Coordination Behaviors of Cu$^{2+}$ With Azo Dye Acid Black 10B

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Abstract. This study mainly explored the coordination relationship between Cu$^{2+}$ and functional groups of acid black 10B, including sulfonic group, azo group, amino group, hydroxyl group and nitro group. By means of UV-vis spectrum scanning, FTIR and XPS techniques, the complex reaction process of cooper ion with dye molecule and their precipitate formed during alkali titration were analyzed. The results showed that copper ion had coordination with all the above groups, and its coordination with azo group and sulfonic group can be able to form a closed ring structure similar to chelate. The spectra characteristics of precipitate revealed that copper ions could play bridging role between amino and hydroxyl and its coordination process would be affected by the pH value of the solution.

1. Introduction

As a transition metal element, copper ion (II) can coordinate with various organic compounds (such as humic acid, chitosan, dyes, etc.) in water and soil to form complexes[1-3]. In these organic compounds, amino, hydroxyl, carboxyl, sulfonic, azo, carbonyl, quinone and sulphhydryl groups, which are rich in nitrogen, oxygen and sulfur, are the possible binding sites of copper ions. Researches show when copper ions coordinate with organic compounds, its activity, solubility and mobility will be greatly changed[3,4].

In recent study, we found that the soluble complex formed by copper ion and azo dye acid black 10B is easy to precipitate under near neutral condition. Considering that copper salt is a common mordant in dyeing process, it often coexists with dye molecules in textile industrial wastewater. Therefore, carrying out the precipitation operation on this kind of complex is of great significance for the simultaneous removal of dyes and heavy metal ions.

With regards to the complex reaction of copper ion with acid black 10B, there had some reports previously[3,5], but it mainly focus on the adsorption aspects. There was no studies mentioned its precipitate behaviors. UV–vis spectroscopy, FTIR and XPS are the commonly used technologies to analyze copper coordination. According to previous reports, FTIR and XPS are very effective in identifying the coordination of copper with sulfonic group and amino group, but sometimes the effect is not very good in judging the azo group. The coordination between copper ion and azo group needs to be decided by UV-Vis spectroscopy. In our study, besides the formation of precipitate, we also observed a special phenomenon, that is, the color of the mixing solution of copper ion and acid black 10B would change with time in the complexation stage. Preliminary analysis by UV-Vis spectroscopy has demonstrated that the color's change of the solution is related to the coordination of the main chromogenic group (azo group) of the dye. In order to further explore the coordination relationship,...
between copper ions and the functional groups of acid black 10B, next, we mainly carried out two aspects of work, one was to keep on tracking their complexation reaction process by using UV-Vis Spectrum scanning, the other was to analyze the precipitates of complexation reaction by using FTIR and XPS technology, and combine with the result of UV-Vis spectrum scanning to elaborate their coordination relationship.

2. Materials and methods

2.1. Reagents and drugs

Azo dye acid black 10B (CAS No.1064-48-8) is purchased from Shandong Yousuo Chemical Technology Co., Ltd. Its molecular formula is C_{22}H_{16}N_{2}Na_{2}O_{11}S_{3}, the molecular weight is 616.5, and the molecular structure is as follows:

![Molecule structure of acid black 10B.](image)

CuCl_{2}·2H_{2}O (analytical grade) is purchased from Shanghai Aibi Chemical Reagent Co., Ltd. NaOH (analytical grade) is purchased from Tianjin Kaitong Chemical Reagent Co., Ltd. Deionized water is made by the laboratory.

2.2. Complex precipitation experiment

Prepare 0.1mol/L CuCl_{2} solution and 20mg/L acid black 10B solution. Add 1ml CuCl_{2} solution into 100ml acid black 10B solution at room temperature, record the initial pH value (pH meter, PHS-25, Leici, Shanghai) and observe the change of solution color. After 1h, to titrate with 0.1mol/L NaOH solution, and record the change of pH value of the solution. As the solution began to precipitate, use colorimeter (XZ-0101s, Leigu, Shanghai) to detect the change of solution’s chroma and calculate the decolorization rate. Stop titration when the decolorization rate reaches stable. The formula of decolorization rate is as follows:

\[ R = \frac{c_0 - c_t}{c_0} \times 100\% \]

where \( R \) is the decolorization rate (%), \( c_0 \) is the initial chroma of acid black 10B solution, \( c_t \) is the chroma of supernatant at time \( t \).

2.3. UV-Vis Spectrum Scanning

Add 1ml of 0.1mol/L CuCl_{2} solution into 100ml of 20mg/L acid black 10B solution. Scan the mixing solution by Uv-2802pc spectrophotometer (Unico, Shanghai, China) when react 30s, 6min, 12min, 18min, 24min, 30min, 36 min, 45min and 1h respectively. The scanning wavelength range is 220-700nm, the fixed slit width is 2nm, and the scanning speed is 1000nm/min. As a control, the original solution of acid black 10B (20mg/L) with no CuCl_{2} is also scanned.

2.4. FTIR and XPS detection

Prepare the complexation precipitate according to the method in 2.2, collect the precipitate by centrifugation, and wash it with deionized water for three times. After that, put the precipitate into a vacuum oven for drying (temperature 25 °C). When it is completely dry, take it out and grind for standby.

In this study, Vertex 70 FTIR spectrometer (Bruker, Germany) and Escalab 250 Xi (Thermo Scientific, USA) X-ray photoelectron spectrometer were used to test the samples. FTIR needs the
sample to be prepared by adopting potassium bromide pressing method. The wave number range of the instrument is 400-4000 cm\(^{-1}\), and the resolution is 4 cm\(^{-1}\). XPS is used to analyze the changes of electronic binding energies of N, O, S and the newly introduced Cu and Cl. The working parameters of XPS are as follows: the K\(\alpha\) spectral line of Al target is used as the excitation light source, the Cl\(1s\) electronic peak of carbon element (284.6 ev) is used as the reference, the power of Al target anode is 300 W, the working voltage and current are 15 kV and 20 mA respectively. High resolution scanning through energy is adjusted to 30 ev. The measurement accuracy of electron binding energy is ± 0.1 eV. Gaussian fitting method is used to deconvolute the peaks.

3. Results and discussion

3.1. Complexation precipitation behaviors

First, after added 1 ml of CuCl\(_2\) solution, the initial pH value of mixing solution was recorded as 5.54. In one hour's complexation reaction, the color of the solution changed from dark blue to blue purple, and finally to purplish red. In the subsequent alkali titration, when the pH value increased to 6.24, the solution began to precipitate, and accompanied by obvious decolorization. As the pH value increased to 6.75, the decolorization rate remained stable and reached 95.6%.

3.2. UV-visible spectrum analysis

Figure 2 shows the UV-vis scanning spectrums of the raw solution of acid black 10B and the mixed solution added with copper ions. As shown in the Figure, there are two obvious absorption peaks of the raw solution. In the visible region, the strong absorption peak at 618 nm is corresponding to azo bond structure, while the peak of 321 nm in the ultraviolet region is corresponding to benzene ring structure and naphthalene ring structure[6].

![Figure 2. UV-Vis scanning spectrums of complex reaction.](image)

After added copper ion, the two absorption peaks changed obviously. During the first 30 s, not only their intensities decreased, but also the positions shifted. The absorption peak of azo structure was blue shifted, while that of benzene ring and naphthalene ring was red shifted. With the extension of reaction time, the offset degree increased continuously. When the reaction time reached 1 h, the absorption peaks at 618 nm and 321 nm almost disappeared, and two new absorption peaks were formed in the wavelength range of 521-527 nm and around 361 nm.

The absorption peak in the visible region is produced by the lone pair electron transition on the nitrogen atom in the azo double bond, i.e. \(n \rightarrow \pi^*\). The blue shift of the absorption peak in the visible region indicates the coordination between copper and azo double bond. When the nitrogen atom
coordinates with copper ion, the lone pair electrons on the nitrogen atom will enter the empty orbit of copper ion. As the lone pair electrons transfer to the antibonding orbit, the energy level will increase, and thus the absorption peak will be blue shifted. So, it can be concluded that the color’s change of the solution mentioned above is related to the coordination of azo group.

The absorption peak in the ultraviolet region is produced by the \( \pi \) electron transition in the conjugated system of benzene ring and naphthalene ring, i.e. \( \pi \rightarrow \pi^* \). The red shift of the absorption peak in the ultraviolet region indicates that the conjugated system increases and the electron transition energy level decreases. Considering that the azo group and sulfonic group connected on the naphthalene ring are in the ortho position, it is possible that copper ion can enhance the conjugated system of naphthalene ring by coordinating with these two groups to form a ring closed structure similar to a chelate (as shown in Figure 3). In view of the negative charge character of sulfonic acid group, its affinity with copper ion should be stronger than that of azo group. Therefore, we inferred that the order of reaction between them is that, copper ions coordinate with sulfonic acid group first, and then with azo group.

3.3. XPS spectra analysis
Figure 4(a) is the full scan XPS spectra of raw dye. As shown in the Figure, the binding energies (BEs) of C1s, N1s, O1s and S2p are 284.6eV, 399.4eV, 531.9eV and 168.0eV, respectively.

![Figure 3. The coordination of Cu²⁺ with azo and sulfonic groups.](image)
Figure 4. XPS spectra of raw dye.

Figure 4(b)-(d) show the XPS spectra of N1s, O1s, and S2p. The spectra of N1s are deconvoluted into four different component peaks. Peaks of N1 (399.4 eV), N2 (400.6 eV), N3 (405.8 eV) are related to amino (-NH₂), azo group (-N=N-) and nitro (-NO₂), respectively. Here, N4 (402.6 eV) could be seen as a satellite peak. Meanwhile, The spectra of O1s are deconvoluted into three component peaks. Peaks of O1 (531.46 eV), O2 (532.38 eV) and O3 (533.20 eV) are correspondence to sulfonic acid group (-SO₃), hydroxyl (C-OH) and gaseous water molecule (H₂O). The XPS spectra of S2p could be dissected to two peaks. S1 (168.5 eV) and S2 (169.7 eV) S1 are correspondence to the two sulfonic acid groups at different positions in naphthalene ring.

Figure 5(a) is the full scan XPS spectra of precipitate. Compared with raw dye, the BEs of N1s, O1s, S2p in precipitate shift to 399.6 eV, 531.8 eV and 167.9 eV, respectively. In addition, copper (933.3 eV) and chlorine (198.2 eV) are also detected in the full spectrum scanning of precipitate. Figure 5(b)-(f) show the XPS spectra of Cu2p, N1s, O1s, S2p, and Cl2p. As shown in Figure 5(b),
Both peaks of Cu(1) (934.4 eV and 954.6 eV) and Cu(2) (932.6 eV and 952.4 eV) are correspondence to Cu$^{2+}$. Obviously, the BEs of Cu2p3/2 in precipitate are smaller than the Cu2p3/2 (935.2eV)[7] of CuCl2:2H2O. It indicated that the coordination of copper ions occurred. Compared with copper (1), the binding energy of copper (2) is lower, which means higher electron cloud density occurred around Cu(2). For the N1s and O1s, the BEs of N1, N2 and N3 shift from 999.4eV, 400.6eV, 405.8eV to 399.6eV, 400.9eV and 405.4eV. Meanwhile, the BEs of O1 and O2 shift from 531.8eV, 533.3eV to 531.5eV and 533.8eV. Its worth to note that there has a new fitting peak of O1s at 531.7eV. In view of the influence of pH value, bivalent copper ion in solution would hydrolyze and to produce Cu(OH)$^+$ and Cu(OH)$_2$$^{2+}$ species[8]. So, we think the peak (531.7eV) of O1s arising from the hydroxyl coordinated with copper. Except for the O1s and N1s, the BEs of S1 (168.5eV) and S2 (169.7eV) also shift to 167.8eV and 169.1eV. Through the above analysis, it could basically determine that copper ion in precipitate had all coordination with azo double bond, sulfonic group, nitro group, hydroxyl group and amino group.

As far as Cl2p is concerned, the binding energy of Cl2p in CuCl2 is 199.2 eV[7]. However, there shows two peaks of Cl2p (199.8 eV and 198.2 eV) in Figure 5(f). According to the theory of Alvarez-Puebla[8], as the copper ions coordinate with the dye molecules, the excess chloride ions would further combine with the remaining free copper ions to form [CuCl4]$^{2-}$. So, we speculate that Cl(1) with lower BE might be coordinate with copper as [CuCl4]$^{2-}$; while that of Cl(2) with higher BE as Cu'(OH) Cl$^-$.  

3.4. FTIR analysis
Figure 6 shows the infrared spectra of the two samples. For the raw dye, it shows strong spectral absorption in the range of 3000-3700cm$^{-1}$, and the maximum absorption peak is 3444cm$^{-1}$, which is mainly caused by the stretching vibration of -OH and -NH[9]. 1635cm$^{-1}$, 1485cm$^{-1}$ and 1283cm$^{-1}$ are the characteristic absorption peaks of benzene ring structure, which are related to the stretching vibration of C=C[10,11]. In addition, 1572cm$^{-1}$ corresponds to the bending vibration of -NH, 1331cm$^{-1}$ is the stretching vibration of N=O, 1383cm$^{-1}$ and 1419cm$^{-1}$ are generated by the coupling of -OH bending vibration and -CH bending vibration [10]. The absorption peaks of 1173cm$^{-1}$, 1140cm$^{-1}$, 1049cm$^{-1}$ and 640cm$^{-1}$ are related to the vibration of sulfonic group (-SO3). Among them, 1713cm$^{-1}$, 1049cm$^{-1}$ and 640cm$^{-1}$ are generated by the coupling of valence vibration of S-O bond and valence symmetry vibration of -SO3 group [3], and 1140cm$^{-1}$ is the stretching vibration of S=O[12]. According to the relevant reports[10,13], the absorption peak of azo bond (-N=N-) is in the range of 1618-1630cm$^{-1}$. Unfortunately, we did not find the related peaks in the Figure It might be covered by the strong peak of benzene ring structure.
Compared with the raw dye, the main change of the infrared spectrum of the precipitate is that, the peak intensity of 3000-3700cm\(^{-1}\) decreased, while the peaks at 1572cm\(^{-1}\) and 1419cm\(^{-1}\) disappeared. These indicate that both the amine group and hydroxyl group on naphthalene ring are affected by the copper coordination. In addition, the peak at 1383cm\(^{-1}\) weakened and shifted to 1385cm\(^{-1}\), which means that the coordination between copper and oxygen destroys the coupling effect of the original OH bending vibration and CH bending vibration. Considering that the two groups are in the ortho position, copper ions might be able to coordinate with them by means of bridging. In view of the fact that the complexation reaction is carried out under acidic conditions, copper ions would coordinate with protonated amino groups first through ion exchange, and then again to combine with ionized hydroxyl groups during alkali titration. Additionally, the peak at 1485cm\(^{-1}\) weakens obviously and shifts to 1500cm\(^{-1}\), which indicates that the structure of benzene ring is also affected. 1173cm\(^{-1}\), 1105cm\(^{-1}\) and 640cm\(^{-1}\) are the characteristic peaks of -SO\(_3\) group, which shift to 1186cm\(^{-1}\), 1109cm\(^{-1}\) and 654cm\(^{-1}\) respectively. The overall shift of these peaks to higher wave numbers indicates that the sulfonic group is coordinated with copper ion. 1331cm\(^{-1}\) is related to the stretching vibration of nitro group. Its shifting from 1331cm\(^{-1}\) s to 1337cm\(^{-1}\) means copper ion might has coordination with -NO\(_2\). It can be seen that these conclusions are basically consistent with the results of XPS.

4. Conclusions
This study emphasized the coordination relationship between Cu\(^{2+}\) and acid black 10B. By means of UV-vis spectrum scan, FTIR and XPS detection and analysis, we could draw the following conclusions,

Firstly, by the tracking scan of the UV-vis Spectrum, it can be determined that the color change of the solution is related to the coordination of azo group. Both azo group and sulfonic acid group coordinated with copper ion, and they could form a ring closed structure similar to chelate.

Secondly, through the spectra analysis of the complex precipitate, it can be judged that, except for the azo group and sulfonic group, copper ion also has coordination with amino group, hydroxyl group and nitro group. With regards to the coordination of copper ion with amino and hydroxyl groups, we speculated that there exists bridging mode among them, and its combine process would be affected by the pH value of the solution.

Based on the above conclusions, We inferred the structure of the complex precipitate might be as follows (Figure 7). Whether this is accurate or not needs further argument.
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