Study On the Degradation Mechanism of 2-Amino-4-Acetaminoanisole From Wastewater by Nano-Fe3O4 Catalyzed Heterogeneous Fenton System

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Abstract

Wide use of 2-Amino-4-Acetaminoanisole (AMA) as a coupling component in the synthesis of many commercial dyes leads to the generation of AMA dyed wastewater. Discharge of untreated AMA dyed wastewater could bring environmental concerns. The present study featured H$_2$O$_2$ heterogeneous Fenton system to degrade 2-Amino-4-Acetaminoanisole from wastewater using nano-Fe$_3$O$_4$ catalyst prepared via the co-precipitation method. Based on a single factor and taking the AMA removal rate as the response value, the Box-Behnken (BBD) response surface method was used to investigate the individual effects of Fe$_3$O$_4$ dosage, H$_2$O$_2$ dosage, initial pH, and reaction time. For the interaction study, the experimental data were processed with Design-Expert 10.0 software to obtain a quadratic response surface model. The results showed that the order of the influence of the four independent variables on the response value is as follows: nano-Fe$_3$O$_4$ dosage > H$_2$O$_2$ dosage > reaction time > pH. The obtained mathematical model exhibited a high degree of fit with the maximum AMA removal efficiency reaching to 100%. The optimal reaction conditions considered in this study are 1.70 g/L of Nano-Fe$_3$O$_4$ dosage, 53.52 mmol/L of H$_2$O$_2$ dosage, pH 5.14 and 388.97 mins as system reaction time. Furthermore, HPLC-MS was employed to analyze the degradation mechanism of AMA and the reaction intermediate products. Findings of this research provides fundamental theory and could guide subsequent practical AMA treatment during wastewater treatment.

1. Introduction

Aniline is an important pollutant in industrial wastewater (Chen S. et al. 2009; Naushad et al. 2016; Wang L. et al. 2007), and is listed as one of the priority pollutants by the U.S. Environmental Protection Agency and the Chinese Ministry of Environmental Protection (Wang D. et al. 2011). Aniline is also included in "14 key environmental pollutants blacklist" by the European Union (Bi and Huang 2013). Aniline compound is a highly toxic substance with hazardous properties belonging to category 6.1 toxic substances with carcinogenic, teratogenic, and mutagenic effects (Emtiazi et al. 2001). Improper contact with aniline compounds can cause hypoxia in the human tissues and damage the central nervous system, cardiovascular system, and other organs. It is even lethal in severe cases. Improper discharge of aniline-containing wastewater could cause serious pollution to the surrounding environment (Xie et al. 2012). 2-amino-4-acetaminoanisole (AMA) is one type of aniline, the main downstream products of which include Disperse Blue HGL, Disperse Blue 79, and other dyes (Sekar 1996). The process of producing such products results in a large number of by-products like 2-nitro-4-methoxyaniline and 3-nitro-4-methoxyaniline. Meanwhile, the wastewater also contains a high level of sulfuric acids and acetic acid. In the light of the above, it is necessary to develop an efficient and economical method for the treatment of 2-amino-4-acetaminoanisole production wastewater.

The remediation of this type of wastewater faces great challenge (Sekar 1996). The commonly used treatment methods include adsorption (Fakhri 2017; Ghadiri et al. 2020), electrochemistry (Shang et al. 2020), photocatalytic oxidation (Haspulat Taymaz et al. 2021; Kumawat et al. 2019), and biodegradation
Some of these technologies have the disadvantages of low efficiency, secondary pollution, and high-cost concerns. As aniline and its derivatives are recognized as hard-to-degrade organic compounds, it is usually necessary to use a strong oxidant to assist degradation (Benito et al. 2017; Ku et al. 2010; Yan J. et al. 2011). Advanced oxidation processes (AOPs) can be used as an effective and feasible technology to remove organic pollutants, by generating active hydroxyl radicals (·OH) to achieve the purpose of degradation (Chaturvedi and Katoch 2020; Haspulat Taymaz et al. 2021; Yan Z. et al. 2021).

Yang et al. (Yang C. et al. 2021) prepared Fe (II)-nano-Fe$_3$O$_4$@PAC heterogeneous Fenton catalyst (MFC) by coprecipitation impregnation method, and reported that MFC is an effective catalyst in the Fenton process for aniline degradation. The degradation and mineralization rate of 5 mg / L aniline solution reached 91.2% and 75.77% within 30 min, respectively. In addition, Fe$^{2+}$/Fe$^{3+}$ on the surface of MFC and Fe$^{2+}$/Fe$^{3+}$ in the solution affected the degradation of aniline. Using SnO$_2$-Sb$_2$O$_3$-pto / Ti anode, aniline was effectively degraded in alkaline medium with pH 11.0 by electrocatalytic oxidation (Li et al. 2003). Duran A et al. (Duran et al. 2018) also studied the degradation of aniline aqueous solution by the combination of solar energy/TiO$_2$ system and electron acceptors (such as Na$_2$S$_2$O$_8$ and/or H$_2$O$_2$). It was found that the solar / TiO$_2$ / Na$_2$S$_2$O$_8$ process is more effective than the solar/TiO$_2$/H$_2$O$_2$ process.

In the Fenton oxidation process, Fe$_3$O$_4$ nanoparticles (MNPs) catalyze H$_2$O$_2$ to generate hydroxyl radicals through their inherent peroxidase-like activity. Not only the generation of hydroxyl radicals but a large number of Fe$_3$O$_4$ nanoparticles in the solid phase can still be present in the solution and can be easy to reuse (Munoz et al. 2015). Hydroxyl radicals as strong oxidants have the ability to decompose most organic pollutants. Existing studies have shown that the heterogeneous Fenton system with nano- Fe$_3$O$_4$ catalyzed by H$_2$O$_2$ can be used for the degradation and removal of organic pollutants (Chen F. et al. 2017; Yang C. et al. 2021; Yang Z. et al. 2018) such as antibiotics, azo dyes (Benabbas et al. 2021), and aniline, and the decolorization of wastewater (Xu et al. 2018). However, its application in the degradation of AMA has not been reported yet.

In the present study, a nano-Fe$_3$O$_4$ catalyst was prepared based on the co-precipitation method, and the degradation performance of the catalyst in the H$_2$O$_2$ heterogeneous Fenton system on AMA was studied. Furthermore, the degradation mechanism of AMA was also analyzed in this study.

2. Materials And Methods

2.1 Reagents and materials

All reagents are chromatographically pure and analytically pure. These include 3-amino-4-methoxyacetanilide standard product (content > 98.0%, Tokyo Chemical Industry Co., Ltd.); Acetonitrile (99.0%, Sigma-Aldrich); methanol (99.0%, Sigma-Aldrich); dichloromethane (99.0%, Sigma-Aldrich); ferrous sulfate (FeSO$_4$·7H$_2$O, Tianjin Damao Chemical Reagent Factory); iron (FeCl$_3$·6H$_2$O, Tianjin Tianli
Chemical Reagent Co., Ltd.); and ammonia (25% w/v, Sigma-Aldrich). Ultrapure water was used throughout the experimentation. In addition, various lab instruments facilitated the study. These include XZ-10DTD ultrasonic cleaning instrument (Ningbo Xinzhi Biological Technology Co., Ltd); UGC-24C water bath nitrogen blowing instrument (Nanjing Emmanuel Instrument Equipment Co., Ltd); HH-S11-2-3 electric heating constant temperature water bath (Shanghai Yuejin Medical Equipment Factory); PHB-5 handheld pH meter (Hangzhou Dewei Instrument Technology Co., Ltd); and 84-A1 six-link magnetic stirrer (Shanghai Hongyi Instrument Equipment Co., Ltd).

2.2 Preparation of Nano-Fe₃O₄

Fe₃O₄ nanoparticles were prepared by coprecipitation method. Briefly, a certain amount of FeSO₄·7H₂O and FeCl₃·6H₂O with the molar ratio of 3:4 was dissolved in 700 ml ultrapure water and the total iron concentration of 0.1 mol/L was generated. The solution was then transferred to a 1000 ml round bottom flask, and connected with a gas pipe, a pH meter, and a mechanical stirring paddle. The gas flow rate was controlled to 0.1 L/min and the dissolved oxygen in the water was removed for 10 min. The mechanical stirring speed was gradually increased to 2000 R/min. NaOH solution was also gradually added into the above mixed solution and the stirring speed was maintained. When pH reached 6.5, a black colloidal substance appeared, and NaOH solution continued to be added until pH reached 13.0. This state was kept and stirred for 30 min. The pH probe was then replaced with a thermometer with continued stirring. After heating to 80 °C, the high temperature was kept for 30 min to crystallize the material. After the mixture was reduced to room temperature, the solid particles were separated by the magnetic field and cleaned several times with ultrapure water. The pH of the supernatant was eventually dropped to 7. The magnetic particles were evenly dispersed in the anaerobic reagent bottle filled with ultrapure water. After each use of the catalyst, the high purity nitrogen was blown for 15 min to remove oxygen, and the nano-Fe₃O₄ particles were stored in the anaerobic closed water environment.

2.3 Characterization of the catalyst

The phase analysis of the material was carried out by X’PERT PRO X-ray diffractometer (Panako, Netherlands) using the Cu target radiation, 40kV as the test voltage, 40mA as the current, and the scanning range of 10°~90° (2theta). At different scales and magnifications, the morphologies of the samples were analyzed by SU8010/S4800 (Japan/Hitachi) high-resolution cold-field emission scanning electron microscope (SEM) with a working voltage of 5kV and a resolution of 1.3nm. SEM analysis was accompanied with an energy dispersive X-ray spectroscopy (EDS) to determine the elemental composition of the catalyst.

2.4 AMA wastewater indicator monitoring

AMA was determined by Agilent 1260 high-performance liquid chromatography equipped with Zorbax Eclipse Plus C18 chromatographic column (column length 150 mm, inner diameter 4.6 mm, particle size 3.5 µm). The experimental conditions were as follows: column temperature: 40 °C; injection volume: 5µL; detection wavelength: 254 nm and flow rate: 1.2 mL/min. The Mobile phase was a mixture of
methanol/ammonium acetate buffer (v/v: 33/67) with 1 g/L of ammonium acetate buffer. The wastewater studied in this project comes from the mother liquor water of a dyeing and chemical company in China. The wastewater production process is that para-anisole undergoes acetylation, nitrification, and other reactions, and then undergoes reduction, precipitation, centrifugation, drying, and other processes to finally obtain 2- Amino-4-acetamido anisole. Due to the long production line, wastewater was generated in each process. Preliminary determination of the composition indicators of the wastewater was carried out, as shown in Table 1.

| AMA wastewater indicators | COD (mg/L) | Chroma (pcu) | pH |
|---------------------------|------------|--------------|----|
| AMA (µg/L)                | 4800       | 39150        | 7.7|
| 3.04×10^5                |            |              |    |

2.5 Single factor test and response surface method

The single-factor method was used to study the effects of the dosage amount of H_2O_2, the dosage amount of Fe_3O_4 particles, pH, reaction time, and reaction temperature on AMA removal rate. For instance, taking the influence of the amount of H_2O_2 on the removal of AMA, the experimental steps were first to control the amount of Fe_3O_4 nanoparticles to 2 g/L at room temperature 22 °C and added to a three-necked flask containing AMA production wastewater. To the above solution, the H_2O_2 solution was added at the dosage of 5, 10, 25, 50, 75, 100, 125, 150 mmol/L, respectively, and stirred continuously for 360 minutes. The removal rate of AMA can be obtained according to formula (1).

\[ R = \left( \frac{\rho_0 - \rho_t}{\rho_0} \right) \times 100\% \]  

(1)

where \( \rho_0 \) is the initial mass concentration of AMA (µg/L); \( \rho_t \) is the mass concentration of AMA after treatment, µg/L.

The removal rate of AMA degradation by Fe_3O_4 nanoparticles was determined by controlling the pH of the solution, the dosage of Fe_3O_4 nanoparticles, reaction time, and temperature. According to the analysis of single-factor experiment results, box Behnken was used to design the experiment. The dosage of nano-Fe_3O_4, H_2O_2, pH, and reaction time were set as independent variables, and the concentration of AMA was used as the response value. The single and interactive effects of the dosage of nano-Fe_3O_4, the dosage of H_2O_2, pH, and reaction time were investigated. Design expert 10.0 software was used to process experimental data and analyze the best experimental conditions.

3. Results And Discussion

3.1 Characterization of nanometer Fe_3O_4 catalyst
Figure 1 shows the XRD patterns of the as-prepared sample. Compared with the data in the standard card JCPDS(NO.65-3107), it can be seen that there are no other miscellaneous peaks. The pure phase magnetite Fe$_3$O$_4$ with cubic inverse spinel structure is obtained, and the highest diffraction peak of the crystal plane is near 35.56° (2285). The as-synthesized sample has shown sharp diffraction peaks, high signal-to-noise ratio, and good crystallinity. Figure 2 depicts an SEM scan image and EDS analysis of the as-prepared sample. Figure 2 (a), (b), and (e) show the even distribution of Fe and O, with a ratio of about 3:4. This indicates that the as-prepared sample could be Fe$_3$O$_4$.

### 3.2 Feasibility Study

Parallel experiments were carried out in a Fenton-like system catalyzed by nano-Fe$_3$O$_4$ and Fenton system catalyzed by FeSO$_4$, and the removal efficiencies of the two catalysts were compared under the same conditions. At room temperature of 22 °C, the dosage of Fe$_3$O$_4$ nanoparticles and FeSO$_4$ was firstly set to 2 g/L, which were added into three flasks containing AMA production wastewater. To the above mixture, the H$_2$O$_2$ solution was then added at various dosages of 5, 10, 25, 50, 75, 100, 125 and 150 mmol/L, respectively. The solution was continuously stirred for 360 mins. The indexes of AMA production wastewater treated by the two systems were determined, as shown in Fig. 3.

As shown in Fig. 3 (a), (b), and (c), the Fenton-like system of nano-Fe$_3$O$_4$ and the Fenton system of FeSO$_4$ have obvious treatment effects on AMA, COD, and chromaticity in AMA production wastewater. The treatment efficiency of nano-Fe$_3$O$_4$ microspheres is obviously better than that of FeSO$_4$ in terms of AMA degradation and COD removal, indicating that nano-Fe$_3$O$_4$ microspheres are investigable in AMA wastewater treatment process.

During the change of H$_2$O$_2$ solution dosage from 5 to 150 mmol/L in Fig. 3, the removal of AMA and COD first decreased and then increased whereas the chromaticity decreased to nearly complete removal. The best AMA removal efficiency was achieved at 75 mmol/L dosage of H$_2$O$_2$ solution. The removal rate of AMA, COD and Chromaticity reaches 99.74%; 95.00% and 99.80%, respectively. The concentration of AMA and COD reached 804.35 g/L and 240 mg/L, respectively. While the chromaticity was 78 pcu. With the continual increase of H$_2$O$_2$ dosage, the removal rate of AMA began to decrease. The experimental results revealed that increasing the dosage of H$_2$O$_2$ can produce more ·OH radicals, which eventually enhance the removal rate of AMA. However, the addition of too much H$_2$O$_2$ results in ·OH consumption, which generates less oxidizing HO$_2^·$. HO$_2^·$ can not only react with H$_2$O$_2$ to prevent it from generating ·OH but also it can react with ·OH to prevent it from degrading AMA. Successful catalytic oxidation of AMA in the Fenton system was attained at 75 mmol/L, which could be considered as the optimum dosage of H$_2$O$_2$.

### 3.3 Single Factor Test

#### 3.3.1 Effect of pH on Removal Efficiency
To study the effect of pH alteration on the Fenton removal of the AMA, COD and chromaticity, 2 g/L of the nano-Fe$_3$O$_4$ catalyst along with 75 mmol/L of H$_2$O$_2$ solution was subjected into the system at the reaction temperature of 22 ℃. The reaction time was set to 360 mins. The pH range of 2–9 was considered in the experiment. Figure 4 (a), (b), and (c) depicts the experimental results.

With the pH rising from 2 to 9, removal of both AMA and COD initially increases and then decreases gradually whereas the chromaticity removal gradually declines. The maximum removal efficiency of AMA, COD and Chromaticity appeared at the pH of 5 with respective removal rates of 99.99%, 94.61% and 99.98%. The concentration of AMA and COD were 15.76 g/L and 258 mg/L, respectively; while the initial chromaticity was 8 pcu. The results revealed that Fe$_3$O$_4$ nanospheres have good catalytic activity under weak acid conditions, but the catalytic activity is inhibited under alkaline conditions. Therefore, it can be stated that the best solution pH value for better degradation and removal of AMA in Fe$_3$O$_4$ + H$_2$O$_2$ Fenton system is 5.

### 3.3.2 Effect of Dosage of Nanometer Fe$_3$O$_4$ on Removal Efficiency

The effect of Fe$_3$O$_4$ catalyst dosage on the removal of AMA, COD and Chromaticity was investigated using 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g/L catalyst loading and the results were depicted in Fig. 5 (a), (b), and (c). Apart from pH set to 5, the H$_2$O$_2$ solution dosage along with the temperature and reaction time remains the same as in the case of pH alteration on the removal rate.

As the Fe$_3$O$_4$ catalyst dosage increases from 0.5 g/L to 4.0 g/L, the chromaticity removal rate also increases. The initial increase of Fe$_3$O$_4$ dosage to 1.0 g/L showed strong change in terms of the chromaticity removal rate (Fig. 5 (c)) while the removal rate is almost constant after 1.0 g/L catalyst loading. The removal efficiency of AMA and COD followed similar pattern. Both AMA and COD first increased and then decreased gradually. The maximum removal efficiency for either AMA, COD or Chromaticity was achieved at 1.5g/L Fe$_3$O$_4$ catalyst loading with removal rate of 99.99%, 98.90% and 99.98%, respectively. The concentration of AMA and COD were 10.33 g/L and 54 mg/L, respectively, while the chromaticity was 6 pcu. In line of the above, it can be stated that the best Fe$_3$O$_4$ catalyst dosage for the degradation of AMA in the Fe$_3$O$_4$ + H$_2$O$_2$-like Fenton system is 1.5 g/L.

### 3.3.3 Effect of Reaction Time on Removal Efficiency

The effect of reaction time on the removal of AMA, COD and Chromaticity was studied considering various reaction times (60, 120, 180, 240, 300, 360, 420 and 480 mins). The values for temperature, nano-Fe$_3$O$_4$ dosage, H$_2$O$_2$ solution and pH were kept constant. Figure 6 (a), (b), and (c) depicts the experimental results.

As the reaction time increases from 60 min to 480 min, the removal rates for chromaticity, AMA and COD also increase. When the reaction time reaches 360 min, the removal efficiency does not increase significantly or even decreases to a certain extent. The removal rate for AMA, COD and Chromaticity
reaches 99.99%, 98.50% and 99.85%, respectively. The respective concentration of AMA and COD were 10.46 g/L and 72 mg/L while the chromaticity was 57 pcu. At reaction time of 360 mins, the optimum AMA degradation rate was attained by Fe₃O₄ + H₂O₂ Fenton system.

### 3.3.4 Influence of Temperature on Removal Efficiency

The effect of reaction temperature on Fenton removal of AMA, COD and Chromaticity was also studied by varying temperatures (0, 5, 10, 15, 20, 25, 30 and 35 ℃). The reaction time was set to 360min and other experimental parameters and conditions were kept constant. The results are shown in Fig. 7 (a), (b), and (c).

As the reaction temperature rises from 0 ℃ to 35 ℃, the chromaticity removal rate also rises first and is nearly completely removed after reaching 10 ℃. The removal rate of AMA and COD first increased and then decreased. The best removal rates were attained when the reaction temperature reached 25 ℃. The respective removal rate of COD and Chromaticity were 99.42% and 99.98%. At this reaction temperature, AMA is no longer detectable. COD concentration was detected as 28 mg/L whereas chromaticity was 8 pcu. The results indicated that the reaction temperature affects the activity of hydroxyl radicals. As the reaction temperature rises, the activity of free radicals can be enhanced. However, too high temperature could decompose hydrogen peroxide. Therefore, it can be deduced that the best reaction temperature for degradation and removal of AMA by Fe₃O₄ + H₂O₂ Fenton system is 25 ℃.

### 3.4 Response surface methodology (RSM)

#### 3.4.1 Design and Data

According to the results of a single-factor experiments, the dosage of nano-Fe₂O₄ (A), H₂O₂ (B), pH (C), and reaction time (D) were determined as the main influencing factors. The value range of each factor was 1.0 ~ 2.0 g/L, 50 ~ 100 mmol/L, 4 ~ 6, 300 ~ 420 min, respectively. The concentration of AMA is taken as the response value and recorded as the dependent variable Y. Based on the principle of Box-Behnken central combination design, an experimental formula with 4 factors and 3 levels was designed. See Table 2 for the levels and codes of each factor.
Table 2
Levels of the factors taken for RSM

| Coded value | Name            | Units   | Levels       |
|-------------|-----------------|---------|--------------|
|             |                 |         | -1     0     1 |
| A           | Fe$_3$O$_4$ dosage | g/L     | 1.0  1.5  2.0 |
| B           | H$_2$O$_2$ dosage | mmol/L  | 50  75  100 |
| C           | pH              | -       | 4  5  6    |
| D           | Reaction Time   | min     | 300 360 420 |

Taking the concentration (Y) of AMA as the response value, the experimental data are fitted by polynomial regression analysis, and a typical four-factor quadratic polynomial model can be obtained. The model is as follows:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

Where $\beta_0$ is the constant term representing the center point correction coefficient; $X_i$ is the experimental factor; $\beta_i$ is the linear coefficient; $\beta_{ij}$ is the quadratic term coefficient; $\beta_{ij}$ is the interaction term coefficient; $\varepsilon$ is the residual error of the constructed model.

### 3.4.2 Regression equation and variance analysis

Based on the principle of Box-Behnken central combination design, the experimental scheme was designed, and a total of 29 groups of experiments were carried out. The experimental design scheme and results are shown in Table 3.
Table 3
Responses values for different experiment conditions

| Run | (A) Fe₃O₄ (g/L) | (B) H₂O₂ (mmol/L) | (C) pH | (D) Reaction time (min) | AMA (µg/L) |
|-----|----------------|-------------------|--------|-------------------------|------------|
| 1   | 1.5            | 75                | 5      | 360                     | 10.46      |
| 2   | 1              | 75                | 5      | 300                     | 968.47     |
| 3   | 2              | 75                | 6      | 360                     | 124.79     |
| 4   | 1.5            | 75                | 6      | 300                     | 527.34     |
| 5   | 1.5            | 75                | 4      | 420                     | 122.67     |
| 6   | 2              | 50                | 5      | 360                     | 357.64     |
| 7   | 1              | 50                | 5      | 360                     | 1016.85    |
| 8   | 1.5            | 75                | 5      | 360                     | 9.74       |
| 9   | 1.5            | 75                | 5      | 360                     | 12.14      |
| 10  | 1.5            | 50                | 6      | 360                     | 735.28     |
| 11  | 1.5            | 100               | 5      | 300                     | 288.82     |
| 12  | 1.5            | 75                | 4      | 300                     | 348.91     |
| 13  | 1.5            | 50                | 4      | 360                     | 365.33     |
| 14  | 1.5            | 100               | 4      | 360                     | 259.08     |
| 15  | 1              | 75                | 4      | 360                     | 518.93     |
| 16  | 1              | 75                | 6      | 360                     | 945.93     |
| 17  | 2              | 75                | 5      | 300                     | 177.94     |
| 18  | 1.5            | 75                | 6      | 420                     | 125.14     |
| 19  | 1.5            | 75                | 5      | 360                     | 10.67      |
| 20  | 1.5            | 100               | 5      | 420                     | 72.14      |
| 21  | 1.5            | 50                | 5      | 300                     | 650.98     |
| 22  | 2              | 75                | 5      | 420                     | 76.69      |
| 23  | 1.5            | 100               | 6      | 360                     | 208.61     |
| 24  | 1.5            | 50                | 5      | 420                     | 334.38     |
Using Design-Expert 10.0 software, the experimental data in Table 3 were fitted by quadratic multinomial regression, and the following equation was obtained.

\[
Y = + 12375.257 - 4279.014 \times A - 48.485 \times B - 570.788 \times C - 27.522 \times D + 2.909 \times AB - 274.510 \times AC + 3.999 \times AD - 4.204 \times BC + 0.0167 \times BD - 0.733 \times CD + 1144.219 \times A^2 + 0.351 \times B^2 + 162.892 \times C^2 + 0.030 \times D^2
\]

(3)

From Table 4, it can be seen that the F value of the model is 353.98, which is much greater than 1. This indicates that the model is significant. At the same time, the F values of the four influencing factors, nano-Fe$_3$O$_4$ dosage, H$_2$O$_2$ dosage, pH, and reaction time, are greater than 1, respectively. Similarly, they all have significant effects on the AMA removal rate, and according to the size of the F value, it can be judged that the order of their influence degree is nano-Fe$_3$O$_4$ dosage > H$_2$O$_2$ dosage > reaction time > pH. This implies the nano-Fe$_3$O$_4$ dosage is the key factor affecting AMA degradation. The corresponding P values of nano-Fe$_3$O$_4$ dosage (A), H$_2$O$_2$ dosage (B), pH (C), and reaction time (D) are all less than 0.05, which also show that they have a significant effect on AMA removal. In addition, the P values corresponding to the six interaction situations of AB, AC, AD, BC, BD, and CD are all less than 0.05, indicating the significant effect of the interaction between the dosage of nano-Fe$_3$O$_4$ (A), the dosage of H$_2$O$_2$ (B), pH (C) and reaction time (D). The determination coefficient of the model R$^2$ was found to be 99.72%, which indicates that the probability of the model can explain the change of response value by 99.72%. Compared to the corrected determination coefficient (R$^2$adj = 99.44%), only 0.56% of the response value cannot be predicted by the model. According to the coefficient of variation (CV = 6.85% < 10%), it can be stated that the reliability of the experiment and the accuracy of the model are high. The signal-to-noise ratio is equal to 60.304 > 4, which indicates that there is enough signal and the value is within a reasonable range.
Table 4
ANOVA for Response Surface Quadratic model

| Source         | Sum of Squares | df | Mean Square | F       | p-value | Source | Prob > F |
|----------------|----------------|----|-------------|---------|---------|--------|----------|
| Model          | 2.552E + 006   | 14 | 1.823E + 005| 353.98  | <0.0001 | significant |
| A- Fe₃O₄ dosage | 9.450E + 005   | 1  | 9.450E + 005| 1835.25 | <0.0001 |
| B- H₂O₂ dosage | 3.134E + 005   | 1  | 3.134E + 005| 608.56  | <0.0001 |
| C-pH           | 54050.39       | 1  | 54050.39    | 104.97  | <0.0001 |
| D-Reaction time| 2.834E + 005   | 1  | 2.834E + 005| 550.35  | <0.0001 |
| AB             | 5288.93        | 1  | 5288.93     | 10.27   | 0.0064  |
| AC             | 75355.74       | 1  | 75355.74    | 146.35  | <0.0001 |
| AD             | 57559.21       | 1  | 57559.21    | 111.79  | <0.0001 |
| BC             | 44188.24       | 1  | 44188.24    | 85.82   | <0.0001 |
| BD             | 2496.00        | 1  | 2496.00     | 4.85    | 0.0450  |
| CD             | 7740.48        | 1  | 7740.48     | 15.03   | 0.0017  |
| A²             | 5.308E + 005   | 1  | 5.308E + 005| 1030.81 | <0.0001 |
| B²             | 3.126E + 005   | 1  | 3.126E + 005| 607.02  | <0.0001 |
| C²             | 1.721E + 005   | 1  | 1.721E + 005| 334.26  | <0.0001 |
| D²             | 74122.84       | 1  | 74122.84    | 143.95  | <0.0001 |
| Residual       | 7208.68        | 14 | 514.91      |         |         |
| Lack of Fit    | 7202.46        | 10 | 720.25      | 463.28  | <0.0001 | significant |
| Pure Error     | 6.22           | 4  | 1.55        |         |         |
| Cor Total      | 2.559E + 006   | 28 |            |         |         |

Note: P < 0.01 means the model is "highly significant", P < 0.05 means the model is "significant", P > 0.05 means the model is "not significant", model determination coefficient \( R^2 = 0.9972 \), correction determination coefficient \( R^2_{adj} = 0.9944 \), prediction determination coefficient \( R^2_{pred} = 0.9838 \), coefficient of variation \( CV = 6.85\% \), signal-to-noise ratio = 60.304.

### 3.4.3 Residual Analysis

Residual refers to the error between the predicted value and the actual value given by the model established by the software. Among them, the internalized residual is used to express the degree to which the standard deviation deviates from the actual and predicted response value, which is mainly shown
graphically as to whether each data point is linearly distributed. Foreign student residuals are used to
describe whether each group of data is an outlier relative to the fitted equation. As shown in Fig. 8a, the
experimental data points are evenly distributed on both sides of the fitting straight line, and the data has
no problem. This further confirms that the predicted value is close to the actual value. As shown in Figs.
8b and 8c, the data points are randomly distributed without any regularity, which proves the randomness
of the experimental group. The residual values are all within the range of 3, indicating that there are no
abnormal points in the fitting process, and the experimental operation is reliable. Figure 8d shows a linear
relationship between the actual value of AMA concentration and the predicted value. The experimental
data points are basically distributed on a straight line, which highlights that there is a good linear
relationship between the predicted value and the actual value of the model. Therefore, this implies the
model has good accuracy and persuasion.

3.4.4 Factor effect analysis

To further understand the removal of AMA by experimental factors and the interaction between nano-
Fe$_3$O$_4$ dosage, H$_2$O$_2$ dosage, pH, and reaction time, a quadratic response surface diagram was drawn
using software, as shown in Fig. 9.

As portrayed in Fig. 9, when one factor is fixed, the response value always increases first and then
decreases with the change of another factor. This explains that each factor has an optimal value within
the experimental level range. Any two factors taken as the central values, the contour lines corresponding
to the response surface are elliptical rather than circular, which confirms the obvious interaction between
the four factors. The optimal values of the model are 1.70 g/L of nano-Fe$_3$O$_4$ dosage, 53.52 mmol/L of
H$_2$O$_2$ dosage, pH of 5.14, 388.97 min as the reaction time, and −105.83 g/L, the concentration of AMA.
The negative concentration of AMA could be linked to the removal efficiency which reached the highest
extent under the set condition. This highlights that AMA has been completely degraded and removed
under this condition.

3.5 Degradation Mechanism

Figure 10 indicates mass spectrogram of AMA degradation in nano-Fe$_3$O$_4$ + H$_2$O$_2$ Fenton system. Before
the reaction starts, only AMA was present in the solution with the mass-to-charge ratio (m/z) of 180. After
10 min of Fe$_3$O$_4$ catalytic reaction, the compounds with m/z of 237, 196, and 154 appeared on the mass
spectrogram. According to the intermediate product and accessory product 12 in the production process
of AMA, the compound with m/z of 237 can be judged to be 2, 4-diaminoanisole while the compound
with m/z of 196 is presumed to be the compound generated by ·O$_2^-$ and ·OH radicals destroying the C
bond at the para-position of the amino group in AMA. Subsequently, the acetamido functional group of
the compound was oxidized by ·O$_2^-$ and ·OH radicals to form a compound with m/z of 154. When the
reaction proceeded for 30 min, new compounds were produced, which were compounds with m/z of 165,
141, 124, and 112, respectively. According to the AMA production method, the compound with m/z of 165
can be judged to be p-methoxy acetanilide. The acetamido functional group of p-methoxy acetanilide can
then be oxidized by ·O$_2^-$ and ·OH radicals to form p-amino anisole with m/z of 124. At the same time, the
compound with m/z of 154 could be further oxidized to form a compound with m/z of 141 and resorcinol with m/z of 112.

With the change of reaction time from 30 min to 240 min, each substance was gradually degraded. Over time, various substances are eventually degraded into small molecular organic substances such as H₂O and CO₂. Only resorcinol with m/z of 112 was found in the final mass spectrogram, and it can be inferred that the possible degradation routes of AMA are the three routes in Figure 11.

4. Conclusions

In this research, the nano-Fe₃O₄ catalyst was successfully prepared by the co-precipitation method, and the catalytic degradation performance of the catalyst for 2-amino-4-acetylaminoanisole production wastewater in an H₂O₂ heterogeneous Fenton-like system was studied. Optimized by response surface methodology, the results revealed that the Fenton-like system of nano-Fe₃O₄ possesses better degradation efficiency. The nano-Fe₃O₄ system was better than the FeSO₄ + H₂O₂ Fenton system in terms of AMA, COD and chromaticity removal. The treatment effect of nano-Fe₃O₄ microspheres is significantly better than that of FeSO₄. Through a single factor experiment, the factors affecting the removal rate of AMA, COD and chromaticity were preliminarily analyzed to obtain the optimal values. The BBD method was employed to optimize the response surface analysis. The results revealed that the four factors (nano-Fe₃O₄ dosage, H₂O₂ dosage, pH, and reaction time) had obvious interaction in the process of removing reductants. The optimal values of the model are 1.70 g/L of nano-Fe₃O₄ dosage, 53.52 mmol/L of H₂O₂ dosage, pH of 5.14, 388.97 min as the reaction time, and −105.83 g/L, the concentration of AMA.

Mass spectrogram of AMA degradation course in nano-Fe₃O₄ + H₂O₂ Fenton system was also investigated in this study. Two possible degradation pathways of AMA were deduced. One is the oxidation by ·O₂⁻ and ·OH radicals to remove acetamino functional groups, and then amino functional groups to resorcinol or Hydroquinone. The other pathway is to use ·OH radical to remove acetamino and methoxy functional groups. Finally, the resultant compounds in the two pathways can be further transformed chemically to H₂O, CO₂, and other small organic compounds through the destruction of the benzene ring. This study on the degradation mechanism of AMA can provide guidance for the same type of high concentration wastewater, and can also be further improved on the basis of this method, so as to achieve the purpose of popularization and application.

Declarations

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Figures
Figure 1

XRD patterns of magnetic Fe3O4 nano-spheres
Figure 2

SEM and EDS analysis of magnetic Fe3O4 nano-spheres
Figure 3

Removal of indexes in Fe₃O₄/FeSO₄ catalyst system

(a) AMA removal in Fe₃O₄/FeSO₄ catalyst system  
(b) COD removal in Fe₃O₄/FeSO₄ catalyst system  
(c) Chroma removal in Fe₃O₄/FeSO₄ catalyst system

(a) Effect of pH on the removal of AMA  
(b) Effect of pH on the removal of COD  
(c) Effect of pH on the removal of Chroma
Figure 4

The influence of pH on the removal rate of each index

(a) Effect of Fe₂O₃ dosage on the removal of AMA  (b) Effect of Fe₂O₃ dosage on the removal of COD  (c) Effect of Fe₂O₃ dosage on the removal of Chroma

Figure 5

The influence of Fe₃O₄ dosage on the removal efficiency of each index

(a) Effect of Reaction time on the removal of AMA  (b) Effect of Reaction time on the removal of COD  (c) Effect of Reaction time on the removal of Chroma

Figure 6

The influence of reaction time on the removal rate of each index

(a) Effect of temperature on the removal of AMA  (b) Effect of temperature on the removal of COD  (c) Effect of temperature on the removal of Chroma

Figure 7
The influence of temperature on the removal rate of each index

Figure 8

Relationships between a): internally studentized residuals and the normal probability; b): internally studentized residuals and the predicted values; c): internally studentized residuals and the experimental numbers; d): actual and predicted decolorization rate of wastewater.
Figure 9

Response surface diagram of the interaction of any two of the four factors. Interactions between: a) nano-Fe3O4 dosage and H2O2 dosage; b) nano-Fe3O4 dosage and pH; c) nano-Fe3O4 dosage and reaction time; d) H2O2 dosage and pH; e) H2O2 dosage and reaction time; f) reaction time and pH.
Figure 10

Mass spectrogram of Fe3O4 catalytic degradation of AMA by H2O2: (a) 0 min; (b) 10 min; (c) 30 min; (d) 60 min; (e) 120 min; (f) 240 min.
Figure 11

Degradation pathway of Fe3O4 catalyzed H2O2 degradation of AMA