

Interference and Elimination of Fe³⁺ During Spectrophotometric Testing of Typical Pollutants in Coking Wastewater

Fengcheng Jiang^{1,2}, Yao Qiu¹, Mingshi Wang¹, Shuguang Zhao², Yahui Xu², Manman Xu², Chuanbing Zhang^{2,*}

¹School of Resources and Environment, Henan Polytechnic University, Jiaozuo 454003, China

²Huaxia Besince Environmental Technology Co., Ltd., Zhengzhou 450008, China

*Corresponding Author

ABSTRACT

As typical pollutants in coking wastewater, pyridine, indole, quinoline, and phenol have the advantages of rapidity and accuracy when determined in aqueous solution using UV spectrophotometry, but the presence of other substances in the water can interfere with the results. In this study, the spectrophotometric detection of pyridine, indole, quinoline, and phenol in coking wastewater was interfered with by Fe³⁺. To minimize this interference, hydroxylamine hydrochloride (HA) was selected as a masking agent to eliminate the interference of Fe³⁺ on the detection. The results indicated that spectrophotometric determination was significantly affected by Fe³⁺, and the level of interference increased with the concentration of Fe³⁺. HA can effectively reduce the absorbance of Fe³⁺ in the wavelength range of 250-350 nm. It exhibits a strong masking effect on the determination of Fe³⁺ in indole and phenol solutions, but it hampers the detection of pyridine and quinoline. HA has a better elimination effect on the interference of different concentrations of Fe³⁺, which can make the relative error of the determination results of indole and phenol less than 5% and 10%, respectively.

KEYWORDS

Coking wastewater; spectrophotometry; Fe³⁺; hydroxylamine hydrochloride; masking.

1. INTRODUCTION

Spectrophotometry is a method for qualitative and quantitative analysis of a substance based on the absorbance of the substance measured at specific wavelengths^[1]. Compared to chromatography and fluorescence analysis, spectrophotometry doesn't necessitate large analytical instruments, offers cost-effective usage, and enables rapid on-site detection, thus enhancing its applicability^[2-4]. However, during the actual determination process, turbidity, organic matter, and metal ions present in water samples can interfere with concentration determination results^[5-7]. Iron, ranked as the fourth most abundant metallic element in the earth's crust^[8], is prone to redox reactions that release Fe³⁺ into water during common water treatment processes. For instance, in the treatment of wastewater using various Fenton and Fenton-like techniques, the utilization of iron activators, whether homogeneous (Fe²⁺) or heterogeneous (Fe⁰, Fe₃O₄, etc.), leads to an elevation in the concentration of Fe³⁺ in the water^[9, 10]. Fe³⁺ absorbs light within the wavelength range of 250-350 nm^[11], and therefore, in the determination of ultraviolet absorbance of some substances, the presence of Fe³⁺ will interfere with the results.

Masking is a method of eliminating the interference of co-existing ions by adding a masking agent to the rapid chemical analysis, which has the advantages of simple operation and rapidity. Commonly used masking agents for Fe^{3+} in various tests include fluoride ion, ethylenediaminetetraacetic acid, and hydroxylamine hydrochloride(HA)^[12-14]. Unlike fluoride ion and ethylenediaminetetraacetic acid, which mask Fe^{3+} by forming stable complexes, HA reacts with Fe^{3+} through its strong reducing property, rapidly reducing Fe^{3+} concentration in solution, and HA has a low absorption in the UV wavelength band^[15]. Additionally, in oxidative water treatment technologies like Fenton involving iron, excessive HA can halt pollutant degradation reactions and serve as an oxidizing agent^[16]. Thus, choosing HA as a masking agent is advantageous.

Considering the complexity of coking wastewater, this study selected pyridine, indole, quinoline, and phenol as research subjects. We assessed how various concentrations of Fe^{3+} affect the accuracy of measuring these pollutants. Additionally, we investigated and confirmed the ability of HA to mask the absorbance of Fe^{3+} and its impact on pollutant detection. This study presents a viable method for eliminating interference during the determination of Fe^{3+} , a common pollutant in coking wastewater, using spectrophotometry in the advancement of water treatment technologies.

2. MATERIALS AND METHODS

2.1. Materials

All chemicals were of reagent grade and used as received without further purification. Indole ($\text{C}_8\text{H}_7\text{N}$), phenol ($\text{C}_6\text{H}_6\text{O}$) were purchased from Sinopharm Chemical Reagent Co. Ltd. pyridine ($\text{C}_5\text{H}_5\text{N}$), quinoline ($\text{C}_9\text{H}_7\text{N}$) were purchased from Tianjin Komeo Chemical Reagent Co. Ltd. ferric nitrate ($\text{Fe}(\text{NO}_3)_3$), and hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) were purchased from Shanghai Yi'en Chemical Technology Co. The experimental water was ultrapure water prepared using an ultrapure water preparation system(Molgene18200 China).

2.2. Interference of Fe^{3+} with the determination of pollutant solution concentrations

The absorbance of different concentrations of pyridine, indole, quinoline, and phenol solutions were measured at wavelengths of 256 nm, 269 nm, 313 nm, and 270 nm using ultra-pure water as a reference, and a UV-Vis spectrophotometer(U-2900, Japan).

Four experimental groups comprising pyridine, indole, quinoline, and phenol were established using 24 colorimetric tubes. Each group was initially supplied with 5.0 mL of a 0.5 mM pollutant solution across six tubes. Subsequently, 0, 0.2, 0.5, 1.0, 2.0, and 4.0 mL of 0.5 mM Fe^{3+} solution is added, followed by the addition of ultrapure water to achieve a final volume of 10 mL. The actual pollutant concentration is denoted as C_0 , while the concentrations measured by UV spectrophotometry were denoted as C_m . The effect of Fe^{3+} on each compound was evaluated by the ratio C_m/C_0 .

2.3. Masking effect of different concentrations of HA on Fe^{3+} interference

To study the masking effect of different concentrations of HA on the absorbance of Fe^{3+} solutions, the absorbance of the mixed solutions at different wavelength conditions was determined when the concentration ratio of HA to Fe^{3+} ($C(\text{HA})/C(\text{Fe}^{3+})$) in the mixed solutions was 0, 0.4, 1, 1.6, 2, and 3, respectively.

The impact of HA on mitigating Fe^{3+} interference in pollutant concentration determination was assessed through its addition. Four sets of experiments were conducted using five colorimetric tubes each, containing pyridine, indole, quinoline, and phenol. To each tube, 5.0 mL of 0.5 mM pollutant solution was added, followed by 2 mL of 0.5 mM Fe^{3+} solution and varying concentrations of HA. These concentrations ensured the ratios of HA to Fe^{3+} ($C(\text{HA})/C(\text{Fe}^{3+})$) to be 20, 40, 60, and 80,

respectively. The efficacy of HA in eliminating Fe^{3+} interference during pollutant concentration determination was assessed by the ratio C_m/C_0 .

2.4. Effect of HA on pollutant determination

The mixed solutions of various pollutants with HA were prepared separately, and the absorbance of these solutions at different wavelengths was measured and compared to solutions without HA to assess the impact of HA as a masking agent on the determination results.

2.5. Effect of HA on the elimination of interference with different concentrations of Fe^{3+} in pollutant solutions

The interference elimination effect of HA on different concentrations of Fe^{3+} during the determination of pollutant concentration was verified when the Fe^{3+} concentration in pyridine, indole, quinoline, and phenol solutions were 0.1, 0.2, 0.5, 1, 1.5, and 2 mM, respectively.

3. RESULTS AND DISCUSSION

3.1. Standard curves for pyridine, indole, quinoline, and phenol

The absorbance of different concentrations of pyridine, indole, quinoline, and phenol standard solutions was measured at specific wavelengths, and the results showed that the standard curves of the four pollutants were well-fitted, and the R^2 was greater than 0.999. The spectrophotometric method can accurately determine the concentrations of pyridine, indole, quinoline, and phenol in water.

3.2. Interference of Fe^{3+} in the determination of the concentration of pyridine, indole, quinoline, and phenol solutions

Various concentrations of Fe^{3+} were added to solutions of pyridine, indole, quinoline, and phenol to assess the level of interference. As depicted in Fig. 1, the presence of Fe^{3+} induces considerable interference with pollutant concentration measurements, leading to significantly inflated values compared to the actual concentrations. The interference with the results of the four pollutant measurements follows a descending order when the concentration of Fe^{3+} in a water sample is fixed: pyridine, quinoline, phenol, and indole; at a Fe^{3+} concentration of 0.01 mM, the interference in determining phenol and indole is minimal, with determination errors within 3%. As the Fe^{3+} concentration in the water samples rises, the errors in C_m and C_0 increase. When the Fe^{3+} concentration in the solution reaches 0.2 mM, the measured values for pyridine, indole, quinoline, and phenol concentrations are approximately 2.58, 1.19, 2.40, and 1.84 times higher than the actual values, respectively. Thus, masking Fe^{3+} is imperative for the accurate determination of pyridine, indole, quinoline, and phenol concentrations in Fe^{3+} -containing water samples.

3.3. Masking effect of HA on Fe^{3+} and its influence on the results of pollutant concentration determination

The masking effect of HA on Fe^{3+} was investigated by testing Fe^{3+} solutions with varying HA concentrations across different wavelengths, as depicted in Fig. 2. HA addition markedly decreases Fe^{3+} absorbance within the 250-350 nm wavelength range. Higher HA concentrations correlate with lower absorbance, when the concentration ratio of HA to Fe^{3+} reaches 3, it can mask most of the UV absorbance of Fe^{3+} . This is primarily attributed to HA's strong reducing properties, enabling it to convert Fe^{3+} in solution to Fe^{2+} , thereby minimizing its interference with UV absorbance. Thus HA has the potential to eliminate Fe^{3+} interference during testing.

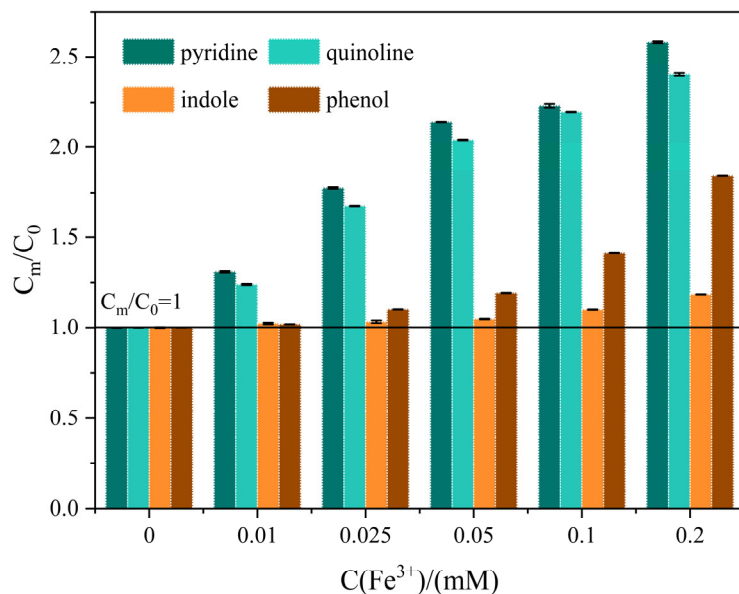


Figure 1. Influence of Fe³⁺ concentration on determination of pollutants in coking wastewater

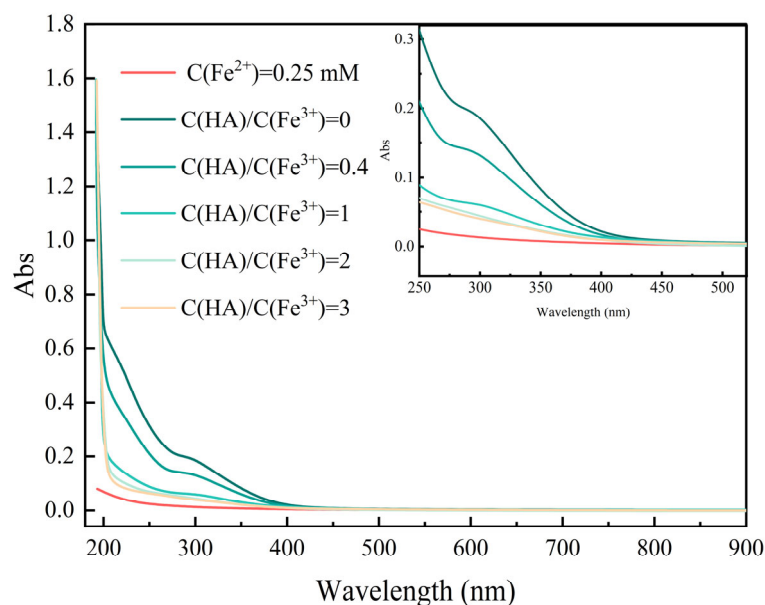


Figure 2. Masking effect of HA on Fe³⁺

The impact of varying concentrations of HA on mitigating Fe³⁺ interference during pollutant determination was studied at a Fe³⁺ concentration of 0.1 mM. In Figure 3(a), under the interference of Fe³⁺ interference, the measured concentrations of pyridine, quinoline, indole, and phenol were notably higher than the actual concentration of 0.25 mM, being 0.56, 0.53, 0.28, and 0.35 mM, respectively. Upon the addition of HA, interference in the measurements of indole and phenol was notably mitigated, aligning the measured values with the actual concentrations. However, increasing HA concentration did not notably enhance interference elimination. The determination errors for phenol and indole remained within 10%, whereas those for quinoline and pyridine exceeded 110%. Fe³⁺ interference was deemed significantly mitigated when the error between measured and actual values remained within 10%. It's evident that at C(HA)/C(Fe³⁺)=10, HA effectively mitigates Fe³⁺ interference during phenol and indole determination, while interference persists in pyridine and quinoline determination (C_m/C₀>110%).

To investigate this phenomenon, full-wavelength scans of pyridine, indole, quinoline, and phenol solutions were conducted both with and without the addition of HA. The comparative results are depicted in Fig. 3(b). Compared to phenol and indole, the absorption curves of pyridine and quinoline mixed solutions with HA show varying degrees of shift, particularly at the wavelength of maximum absorbance.

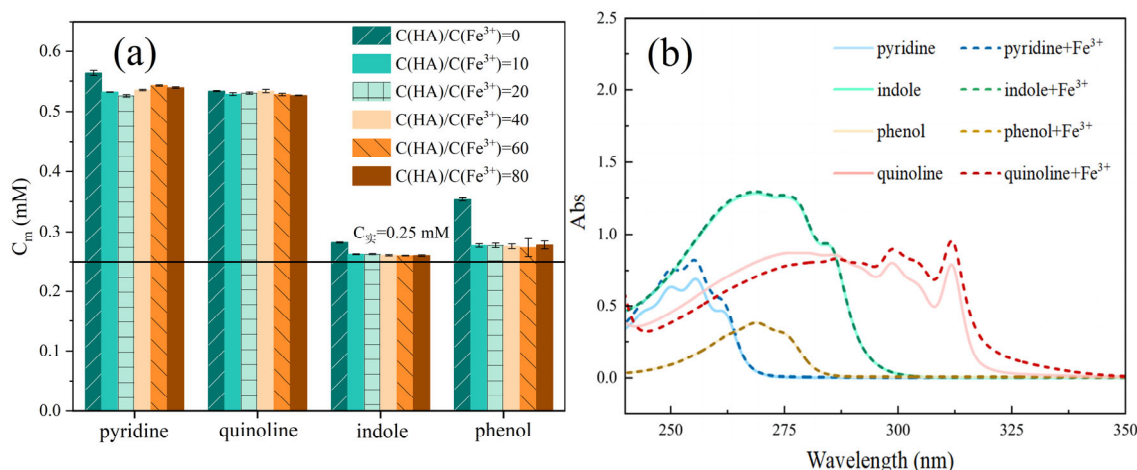


Figure 4. (a) Elimination effect of HA in Fe^{3+} during testing of pollutants; (b) Effect of HA on the absorbance of pollutants

3.4. Effect of HA on the elimination of Fe^{3+} at different concentrations

The effect of HA on eliminating interference from various concentrations of Fe^{3+} during phenol and indole determination is illustrated in Fig. 4. With the addition of HA, the interferences generated by different concentrations of Fe^{3+} were effectively suppressed, which indicates that the interference elimination of Fe^{3+} by HA has a wide range of concentration applicability. When Fe^{3+} concentration ranged from 0.1 to 2 mM, C_m/C_0 was $<10\%$. The masking effect of HA on Fe^{3+} in the indole test surpassed that in phenol, with a testing error of around 5%, owing to Fe^{3+} 's lesser interference on indole determination compared to phenol (Fig. 1). The masking effect of HA on Fe^{3+} did not significantly improve with the increase of the $C(\text{HA})/C(\text{Fe}^{3+})$ ratio from 10 to 700, consistent with findings in Section 3.4. Thus, adding HA at 10 times the amount of Fe^{3+} is adequate for interference elimination.

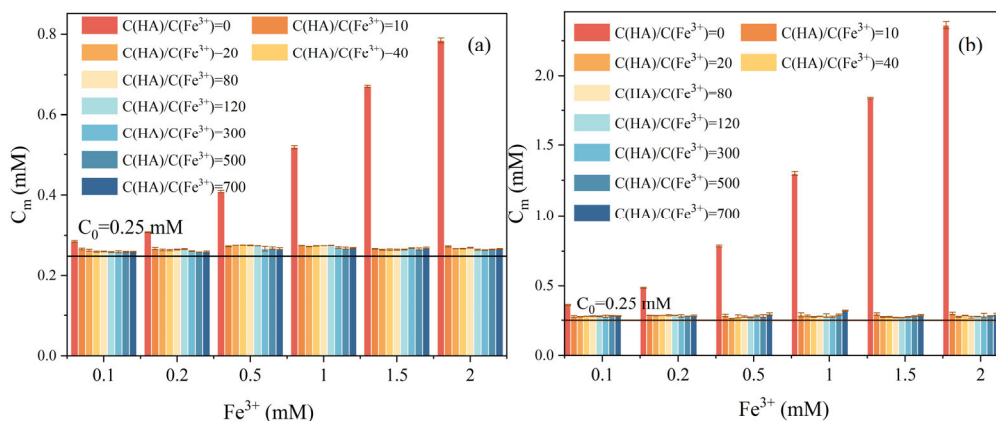


Figure 4. Effect of HA on the elimination of Fe^{3+} interference at different concentrations in the determination of indole(a) and phenol(b)

4. CONCLUSIONS

In the determination of typical pollutants in coking wastewater by spectrophotometry, the presence of Fe^{3+} can cause significant relative errors in quantifying pyridine, indole, quinoline, and phenol. Moreover, the higher the concentration of Fe^{3+} , the greater the determination error. At equivalent concentrations, Fe^{3+} affects pollutant test results in the order of pyridine, quinoline, phenol, and indole. HA itself significantly interferes with the testing of pyridine and quinoline, rendering it unsuitable as a masking agent for Fe^{3+} in the determination of these substances in water. However, it exhibits a superior capacity to mitigate Fe^{3+} interference in the determination of phenol and indole in water. When the concentration ratio of HA to Fe^{3+} exceeds 10, it effectively mitigates the interference of 0.1~2 mM Fe^{3+} on the testing of indole and phenol. This ensures that the relative errors in phenol and indole determination remain within 10% and 5%, respectively. Moreover, excessive addition of HA does not impact pollutant test results.

ACKNOWLEDGMENTS

This work was supported by Key Research & Development and Promotion of Special Project (Scientific Problem Tackling) of Henan Province (222102320102, 232102320141), Project funded by China Postdoctoral Science Foundation (2023M731170), Major Science and Technology Special Projects of Henan Province (221100320200), Key Research and Development Program of Hunan Province (231111320200), Doctoral Fund Project of Henan Polytechnic University (39B2022-39)

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