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Acetylacetone as A Potential Chemosensor for Rapid Detection of Cu(II) in Aqueous Media

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Abstract. Monitoring of Cu(II) ions is one of the most critical issues in wastewater treatment. Since the application of diketone-derived compounds as the Cu(II) chemosensor has not been addressed yet, in this present work, acetylacetone (penta-2,4-dione) was employed as the chemosensor to detect Cu(II) ions in the aqueous media. Ultraviolet (UV)-visible spectra showed that the blue colored-Cu(II) solution gave absorption at 811 nm, while the acetylacetone only gave absorption at UV region of 272 nm. Interestingly, the blue Cu(II) solution immediately turned to green solution after the addition of Cu(II) solution into the ligand solution, giving a new peak at 748 nm due to formation of Cu(II)-acetylacetone complex. This large blue shifting suggested the potential application of the acetylacetone as a colorimetric sensor of Cu(II), which gives benefit in the rapid detection. The limit of detection (LoD) and limit of quantification (LoQ) were found to be 0.15 and 0.51 mM, respectively. Furthermore, the presence of other metal ions, such as Na(I), K(I), Mg(II), Mn(II), Ni(II), Al(III), Au(III) and La(III), could be neglected since they gave low extents of interferences up to less than 10%. These results demonstrated that the acetylacetone is a potential chemosensor for Cu(II) detection in the aquatic environment.

1. Introduction

Heavy metals pollution is one of the most serious problems in the aquatic environment. This kind of pollution came from many sources, such as industries, energies, and so on [1]. Copper as one of the most abundant heavy metal ions is pivotal in our daily life because it is massively used for electronic appliances. In the environment, copper is mostly found in cationic form as Cu(II) ions, and they contaminate the aquatic environment [2-4]. An excessive amount of Cu(II) intake could lead to several health problems, such as anemia [5], irritation [6], and liver dysfunction [7]. Because of these negative effects, Cu (II) ion monitoring is a critical issue in wastewater treatment.

Many pieces of research have been done to monitor the Cu(II) concentrations either in the laboratory or environmental samples using a chemosensor agent due to the simple procedure. Phapale *et al.* synthesized a chemosensor for Cu(II) and Fe(III) recognition using pyrene based molecules [8], while Patil *et al.* employed phthalimide based compound for Cu(II) detection using spectrophotometer [9]. The drawbacks of these researches were the complicated and time-consuming synthesis process. Furthermore, the pyrene compounds are highly toxic to our environment, and thus other simple and non-toxic chemosensor agents should be evaluated.



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On the other hand, diketone-based molecules are simple and environmentally friendly chemical, which are able to act as chelating agents for certain metal ions. Among them, 1,3-diketone compounds are potential to be a Cu(II) ions chemosensor because they form a stable complex with Cu(II) ions [10] and they have been thoroughly investigated for Cu(II) extraction through a liquid-liquid extraction process [11]. Even though the complexation of Cu(II) and 1,3-diketone derivatives have been extensively studied, the usage of diketone derivatives as chemosensor agent for Cu(II) detection and quantification in the aqueous media has not been addressed yet. Therefore, in this work, a simple 1,3-diketone derivative, acetylacetone (penta-2,4-dione), was applied as a chemosensor agent for Cu(II) detection and quantification in the aqueous media. At first, the ultraviolet-visible (UV-vis) spectra of the ligand before and after addition of Cu(II) ions at various concentrations were recorded to determine the limit of detection (LoD) as well as the limit of quantification (LoQ). Afterwards, the interference effect due to the presence of the other metal ions was also studied.

2. Experiment

2.1. Materials

All of the used chemicals, such as acetylacetone (Merck, China), acetonitrile (Merck, Germany), CuCl₂ (Merck, UK), NaCl (Merck, Denmark), KCl (Merck, USA), MgCl₂ (Merck, Germany), MnCl₂ (Merck, Germany), NiCl₂ (Merck, Germany), AlCl₃ (Merck, Germany), AuCl₃ (Merck, Germany) and LaCl₃ (Merck, UK) salts were purchased in pro analytical grade and used without further purification. The chemical structure of acetylacetone (penta-2,4-dione) ligand is shown in Figure 1.

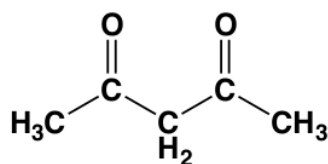


Figure 1. Chemical structure of acetylacetone ligand.

2.2. Evaluation of Cu(II) detection using acetylacetone as the chemosensor agent

A 50 mM solution of acetylacetone was prepared by dissolving 0.51 mL of acetylacetone (MW: 100.13 g mol⁻¹) in 100 mL of H₂O:CH₃CN mixture in 1:1 volume ratio (v/v). Then 1 mL of the ligand solution was then mixed with 1 mL of 10 mM CuCl₂ solution in H₂O:CH₃CN 1:1 v/v media. The absorbance of the solution was measured using a UV-visible spectrophotometer (UV-Vis, JASCO V-760) at 200–900 nm.

2.3. LoD and LoQ measurements of Cu(II) detection with acetylacetone

The LoD and LoQ values of Cu(II) sensing with acetylacetone were determined using a calibration curve. The ligand solution was mixed with CuCl₂ solution at various concentrations (1, 2, 3, 4, 5, and 6 mM) in 1:1 volume ratio. The absorbance of each solution was measured with UV-Vis spectrophotometer. The calibration curve was obtained by plotting the absorbance of the solution at 748 nm versus the Cu(II) concentrations. The LoD and LoQ values were calculated using equations (1) and (2), whereas σ is the standard errors of the blank solution while a is the slope of the calibration curve, respectively.

$$\text{Limit of Detection (LoD)} = \frac{3 \sigma}{a} \quad (1)$$

$$\text{Limit of Quantification (LoQ)} = \frac{10 \sigma}{a} \quad (2)$$

2.4. Interference study of Cu(II) sensing in the presence of other metal ions

The mixture of binary metal ions, i.e. Cu(II) and each metal ion of (Na(I), K(I), Mg(II), Mn(II), Ni(II), Al(III), Au(III), or La(III)) was prepared by mixing 300 μL of 10 mM Cu(II) solution, 300 μL of 10 mM other metal ion solution, and 400 μL mixture of $\text{H}_2\text{O}:\text{CH}_3\text{CN}$ 1:1 v/v to obtain a bimetal solution at 0.3 mM concentration for each metal ions. Then the 1 mL of the ligand solution was added into the binary metal solution. The absorbance of the mixture was measured using the UV-vis spectrophotometer. The percentage of interference was calculated by equation (3), where $[\text{Cu(II)}]_{\text{initial}}$ and $[\text{Cu(II)}]_{\text{interference}}$ showed the concentration of detected Cu(II) in the absence and presence of other metal ions.

$$\text{Extent of Interference (\%)} = \frac{[\text{Cu(II)}]_{\text{initial}} - [\text{Cu(II)}]_{\text{interference}}}{[\text{Cu(II)}]_{\text{initial}}} \times 100 \quad (3)$$

3. Results and Discussion

In the present work, acetylacetonone was employed as the chemosensor agent for Cu(II) detection in $\text{H}_2\text{O}:\text{CH}_3\text{CN}$ 1:1 v/v media. The Cu(II) ion solution has a blue color, however, interestingly, after the addition of Cu(II) solution into the ligand solution, the color of the mixture was immediately changed to green color. The photographic images of the ligand and Cu(II) solutions and their mixture are shown in Figure 2. The color changes would indicate the difference in their UV-Vis absorption spectrum. Figure 3 shows the UV and visible spectra of the acetylacetonone ligand before and after the addition of Cu(II). As shown in Figure 3(a), the acetylacetonone has an absorbance peak in the UV region at 272 nm. This absorbance peak shall correspond to $n \rightarrow \pi^*$ electronic transition of carbonyl group [12]. After the addition of Cu(II), the absorbance of that peak was quenched and shifted to 282 nm. Furthermore, a new peak on the visible region at 748 nm was observed and this peak was obviously different from either the acetylacetonone ligand (no absorption peak at visible region) or the Cu(II) solution (an absorption peak at 811 nm). The quenching and shifting phenomena may correspond to the stable complexation between acetylacetonone and Cu(II) ion forming a Cu-acetylacetonone complex at room temperature. The spectral changes were observed within a second, demonstrating that rapid sensing of Cu(II) ions was achieved.

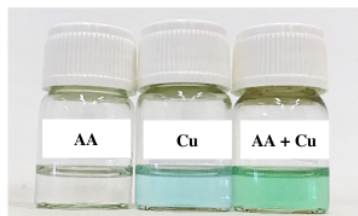


Figure 2. Photographic images of the acetylacetonone solution (AA), Cu(II) solution (Cu), and their mixture (AA + Cu) solution.

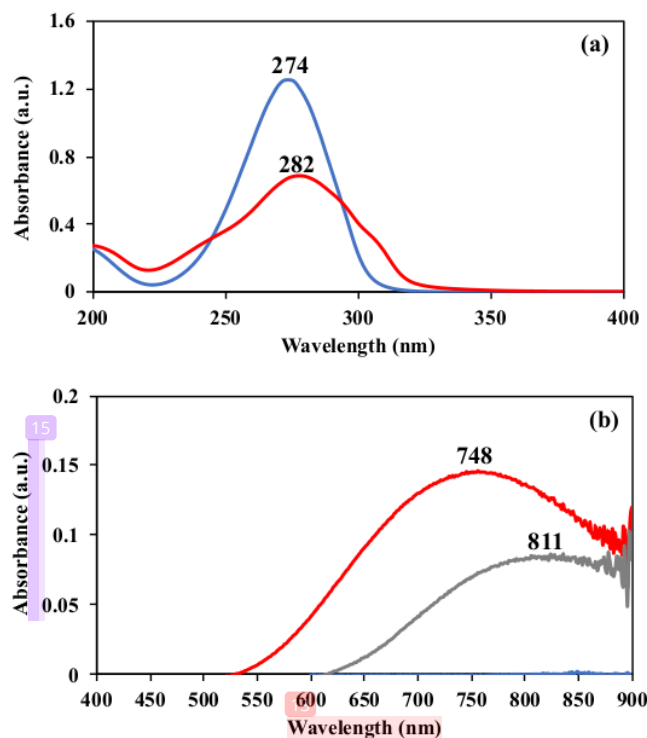


Figure 3. (a) UV spectra of acetylacetonone before (blue line) and after (red line) the addition of Cu(II) solution. (b) Visible absorption peak of acetylacetonone solution (blue line), Cu(II) solution (grey line) and their mixture (red line).

The new absorption peak at the visible region of 748 nm gave us information about the successful detection of Cu(II) by the acetylacetonone via the formation of the Cu(II)-acetylacetonone complex. In order to investigate the possibility to quantify the Cu(II) concentrations by monitoring the intensity of this new absorption peak, the absorbance of the solution at 748 nm was plotted against the Cu(II) concentrations, which were varied to 0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mM. The plot of this calibration curve is shown in Figure 4. It was clear that a strong linear correlation between the concentration of Cu(II) and absorbance of the mixture at 748 nm could be observed with R^2 value of 0.9959.

In order to evaluate the performance of the acetylacetonone, the LoD and LoQ values for Cu(II) sensing application were determined using equations (1) and (2) aforementioned above. The LoD and LoQ of acetylacetonone were found to be 0.15 and 0.51 mM, respectively. These values are good enough since they are smaller than 1 mM, suggesting that the acetylacetonone could be potential for detection of wastewater treatment containing Cu(II) with such concentration range limit. Further study was then also carried out to investigate the effect of other metal ions on the Cu(II) detection and quantification. The Na(I) and K(I) ions were selected as the representative of monovalent cations, the Mg(II), Mn(II), and Ni(II) ions were selected as the representative of divalent cations while the Al(III), Au(III) and La(III) ions were selected as the representative of trivalent cations.

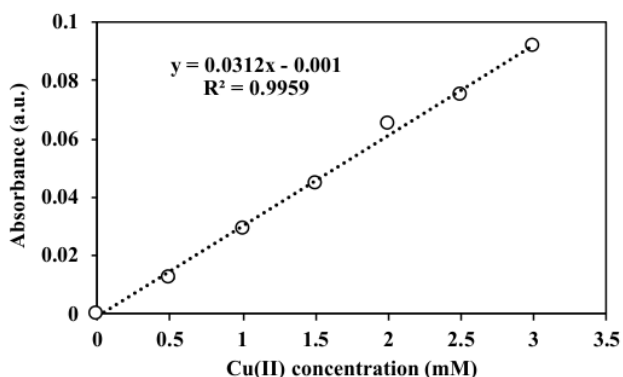


Figure 4. Calibration curve of Cu(II) sensing using acetylacetone as the chemosensor agent.

The photograph images of the ligand solution after the addition of each metal ion are shown in Figure 5. It gave clear evidence that the color changes were observed only for Cu(II) ion and Au(III) ions. While the yellow color of the ligand after addition of Au(III) ions was caused by the initial color of Au(III) ions solution, the green color of the Cu(II)-acetylacetone complex did not come from the color of Cu(II) since the Cu(II) solution was originally blue in color. This result strongly indicated that the acetylacetone was only highly selective for Cu(II) ions.

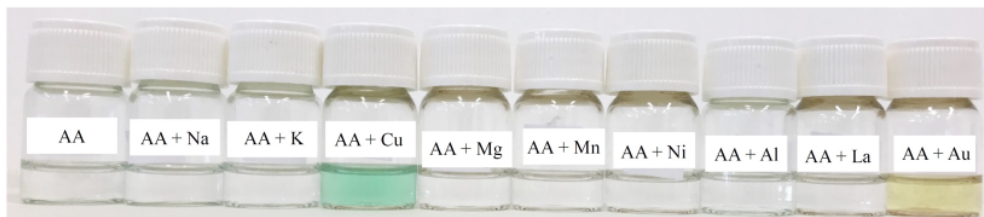


Figure 5. The photographic images of the acetylacetone solution (AA) mixture with the various metal ions. From left to right: ligand only and ligand after addition of Na(I), K(I), Cu(II), Mg(II), Mn(II), Ni(II), Al(III), La(III) and Au(III) ions, respectively.

The interference of the other metal ions, *i.e.* Na(I), K(I), Mg(II), Mn(II), Ni(II), Al(III), Au(III) and La(III) on the Cu(II) quantification was studied by measuring the absorbance of Cu(II)-acetylacetone complex at 748 nm in the absence and presence of other metal ions. Figure 6 shows the absorbance of the Cu(II)-acetylacetone complex in the absence and presence of the other metal ions in the aqueous media. It was found that the absorbance of Cu(II)-acetylacetone complex was not much affected by the presence of other metal ions, as indicated by similar absorbance values. The data labels shown in the Figure 6 represent the extent of interference of other metal ions in the of Cu(II) quantification. The extent of interference for monovalent cations, *i.e.* Na(I) and K(I) ions were 0.69 and 4.97%, respectively. The extent of interference for divalent cations, *i.e.* Mg(II), Mn(II), and Ni(II) ions were 3.79, 9.82, and 6.46%, respectively, while the extent of interference for trivalent cations, *i.e.* Al(III), Au(III) and La(III) ions were 9.00, 4.01, and 4.66%, respectively. Even though there was no clear correlation on the effect of the cations to the extent of interference, it is worthy to note that the presence of the other metal ions in general gave a low extent of interference (less than 10%).

Therefore, this study revealed that the acetylacetonone could act as a potential Cu(II) chemosensor agent in the aqueous media with a rapid detection and quantification process.

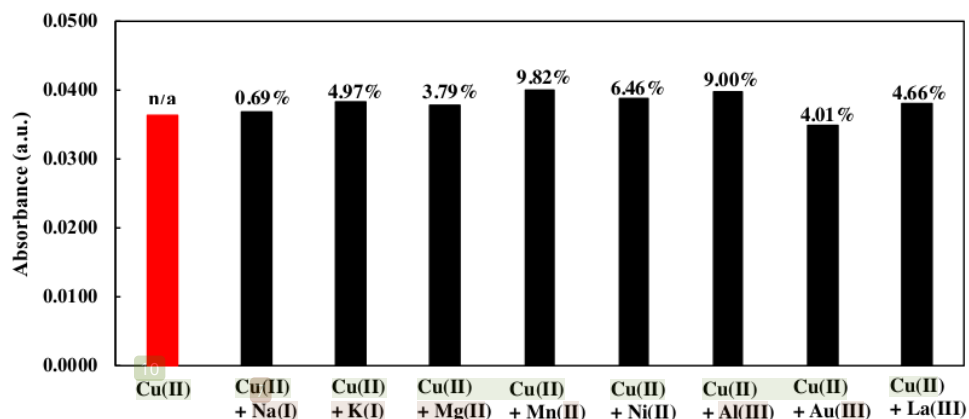


Figure 6. The absorbance at 748 nm of the bimetal solution (Cu(II)+M(n+)) using acetylacetonone as the chemosensor agent. The data labels show the interference extent percentages of other metal ions on the Cu(II) quantification.

4. Conclusions

The acetylacetonone was found as a potential chemosensor agent for Cu(II) detection and quantification in H₂O:CH₃CN 1:1 v/v media. After the addition of Cu(II) ions solution into the ligand solution, the color of the mixture was immediately changed from blue to green color within a second, demonstrating that a rapid sensing of Cu(II) ions was successfully achieved. It was also found that the LoD and LoQ values for Cu(II) sensing using acetylacetonone were 0.15 and 0.51 mM, respectively, which are acceptable values for wastewater containing Cu(II). Furthermore, the presence of the other metal ions gave the extent of interference below 10%, confirming that a selective Cu(II) detection and quantification had been established. These findings showed that acetylacetonone is a potential Cu(II) chemosensor agent with a rapid detection and quantification process in the aqueous media.

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