemical industry, construction industry, and many other fields. But in application, steel is often affected by environmental conditions and corrodes to varying degrees.1 Corrosion of steel brings a series of cost and safety problems. Therefore, various means such as alloys, coatings, corrosion inhibitors, and so on are used to reduce corrosion.2–4 Among these methods, corrosion inhibitors have attracted the attention of many researchers due to their advantages like simple operation and optimal efficiency.5 In the case of organic molecules, if heteroatoms or heterocyclic molecules are present in molecular structures, such molecules have the potential to become corrosion inhibitors.6,7 At present, most of the corrosion inhibitors used are synthetic and are associated with high production costs. If the cost of corrosion inhibitors can be reduced, the application value of corrosion inhibitors will be greatly improved. In some industrial applications that require corrosion inhibitors, the dissolved water of the corrosion inhibitor may not be purified water, especially in the oilfield development industry. In the process of oilfield development, oilfield-produced fluid is often used for reinjection. Oilfield-produced fluids belong to water containing a large amount of organic and inorganic substances; if other wastes that can play a role in corrosion inhibition can be mixed with the produced water, the cost of corrosion inhibitors can be effectively reduced and economic benefits can be improved.

Dyes paint our lives in several industrial aspects, such as textile, leather, and food, among others, whose wide application brings convenience and color into our lives but also results in irreversible damages to the environment and human life.8 Dye-contaminated wastewater is characterized by toxicity, carcinogenicity, mutagenicity, and teratogenicity, which requires specific purification technologies before its discharge.9,10 Physical and chemical decolorization treatments have been applied such as adsorption, oxidation, and biological treatments, whose efficiency is limited by the complicated structure of dye molecules.11 The heterocyclic group within the dye structure owns great potential to serve as a corrosion inhibitor. In addition, mixing dyes in the oilfield reinjection fluid will not significantly increase pollution hazards. For wastewater treatment, after the end of the reinjection, the final produced liquid will be treated uniformly, and the added dye will be purified along with other substances in the water during this process. Therefore, the use of dyes as corrosion inhibitor additives has a research value in the oilfield mining industry.

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In this paper, two dyes are chosen as simulated dye wastewaters used for the protection of P110 steel in 1.0 M HCl against corrosion. Their protection performance is studied through electrochemical and weight-loss methods. Thereafter, the one with better results is used as an ingredient in compound corrosion inhibitors. The effects of compound corrosion inhibitors are also studied. Scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) analysis is used to study the effects of corrosion inhibitors on metal surfaces. In addition to experiments, theoretical calculations have also been used to analyze the molecular structure of dyes and their adsorption configurations on iron surfaces. Actual experiments explain the role of corrosion inhibitors through intuitive phenomena, and theoretical calculations can help explain the phenomena in actual experiments from the perspective of microscopic molecules. The combination of theoretical calculations and actual experiments has a positive effect on explaining the effect of corrosion inhibitors. For the treatment strategy to move into environmental protection and cost reduction, dye-containing wastewaters deserve attempts to be exploited as a corrosion inhibitor additive. Dye wastewater used as an additive for organic corrosion inhibitors can reduce the number of organic molecules with high synthesis costs. If this addition can maintain a satisfactory corrosion inhibition effect, then this will provide a new utilization scheme for dye wastewater. Dye wastewater as an additive for corrosion inhibitors will simultaneously open up new areas of sewage treatment and metal protection.

2. RESULTS AND DISCUSSION

2.1. Electrochemical Measurements of Dyes. 2.1.1. Potentiometric Polarization Curves. To select satisfactory corrosion inhibitors, electrochemical tests are used to evaluate the inhibition efficiency of methylene blue (MB) and methyl orange (MO) when used alone. The potentiometric polarization curves of the two dyes are shown in Figure 1a,b, respectively. It can be seen from Figure 1 that the shape of the polarization curves barely changes when the dyes are added. Therefore, in this case, it can be said that MB and MO have no influence on the corrosion reaction mechanism. After addition of MB, the polarization curve moves downward. The downward translation of the polarization curve indicates a decrease in the corrosion current density, which means that MB can inhibit the corrosion of steel. Unfortunately, for MO, whether added or not, the polarization curve barely shifts. The nontranslation of polarization curves indicates that MO may not play any positive role in corrosion protection.
quantitatively study the inhibition effect, eq 1 can be used to calculate the corrosion inhibitor efficiency ($\eta$):\(^{15}\)

$$\eta (%) = \left( \frac{I_0 - i}{I_0} \right) \times 100$$  \hspace{1cm} (1)

where $i$ is the corrosion current density with inhibitor and $I_0$ is the blank corrosion current density. The results are presented in Table 1 with other parameters of curves.

It can be seen from Table 1 that when MB is added, the corrosion current decreases significantly, and the inhibitor efficiency gradually increases with the increase in the concentration. At 300 mg/L, MB achieved its maximum corrosion efficiency, 77.34%, which is not a desirable value. This result indicates that MB may reduce corrosion, but the protective effect is not significant. MB may help to protect the metal from corrosion when combined with other reagents, but used solitarily, may not be able to efficiently deter corrosion. In addition, if the change of corrosion potential ($E_{corr}$) with and without the inhibitor is greater than 85 mV, the inhibitor can be identified as a cathode type or an anode type.\(^{16}\) If the change of potential is less than 85 mV, the inhibitor is considered a mixed type.\(^{17,18}\) The maximum $\Delta E_{corr}$ of MB is 19 mV, indicating that MB belongs to a mixed-type corrosion inhibitor. This is reflected in the cathode slope and the anode slope ($b_c$ and $b_a$). After adding MB, it can be seen that both cathode and anode slopes are reduced but the reduction is not much pronounced. This phenomenon indicates that MB affects both the cathode and anode reaction corrosion rates.\(^{15,20}\) However, for MO, the corrosion current increases rapidly at a low concentration instead of decreasing, indicating that MO can aggravate metal corrosion. When the concentration of MO is increased by more than 100 mg/L, the corrosion current decreases with the increase in the concentration, which means the destructive effect on the metal by MO decreases. The decrease of corrosion current confirms that MO cannot be used as a corrosion inhibitor for metal at all.

2.1.2. A.C. Impedance Test. By fitting the A.C. impedance results, Nyquist plots can be drawn, which can be used to analyze corrosion inhibition of organic molecules on metal surfaces.\(^{21}\) Nyquist plots of the dyes are shown in Figure 1c,d. It can be seen from Figure 1 that the curve of the corrosion system presents an arc but it is not a perfect arc. This phenomenon is caused by the unevenness and roughness of the sample surface.\(^{22}\) By comparing the length of the long axis of these curves, the effect of the corrosion inhibitor can be preliminarily evaluated.\(^{23}\) In Figure 1c, as the concentration increases, the semimajor axis length of the MB curve increases, indicating that the addition of MB can inhibit the charge transfer in the corrosion reaction hence protecting steel from corrosion. In Figure 1d, with continuous change in MO concentrations, the axes of the curves did not become significantly longer, rather appeared to be more shortened at some concentrations. This phenomenon proves the poor performance of MO in metal-corrosion protection. To quantitatively judge the corrosion protection ability of the dye molecules, the related parameters of A.C. impedance are calculated whilst fitting the curve. All $\chi^2$ values in Table 2 are around 0.01, and the standard deviations of the parameters are all less than 10%, indicating that the data fitting results have a good correlation with the original data. The calculation results are given in Table 2. The efficiency is calculated using eq 2:\(^{24}\)

$$\eta (%) = \left( \frac{R_{ct} - R_{ct}^0}{R_{ct}} \right) \times 100$$  \hspace{1cm} (2)

where $R_{ct}^0$ is the resistance in the blank test and $R_{ct}$ is the resistance calculated from the test with inhibitors. By comparing $R_{ct}$ values, the corrosion inhibition ability of two dyes can be obtained more intuitively. For MB, the $R_{ct}$ value increases with an increase in the concentration, attaining 43.54,

| inhibitors | concentration (mg/L) | $R_s$ ($\Omega$ cm$^2$) | $R_i$ ($\Omega$ cm$^2$) | $C_d$ ($\mu$F/cm$^2$) | $n$ | $\eta$ (%) | $\chi^2$ |
|------------|----------------------|--------------------------|--------------------------|--------------------------|----|-------------|----------|
| MB         | 0                    | 3.391                    | 19.13                    | 87.82                    | 0  | 0.0136      | 75.28    |
|            | 50                   | 4.017                    | 43.54                    | 86.52                    | 0  | 0.0123      | 75.28    |
|            | 100                  | 4.107                    | 55.96                    | 80.95                    | 0  | 0.0125      | 75.28    |
|            | 200                  | 4.138                    | 71.28                    | 81.10                    | 0  | 0.0127      | 75.28    |
|            | 300                  | 4.141                    | 77.76                    | 77.30                    | 0  | 0.0129      | 75.28    |
| MO         | 0                    | 3.610                    | 14.68                    | 85.60                    | 0  | 0.0097      | 75.28    |
|            | 50                   | 3.652                    | 12.29                    | 102.92                   | 0  | 0.0097      | 75.28    |
|            | 100                  | 3.633                    | 12.27                    | 125.57                   | 0  | 0.0100      | 75.28    |
|            | 200                  | 3.746                    | 15.01                    | 132.60                   | 0  | 0.0107      | 75.28    |
|            | 300                  | 3.722                    | 16.39                    | 128.51                   | 0  | 0.0182      | 75.28    |

Table 1. Tafel Curve Parameters of MB and MO

Table 2. A.C. Impedance Parameters of P110 Steel in Different Concentrations of Dyes

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55.96, 71.28, and 77.76 Ω/cm² at 50, 100, 200, and 300 mg/L, respectively. At 300 mg/L, the corrosion inhibition efficiency reaches the maximum, 75.40%. This efficiency reaffirms the earlier deduction that MB just slightly reduces corrosion but not in its entirety. For MO, at the same concentration as MB, $R_{dl}$ values are only 12.29, 12.27, 15.01, and 16.39 Ω/cm², indicating that MO does not have the potential as a metal protective agent. In addition to charge-transfer resistance, the value of $n$ can also be used to determine the character of the device $Q$ in the equivalent circuits. The closer the $n$ value is to 0, the closer the $Q$ value is to pure resistance. As $n$ approaches 1, $Q$ increasingly exhibits the property of pure capacitance. In Table 2, all $n$ values are close to 1, indicating that steel surfaces for all impedances are closer to capacitance. Therefore, the electric double-layer capacitance ($C_{dl}$) can be used to infer the role of molecules in corrosion. For MB, there is a slight change in $C_{dl}$, indicating that the amount of charge on the metal surface is stable. With addition of MO, $C_{dl}$ increased significantly, indicating that the metal surface has an increased ability to hold charges, which is unfavorable for inhibiting the corrosion reaction. This is also one of the reasons for the poor performance of MO in corrosion inhibition.

2.1.3. Mechanism Analysis and Dye Selection. Through electrochemical tests, it can be found that MB has a certain inhibitory effect on the corrosion of steel, but MO has no inhibition effect but rather causes damage to P110 steel. This may depend on the type of two dyes. MB is a kind of cationic dye and has a positive charge in the solution. After MB is adsorbed on the metal surface via the heterocyclic ring in the molecule, due to electrostatic repulsion, it repels the hydrogen ions away from the metal surface, reducing the contact between iron and hydrogen ions. In the corrosion reaction, the hydrogen evolution reaction is an important part, and the reduction of hydrogen ions on the metal surface can effectively reduce the corrosion reaction rate. However, MO is an anionic dye and is negatively charged in the solution, which causes hydrogen ions to be attracted. If the added amount is small, MO is adsorbed on the metal surface, which may increase the concentration of hydrogen ions on the metal surface, resulting in an increase in the reaction rate. The increase in $C_{dl}$ after adding MO can confirm this conclusion. As the added concentration continues to increase, the coverage of the metal surface by MO increases, thus reducing the contact of hydrogen ions, so the damage of MO to steel is weakened at high concentrations.

In both potentiometric polarization and A.C. impedance experiments, MO showed poor performance. Not only did MO not inhibit corrosion but even accelerates the damage to the metal. Therefore, it is deemed unnecessary to continue studying the inhibition performance of MO. In the compound experiment, only MB is used as an additive to combine with DBP so as to test the protective ability of the compound corrosion inhibitor.

2.2. Compound Tests of Dye Wastewater and Organic Corrosion Inhibitors. MB and DBP are selected as the compound inhibitor, and different ratios of corrosion inhibitors (M8D2, M6D4, M5D5, M4D6, and M2D8) with concentrations of 200 mg/L are added to the corrosion solution to test the protective effect. The resulting polarization curves and A.C. impedance graph are given in Figure 2. In Figure 2a, polarization curves of the compound corrosion inhibitors are given, and the corresponding data are listed in Table 3. Comparing the changes of curves, it can be seen that after the addition of corrosion inhibitors, polarization curves obviously shifted downward, indicating that the corrosion rate decreased. Analyzed with comparison to the data in Table 3, it can be seen that when the addition ratio of MB and DBP is 6:4, the corrosion current density drops to its lowest, 0.190 mA/cm², reaching the maximum corrosion inhibition efficiency of 87.65%. At this ratio, the compound inhibitor has the same effect as adding DBP alone. In addition, it can be seen that the maximum corrosion potential change of the

Table 2. Tafel Curve Parameters of Compound Inhibitors at Different Ratios

| mass ratio (MB/DBP) | $i_b$ (mA/cm²) | $i_c$ (V/dec) | $i_{ca}$ (V/dec) | $E_{corr}$ (V) | $\eta$ (%) |
|---------------------|----------------|---------------|------------------|--------------|-----------|
| blank               | 1.537          | -0.166        | 0.152            | -0.398       |           |
| 10:0                | 0.373          | -0.104        | 0.110            | -0.419       | 75.62     |
| 8:2                 | 0.282          | -0.112        | 0.108            | -0.453       | 81.67     |
| 6:4                 | 0.190          | -0.114        | 0.162            | -0.449       | 87.65     |
| 5:5                 | 0.207          | -0.115        | 0.140            | -0.445       | 86.56     |
| 4:6                 | 0.200          | -0.118        | 0.123            | -0.441       | 83.85     |
| 2:8                 | 0.192          | -0.111        | 0.140            | -0.452       | 87.53     |
| 0:10                | 0.191          | -0.128        | 0.176            | -0.420       | 87.59     |
compound inhibitor is 54 mV, less than 85 mV. When MB, DBP, or the compound inhibitor are added, the potential change is also less than 85 mV, indicating that the combination did not change the type of inhibitor, and the compound inhibitor still belonged to the mixed type.

The Nyquist plots and corresponding data obtained from A.C. impedance experiments are listed in Figure 2b and Table 4, respectively. All \( \chi^2 \) values in Table 4 are around 0.01, and the standard deviations of the parameters are all less than 10%, indicating that the data fitting results have a good correlation with the original data. Obviously, the semimajor axis of arc increases no matter what kind of corrosion inhibitor is added, which reflects the good protective effect of the mixed corrosion inhibitor on steel. For corrosion inhibition efficiency, the A.C. impedance data show a similar result to that of the polarization curve: when the ratio is 6:4, the maximum charge-transfer resistance, 131.8 \( \Omega/cm^2 \), is reached, corresponding to the maximum efficiency of 85.48%, which is similar to the effect of DBP (131.1 \( \Omega/cm^2 \) and 85.41%, respectively). In electrochemical experiments, it can be seen that the most satisfactory effect can be achieved when the ratio of MB and DBP is 6:4 (M6D4). For other addition ratios, although similar inhibition effects are achieved (e.g., M2D8), M6D4 is still a more economical choice considering the synthetistic cost of organic corrosion inhibitors. From electrochemical tests, it can be seen that adding MB can reduce the cost while maintaining the protective effect of inhibitors. As for DBP, the mixing will not affect the reaction mechanism and the properties of the inhibitor. The ideal ratio for MB and DBP is 6:4, which will be used for the weightlessness test and SEM-EDS analysis.

2.3. Weight-Loss Measurement. In some applications, the concentration of the corrosion inhibitor is limited to 200 mg/L, so 200 mg/L is selected as the maximum addition amount. The corrosion rates and efficiency of two dyes, DBP and M6D4, are given in Table 5. The inhibition efficiency is calculated using eq 3

\[
\eta \% = \left( \frac{V_0 - V_{\text{corr}}}{V_0} \right) \times 100
\]

where \( V_0 \) and \( V_{\text{corr}} \) (mm/y) are the corrosion rates with and without inhibitors, respectively. From Table 5, it can be seen that without any inhibitor, the corrosion rate reaches 24.61 mm/y. This shows extremely poor performance and steel will quickly fail in this kind of environment. After MB is added to the solution, as the concentration increases, the corrosion inhibition efficiency also increases. At a concentration of 200 mg/L, the maximum efficiency of 74.28% is reached, and the corrosion rate at this time is 6.33 mm/y. This corrosion rate is still unsatisfactory, thus addition of MB singularly can only mitigate corrosion to a limited extent. For MO, similar to observations in the electrochemical experiment, no matter how much the concentration is increased, it is difficult to clearly see the change in the corrosion rate. Therefore, comparing MB and MO, it is obvious that MB is a more valuable corrosion inhibitor. In addition to the two dyes alone, the corrosion rates and inhibition efficiency of DBP and M6D4 are also given in Table 5 (90.61 and 90.45% for DBP and M6D4, respectively). Compared with the case for MB alone, the protective effect is significantly increased. Compared with adding DBP alone, the corrosion inhibition effect has little change. However, considering the cost benefits, mixed corrosion inhibitors are obviously more popular. The effect of compound corrosion inhibitors is much better than that of MB, and it can have almost the same effect as DBP. Considering the synthesis cost of DBP and the environmental-protection value of recycled dyes, this compound corrosion inhibitor has a promising future.

In Figure 3, the samples are shown after weight-loss experiments. By observing samples’ surfaces, the same conclusion as made with results in Table 5 can be drawn: when blank corrosion occurs (Figure 3b), the metal surface corrodes seriously. After adding MB (Figure 3c), the corrosion is reduced but damage can still be clearly seen. When DBP and M6D4 (Figure 3d,e, respectively) are added, the surfaces of specimens can still retain some metallic luster. In the weight-loss experiment, it is once again observed that MB has a good corrosion inhibition effect and MO is not suitable for corrosion protection. In addition, the mixed corrosion inhibitor can have the same protective effect as DBP. Since MB can be obtained from sewage, it can reduce the cost of corrosion inhibitors while remaining environmentally friendly; thus, using MB as an additive is a green and economical corrosion protection method.

2.4. SEM and EDS. SEM is used to characterize the surface morphology of samples to study the influence of organic molecules as corrosion inhibitors on steel surfaces. MO showed very awful performance in both electrochemical and weight-loss experiments and thus, in this study, only MB and DBP compound inhibitors (M6D4) are tested. The results are shown in Figure 4. It can be seen from the surface under blank corrosion (Figure 4a) that the sample is severely damaged, and many corrosion pits and corrosion products appeared. When MB is added (Figure 4b), the pits and damage are significantly reduced, but there are still a small number of them that can be directly observed. This shows that MB can inhibit corrosion damage when added along in solution, but the degree of inhibition is not satisfactory. In Figure 4c, when a compound

Table 5. Results of the Weight-Loss Method

| inhibitor | concentration (mg/L) | \( V_{\text{corr}} \) (mm/y) | \( \eta \% \) |
|-----------|----------------------|-----------------------------|-------------|
| blank     |                      | 24.61                       |             |
| MB        | 50                   | 11.22                       | 54.41       |
|           | 100                  | 9.35                        | 62.01       |
|           | 200                  | 6.33                        | 74.28       |
| MO        | 50                   | 23.82                       | 3.21        |
|           | 100                  | 24.77                       | −0.65       |
|           | 200                  | 24.13                       | 1.95        |
| DBP       | 200                  | 2.31                        | 90.61       |
| M6D4      | 200                  | 2.35                        | 90.45       |
inhibitor is added, the damage on the metal surface almost completely disappeared, which proved that the compound inhibitor achieved satisfactory results.

In general, an organic corrosion inhibitor can protect the metal from corrosion media by forming an adsorption film on the metal surface. To confirm the existence of this adsorption, an EDS test is used to scan the elemental distribution on the metal surface. In Figure 4a, it can be seen that there are a lot of chloride ions on the blank corrosion surface and there are no nitrogen and sulfur elements observed, which shows that metal is seriously affected by corrosion. The small amount of oxygen in the elemental analysis may be due to the oxidation of the surface part during the treating and test. In an MB molecule, N, O, and S elements can be found. After MB is added along as an inhibitor (Figure 4b), N and S appear on the surface, and the distribution of O also increases. The changes in the distribution of surface elements confirm that MB is adsorbed on the metal surface, forming a film that can protect against corrosion. The EDS result of M6D4 is shown in Figure 4c. It can be seen that all of the three elements also appear on the metal surface, and the distribution of the N element increased. In DBP, only N existed; this result shows that DBP and MB are adsorbed on the sample surface together and have a protective effect on metal corrosion. SEM-EDS results confirm that from a microscopic perspective, MB and M6D4 can be adsorbed on the P110 surface and inhibit corrosion.

2.5. Computational Calculation.

2.5.1. Frontier Orbital Analysis. Corrosion inhibitors can prevent metal corrosion by adsorbing on the surface. This process is related to the interaction of electrons between frontier orbitals of organic molecules and vacant d-orbital of metal atoms. To predict the corrosion inhibition performance of organic molecules, the frontier orbital of molecules and their energy need to be calculated. Frontier orbital can be divided into highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The optimized structure and orbital distribution of the two dyes calculated by software are shown in Figure 5. The results of $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ and other parameters (the electronegativity $\chi$ and the global hardness $\zeta$) are listed in Table 6. From $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$, the energy gap ($\Delta E$) can be calculated as per eq 4.
electrons tend to move from molecules to the metal surface.39

In addition to the energy gap, the electron fraction ($\Delta N$) can as well be used to predict the corrosion inhibition ability of organic molecules. To calculate $\Delta N$, a series of calculations are carried out according to the following formulae:\textsuperscript{36,37}

$$\Delta N = (\chi_{Fe} - \chi_{inh}) / 2(\zeta_{Fe} + \zeta_{inh})$$  \hspace{1cm} (5)

$$\zeta = (I - I_{A}) / 2$$ \hspace{1cm} (6)

$$\chi = (I + I_{A}) / 2$$ \hspace{1cm} (7)

$$I = -E_{HOMO}$$ \hspace{1cm} (8)

$$E_{A} = -E_{LUMO}$$ \hspace{1cm} (9)

where $\chi_{Fe}$ and $\zeta_{Fe}$ are 7 and 0, respectively. The $\Delta N$ values calculated are listed in Table 6. The sign of $\Delta N$ can be used to determine the tendency of electrons to transfer between iron atoms and organic molecules.\textsuperscript{38} If $\Delta N$ is greater than zero, electrons tend to move from molecules to the metal surface.\textsuperscript{39} Conversely, electrons are more easily transferred from iron atoms to organic molecules. If for a molecule, the value of $\Delta N$ with an iron atom falls in the range of 0–3.6, then this molecule may have good inhibition performance.\textsuperscript{40} Within the same range, the larger the $\Delta N$ value is, the better the inhibition efficiency the molecule may have. For MB, the $\Delta N$ value is 0.066, which is in the range of 0–3.6, indicating that MB can be used as an inhibitor. However, the value of 0.066 is too low, predicting that the MB’s corrosion inhibition effect may be very limited. As for MO, the $\Delta N$ value is 6.425, which falls without the range of desirable corrosion inhibitors; hence, it can be predicted that MO may provide no protective effect for Fe atoms. Moreover, the electrophilicity parameter $\omega$ and nucleophilicity parameter $\epsilon$ have been calculated by the following formula:\textsuperscript{36}

$$\omega = \chi^2 / 4\zeta = 1 / \epsilon$$  \hspace{1cm} (10)

These two parameters describe the affinity of the molecule to accept or give electrons. A molecule with a larger $\omega$ and a smaller $\epsilon$ is more likely to accept electrons in the interaction. Comparing the electrophilic index and the nucleophilic index of MB and MO, it can be found that MB has a fairly high electrophilicity, indicating that it is easier for MB to get electrons. In contrast, MO has a high nucleophilic number, which means that MO is more inclined to donate electrons.

The difference between the electrophilic and nucleophilic properties of the two leads to the contrast of corrosion inhibition performance. The calculation and the experiment have reached the same results.

2.5.2. Inhibitor Adsorption Simulation. To simulate the interaction between the corrosion inhibitor and the steel surface, an adsorption module is carried out to obtain the adsorption structure and energy for MB, DBP, and M6D4 on a Fe(110) surface. In each of the simulations, the number of molecules used is 10. The simulated spatial structures and their binding energy values are shown in Figure 6. The number of surface molecules in the adsorption structure and the individual binding energy of DBP and MB are given in Table 7. In Table 7, both binding energies of MB and DBP are negative, which means that these structures can be formed spontaneously and have strong interactions. It should be noted that the calculated binding energy is not the adsorption energy in the real environment, and the calculated result shows only the relative trend. Comparing the binding energy of MB and DBP, the binding energy of DBP (−251.56) is stronger than MB (−187.84 kcal/mol). Stronger adsorption often indicates better corrosion inhibition. Therefore, the corrosion inhibition potential of DBP is better than that of MB, which is similar to the conclusions obtained from actual experiments.

Regarding the molecular adsorption configuration, the configuration of organic molecules on the Fe(110) surface shown in Figure 6 is close to parallel to the plane, and this spreading method is related to the distribution of molecular charges. The relatively parallel structure facilitates the organic molecules to provide greater steric hindrance for the corrosion reaction and helps to inhibit corrosion. Due to the resistance of space and charge, not all molecules can be adsorbed on the metal surface. For MB, there are 3 molecules near the surface and 7 molecules away from the surface. Comparing the adsorption situation of MB, DBP, and M6D4, it can be seen that in the adsorption structure of DBP and M6D4, there are fewer free molecules (4 molecules) and more molecules close to the Fe surface (6 molecules). Through simulation results, it

Table 6. Quantum Chemical Calculation Results of Inhibitors

| molecules | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $\Delta E$ (eV) | $\chi$ (eV) | $\zeta$ (eV) | $\Delta N$ | $\omega$ | $\epsilon$ |
|-----------|----------------|----------------|----------------|-------------|-------------|-----------|--------|---------|
| MB        | −7.645         | −6.157         | 1.488          | 6.901       | 0.744       | 0.066     | 16.00  | 0.06    |
| MO        | −0.855         | 0.182          | 1.037          | 0.336       | 0.518       | 6.425     | 0.05   | 18.31   |
can be inferred that DBP and M6D4 can achieve more satisfactory results, which are similar to the results obtained from actual experiments. In the small range of the crystal lattice set by calculations, the number of molecules on the metal surface is the same for M4D6 and DBP alone. The area covered by organic molecules on the Fe(110) surface is relatively close, which means a similar protective effect. Therefore, it is speculated that on a larger metal plane, the corrosion inhibition effects obtained by the two methods of adding corrosion inhibitors will be closer, which is similar to the conclusions obtained from the experiment.

3. CONCLUSIONS

Two dyes, MB and MO, are used to simulate dye wastewater, and their potential as corrosion inhibitors is tested by electrochemical methods. The test results showed that MB has better protection against corrosion of P110 steel in 1.0 M HCl. When a 300 mg/L concentration is added, the maximum corrosion inhibition rate is 77.34%. However, MO does not function as a corrosion inhibitor, rather accelerates corrosion at low concentrations. Therefore, MB is selected for the compounding of corrosion inhibitors. MB and another corrosion inhibitor DBP are mixed in different proportions to test the inhibition effect after mixing. The test results showed that when the ratio of MB and DBP is 4:6, the mixed corrosion inhibitor achieves the same effect as when DBP is added alone (efficiency 85.48%). The weightlessness test, the SEM test, and quantum chemical calculations confirmed that the mixed corrosion inhibitor can be adsorbed on the metal surface to provide a protective effect. This research is an attempt to recycle wastewater. The main purpose of the research is to verify the corrosion inhibition ability of dyes and the synergistic effect between dyes and other organic corrosion inhibitors. If the dye wastewater corrosion inhibition technology is applied in practice in the future, the toxicity of the wastewater will inevitably be a problem that this technology needs to consider. The goal of this research is to propose a feasible way of wastewater reuse. Studies about the contradiction and balance between corrosion inhibition performance and potential toxicity will continue in the follow-up work. In addition, wastewater reinjection development is an existing process in the oilfield development industry. By injecting sewage into the ground to carry out oil displacement, development costs can be effectively reduced. When choosing dye-containing sewage as a corrosion inhibitor to inject water, it can be pretreated in accordance with the relevant standards for oilfield sewage reinjection, and the effect of the corrosion inhibitor can be improved on the premise of reaching the water quality standard. The application of dye molecules in compound corrosion inhibitors can provide a recovery application value for dye wastewater, and can also reduce the synthesis cost of organic corrosion inhibitors. The use of dyes as corrosion inhibitor additives provides future prospective research values in regards to both economic and ecofriendly benefits.

4. MATERIAL AND METHODS

4.1. Material. In all corrosion tests (electrochemistry tests, weight loss, etc.), the selected sample material is P110, and its elemental composition is shown in Table 8. The samples used are customized polished specimens, whose sizes are 40 mm × 13 mm × 2 mm. Before tests, petroleum ether is first used to clean the protective grease from the sample surface, and then samples are washed repeatedly with ethanol and deionized water respectively. After cleaning, samples are dried and weighed at room temperature in a nitrogen atmosphere. All solutions used in this study are prepared using 1 M HCl. Methylene blue (MB) and methyl orange (MO) are used as both cationic and anionic dyes to prepare simulated dye wastewater, and their molecular structures are shown in Figure 7. To test the synergistic effect of dyes and other corrosion inhibitors, decamethylene bis-pyridinium dibromide (DBP) is selected as another component of the mixed corrosion inhibitor, which has been reported in our previous study. The molecular structure of DBP is also shown in Figure 7.

4.2. Electrochemical Tests. In the electrochemical test, a flat corrosion electrolytic cell is used for measurements. All of the electrochemical tests are carried out at 30 °C using a CHI660E electrochemical workstation. In addition, a three-electrode system is used: P110 as a working electrode, Ag/AgCl as a reference electrode, and a platinum plate as a counter electrode. The area of the working electrode is 1 cm². Prior to testing, the sample is soaked in the solution until

| element | C | Si | Mn | Cr | Mo | P | S | Cu | Ni | V |
|---------|---|----|----|----|----|---|---|----|----|---|
| composition | 0.29 | 0.27 | 0.50 | 0.90 | 0.18 | <0.02 | <0.01 | <0.20 | <0.20 | <0.08 |
the open-circuit potential (OCP) reached a stable level. In the potentiodynamic polarization curve test, the scan range and the scan rate are set to be OCP ± 250 mV and 1 mV/s, respectively. In the A.C. impedance test, an alternating current whose amplitude is 0.005 V is applied at the open-circuit voltage with an amplitude of 0.005 V, whose frequency range is from 0.1 to 20 000 Hz. After results are obtained, Zsimpwin software is used for fitting the results. An illustration of the circuits’ setup used is shown in Figure 8. \( R_a \) is the resistance of solution, \( R_c \) is the charge-transfer resistance during corrosion, and \( Q \) is a constant phase element.\(^{44} \) In all tests, each set of experiments is repeated three times. If there is no significant difference between the curves obtained from the three experiments, data processing is performed.

### 4.3. Weight-Loss Experiment

In the weight-loss experiment, the P110 specimen is soaked in corrosion solutions at 30 °C for 3 days. After corrosion, the surface of the specimen is washed sequentially with deionized water and ethanol. Then, the specimen is dried in a nitrogen atmosphere before being weighed. All experiments are repeated three times to ensure accurate results.\(^{5,6} \) When weight loss of specimens is obtained, corrosion rates are obtained using eq \(^ {16} \)

\[
V_{\text{corr}} = \frac{(8.76 \times 10^{4} \times \Delta m)}{(s \times t \times \rho)} \tag{11}
\]

where \( \Delta m \) (g) is the average weight loss of three specimens, \( s \) (cm\(^2\)) is the surface area of samples, which is calculated through the measured value, \( t \) (h) is the corrosion time in hours (72 h), and \( \rho \) (g·cm\(^{-3}\)) is the density of P110 specimens.\(^{37} \) All experiments were repeated three times to reduce errors.

### 4.4. Scanning Electron Microscopy (SEM)

To study the changes of sample surfaces with or without inhibitors, an FEI Quanta 200F scanning electron microscope is used to analyze the surface of the specimens. Before testing, specimens are soaked in a corrosive medium at 30 °C for 3 days and then washed and dried in nitrogen. The concentration of all corrosion inhibitors is determined to be 200 mg/L, which is the standard for corrosion inhibitors in some practical applications. In the SEM test, the surface is magnified by 3000 times to obtain a microscopic image. Thereafter, an energy-dispersive X-ray spectroscopy (EDS) system is used to analyze the elemental distributions.

### 4.5. Computational Studies

Quantum chemical software is used for obtaining the optimal structure of inhibitor molecules and the morphology of corrosion inhibitors on a metal surface. First and foremost, density functional theory is chosen for the optimization of the molecular structure. The generalized gradient approximation (GGA) and exchange–correlation function of Becke–Lee–Yang–Parr (BLYP) functions are used.\(^{17} \) After the optimized structures are calculated, the adsorption simulation module is used to predict the adsorption of corrosion inhibitors on the Fe(110) surface.\(^{18} \) It is worth noting that quantum chemical calculations cannot fully simulate the real corrosion environment, and the calculated results may deviate from actual experiments. The purpose of this calculation is to predict the performance of molecules and study the mechanism of corrosion inhibitors from a microscopic view.

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**Notes**

The authors declare no competing financial interest.

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