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Original Article

Influence of Synthesis Conditions on Crystal Structure and Catalytic Performance of $CoFe_2O_4$ Nanoparticles for Tetracycline Degradation by Persulfate Activation Process

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Abstract: In this research, $CoFe_2O_4$ nanoparticles were systematically synthesized by hydrothermal method, under different synthesis conditions such as variations in pH of the mixture, in reaction time, and in temperature, to study the impact of synthesis conditions on crystal structure and catalytic performance of $CoFe_2O_4$ nanoparticles. The catalytic performance was evaluated though the degradation of tetracycline (TC) using persulfate activation process to figure out the optimal synthesis conditions. The latter were then applied to produce $CoFe_2O_4$ nanoparticles which were subsequently applied for studying the TC degradation process. The obtained results revealed that $CoFe_2O_4$ nanoparticles were successfully produced without significant impurities. pH of the mixture, reaction time, and temperature all contributed to changes in particle size, crystallinity as well as the catalytic performance. Under optimal synthesis conditions (pH 11.0, 180 °C, 12 hour), 66.1% of 10 mg/L TC solution were removed after 60 min. The TC degradation process followed the pseudo-second kinetics model, with R^2 ranging from 0.933 to 0.987, and k values within the range of 0.001 – 0.01 $mg \cdot L^{-1} \cdot min^{-1}$. Thes findings highlight the potential use of $CoFe_2O_4$ catalyst for wastewater treatment application. This research provides a simple approach to design and synthesis of $CoFe_2O_4$ magnetic catalysts for the treatment of antibiotic resdues in water.

Keywords: $CoFe_2O_4$ nanoparticles, persulfate activation, sulfate radicals, tetracycline antibiotic, water treatment, kinetics.

1. Introduction

The rapid increase in global antibiotic use, although essential for modern health care, has caused a growing environmental issue: the persistent contamination of water sources with antibiotic residues [1]. Among the most frequently used antibiotics is tetracycline (TC), which is widely applied in both human and veterinary medicine because of its broad-spectrum efficacy and low cost [2]. However, a

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significant portion of the TC used remains unmetabolized, entering the aquatic environment through wastewater, agricultural runoff, and pharmaceutical waste [3]. Their presence in natural waters not only harms aquatic organisms, but also accelerates the emergence and spread of antibiotic-resistant bacteria and resistance genes, posing a serious risk to public health [4].

Conventional wastewater treatment systems are inadequate regarding the removal of antibiotics, as those systems are primarily designed for bulk organic matters and nutrients [5]. In response, researchers have turned to Advanced Oxidation Processes (AOPs), which generate reactive radicals capable of degrading recalcitrant organic pollutants into begin products such as CO_2 and H_2O [6]. Among AOPs, persulfate ($S_2O_8^{2-}$)-based systems have gained a lot of attention due to their high oxidation potential and longer lifetime of the generated sulfate radicals ($SO_4^{\bullet-}$) [7]. Persulfate is also chemically stable, cost-effective, and easy to handle, making it suitable for large-scale applications.

Persulfate activation can be achieved via thermal, UV, or transition metal catalysis, with heterogeneous catalysts offering the advantages of reusability and reduced secondary pollution [11]. Spinel ferrites, with the general formula MFe_2O_4 (where M is a divalent metal such as Co, Mg, Ni, Zn, or Cu), have emerged as effective persulfate activators [12]. These materials exhibit high chemical stability, tunable magnetic properties, and catalytic activity over a wide range of pH [11]. Among them, cobalt ferrite ($CoFe_2O_4$) stands out due to the synergistic role of Co^{2+} and Fe^{3+} ions in persulfate activation process, as well as its superparamagnetic properties that allow for easy magnetic separation after the treatment process, reducing the treatment cost [11].

However, the catalytic performance of $CoFe_2O_4$ is closely related to its physico-chemical properties, including surface area, crystallinity, particle size, and magnetic properties, all of which are strongly dependent on the synthesis method. Techniques such as co-precipitation, hydrothermal, sol–gel, and microwave-assisted synthesis provide varying degrees of control over these parameters [13]. For example, hydrothermal methods typically yield well-crystalline particles, while co-precipitation is preferred because of its scalability and simplicity [14, 15]. Just recently, Xing et al., [16] produced $CoFe_2O_4$ nanoparticles from Metallic Organic Frameworks (MOF) by using solvothermal method followed by calcination process for the degradation of TC via peroxymonosulfate activation process. That approach presents some interesting outcomes such as high degradation efficiency, short reaction time,… the use of various organic solvents, including harmful ones, the application of high temperature (up to 800 ℃) and more costly chemical (peroxymonosulfate) compared to persulfate would limit the practical applications of $CoFe_2O_4$ nanoparticles produced by such a way. In addition, although, Xing et al., [16] reported the impact of synthesis temperature on TC degradation, they have not yet studied the impact of pH solution and reaction time of the synthesis process on the TC degradation efficiency.

This study aims to fill some gaps by experimentally synthesizing $CoFe_2O_4$ nanoparticles using hydrothermal process under mild conditions and evaluating the impact of material synthesis conditions (temperature, pH, reaction time) on the catalytic performance of $CoFe_2O_4$ in TC degradation by persulfate activation process. Through detailed characterization and performance evaluation, we seek to elucidate the relationship between synthesis parameters, material properties, and catalytic activity. The insights gained will aid in the rational design of efficient, reusable, and scalable catalysts for the remediation of antibiotic-contaminated water, a pressing environmental and public health issue.

2. Experimental

2.1. Chemicals

$Co(NO_3)_2.6H_2O$ (99%), $Fe(NO_3)_3.9H_2O$ (99%), NaOH (99%), were purchased from

Xilong Chemical, China. Tetracycline (99%) methanol (MeOH, 99%), absolute ethanol, tert-butanol (TBA, 99.5%), sodium azide (NaN_3, 99%) were purchased from Sigma Aldrich. All chemicals were used directly without further purification.

2.2. Synthesis of Materials

2.2.1. Synthesis of $CoFe_2O_4$ under Different pH Values

Three grams of $Co(NO_3)_2.6H_2O$ and 8.0 g of $Fe(NO_3)_3.9H_2O$ were simultaneously dissolved in 200 mL of deionized (DI) water. Then, the mixture was stirred for 30 min. The resulting solution was adjusted to pH 9.0, 10.0, 11.0, and 12.0. Then, the solution was vigorously stirred for 4 hour and hydrothermally treated at 180 ºC for 12 hour. The resulting mixture was washed 3 times with DI water, three times with ethanol (90%, wt.). Finally, the solid part was dried at 70 ºC for 24 hours to obtain $CoFe_2O_4$ nanoparticles.

2.2.2. Synthesis of $CoFe_2O_4$ Nanoparticles at Different Temperatures

Two first steps presented in 2.2.1 were applied. Then, the resulting mixture was adjusted to pH 11.0. The solution was then stirred vigorously for 4 hour and hydrothermally treated at 160 ºC, 180 ºC, 200 ºC, and 220 ºC for 12 hours. The resulting mixture was washed three times with DI water, 3 times with ethanol (90%, wt.). Finally, the solid part was dried at 70 ºC for 24 hours to obtain $CoFe_2O_4$ material.

2.2.3. Synthesis of $CoFe_2O_4$ Nanoparticles at Different Reaction Time

Three grams of $Co(NO_3)_2.6H_2O$ and 8 g $Fe(NO_3)_3.9H_2O$ were simultaneously dissolved in 200 mL DI water. Then, the mixture was stirred for 30 min. The resulting solution was adjusted to pH 11.0. Then, the solution was vigorously stirred for 4 hour and hydrothermally treated at 180 ºC for 6 hour, 9 hour, 12 hours, and 15 hours. The resulting mixture was washed three times with DI water, three times with ethanol (90%, wt.). Finally, the solid was dried at 70 ºC for 24 hours to obtain $CoFe_2O_4$ nanoparticles.

2.3. Material Characterization

Structural and chemical properties of the produced materials were characterized by means of X-ray diffraction (XRD), model Miniflex 600, Rigaku, Japan; Energy Dispersive X-ray (EDX) – mapping, model AZtec-Energy, Oxford (UK); and Fourier Transform Infrared Spectroscopy (FT-IR), model Jasco 4600 (Japan) while morphology of the synthesized samples was evaluated by using a scanning electron microscope (SEM), model Hitachi TM4000 plus (Japan).

2.4. TC Degradation Experiments

In order to examine the performance of $CoFe_2O_4$ catalyst regarding the degradation of TC, batch experiments were conducted in a number of conical flasks at room temperature. In a typical run, 100 mL of TC solution (C_0 = 10 mg/L) was transferred to a conical flask before adding 20 mg of $CoFe_2O_4$ catalyst. The mixture was continuously stirred using a magnetic stirrer. Before starting the reaction, a known amount of persulfate solution (3.5 mM) was added to the mixture. 5 mL of the solution was typically sampled with an interval time of 15 min, then directly filtered (0.45 µm) to remove the catalyst and analyzed for residual TC concentration using a UV–VIS spectrophotometer at 358 nm, model UH5300/Hitachi. The effect of antibiotic concentration (5–20 mg/L) was also studied. The degradation efficiency was calculated using the following equation:

$$E(\%)= (C_0-C_t).100/C_0 \quad (1)$$

where C_0 and C_t represent the initial pollutant concentration (mg/L) and the concentration (mg/L) at time t (min), respectively.

3. Results and Discussion

3.1. Influence of Synthesis Conditions (pH Value) on Crystal Structure and Catalytic Performance of $CoFe_2O_4$

X-ray diffraction (XRD) patterns of cobalt ferrite nanoparticles ($CoFe_2O_4$) for samples synthesized at different pH values are shown in Figure 1a. The results show that the pH of the reaction medium strongly affected the formation of the spinel structure and the catalytic performance of the $CoFe_2O_4$ material. XRD spectra of the synthesized samples at pH 9, 10, 11 and 12 in Figure 1a all show characteristic diffraction peaks of the cubic spinel phase of $CoFe_2O_4$, being consistent with the XRD spectrum of pristine $CoFe_2O_4$ from the literature (JCPDS card no. 22-1086), indicating that the basic crystal structure was formed over the entire pH range studied. However, the intensity and sharpness of the diffraction peaks showed obvious differences in the degree of crystallinity and crystal size among the samples. Several structural parameters were calculated using XRD data and are listed in Table 1. The Scherer formula for the crystallite size is:

$$D= K.\lambda/\beta.\cos\theta$$

where K = 0.9, λ, β and θ are the CuKα wavelength, full half-maximum and Bragg angle, respectively [17, 18].

The crystallinity Xc(%) was calculated from the XRD data by separating the integral areas of the crystalline (Acrystalline) and amorphous (Aamorphous) peaks, using the formula:

$$Xc(\%)=A_{crystalline} *100/(A_{crystalline}+A_{amorphous})$$

At pH 9.0, the XRD peaks (Figure 1a) were quite weak, accompanied by high background noise, indicating that the material had rather poor crystallinity, an incomplete spinel structure and that the amorphous or intermediate phase might still exist. This sample also gave the lowest TC removal efficiency 56.8% (Figure 1b), suggesting that the number of Co^{2+} active sites on the surface was insufficient to efficiently activate the persulfate. As the pH increased to 10, the crystallinity was significantly improved, the XRD spectrum (Figure 1a) had higher intensity and sharper peaks, resulting in an increase in removal efficiency to 65.3% (Figure 1b).

The study showed that pH of the solution significantly affected the structure and catalytic activity of $CoFe_2O_4$. At pH 11, the material achieved the highest TC removal efficiency 66.1% (Figure 1b) after 60 min. This might be due to the simultaneous possession of three important characteristics: (1) high crystallinity as shown by sharp XRD peaks (Figure 1a), nanocrystal size of ~6.72 nm (Table 1) optimizing surface area, and pure phase structure without impurities. When increasing pH to 12, although the crystallinity continued to improve, particle agglomeration might occurr (size increased to ~8.67 nm), resulting to a reduction of the active surface area [19]. As a result, the number of catalyst sites directly exposed to persulfate decreased, leading to a slight decrease in removal efficiency to 63.4% (Figure 1b). pH 11.0 was, therefore, the optimal pH for $CoFe_2O_4$ synthesis, helping to form a pure spinel structure with high crystallinity and small particle size, creating a material with a perfect balance between structural properties and catalytic ability, thereby resulting in the highest efficiency of TC antibiotic degradation through persulfate activation process.

Tables 1. Parameters calculated using XRD experimental data

Samples (conditions)	Crystallinity (%)	Crystal size (nm)
pH 9.0	65.1	2.19
pH 10.0	97.6	3.89
pH 11.0	100	6.72
pH 12.0	100	8.67

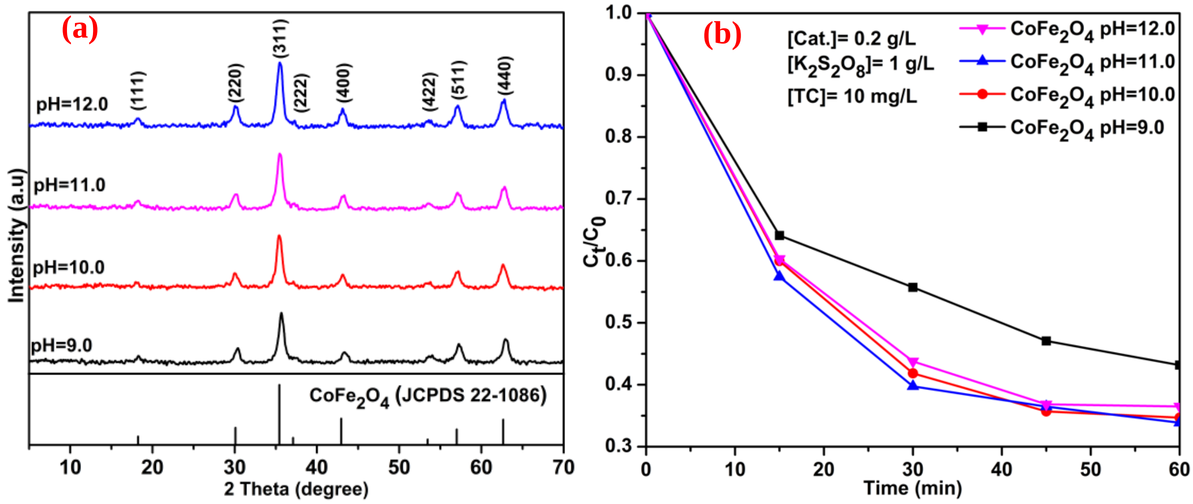


Figure 1. XRD (a), TC decomposition efficiency as a function of pH values (b).

3.2. Influence of Synthesis Conditions (Temperature) on Crystal Structure and Catalytic Performance of $CoFe_2O_4$

The synthesis temperature significantly affected the structure and catalytic activity of $CoFe_2O_4$. XRD analysis (Figure 2a) showed that the samples synthesized from 160 °C to 220 °C all had a typical spinel structure, but the crystallinity was significantly different. The sample synthesized at 180 °C gave the sharpest XRD peak, indicating a complete crystal structure [18, 20, 23], and achieved the highest TC removal efficiency, with 66.1% (Figure 2b). This could be explained by the optimal combination of high crystallinity, small particle size, and many Co^{2+} active centers. The results confirmed that 180 °C was the ideal synthesis temperature to obtain $CoFe_2O_4$ with the best catalytic activity.

However, when the temperature was further increased to 200 °C and 220 °C, although the XRD spectrum showed that the crystallinity continued to increase (Figure 2a), the diffraction peaks became increasingly sharp, the TC removal efficiency respectively decreased to 56.4% and 49.6% (Figure 2b). The main reason could be associated to the fact that at higher temperatures, the crystal growth process was too fast and strong, leading to agglomeration and increased particle size [20] (increasing from 3.35nm at 160 °C to 13.3 nm at 220 °C (Table 2)). Larger particles could lead to a decrease in specific surface area, which in turn reduces the number of catalytic sites on the surface [20]. Since the persulfate activation reaction in this study is a heterogeneous process that occurs on the surface of the material, the decrease in surface area would significantly affect the catalytic performance. Therefore, despite the higher crystallinity, the materials synthesized at 200 °C and 220 °C exhibited lower catalytic activity due to the lack of effective surface-active sites. In conclusion, 180 °C was the optimal synthesis condition for $CoFe_2O_4$ nanoparticles, providing a balance between crystallinity, particle size and surface area – the three key factors determining the catalytic performance in the degradation of TC antibiotic via persulfate activation process.

3.3. Influence of Synthesis Conditions (Reaction Time) on Crystal Structure and Catalytic Performance of $CoFe_2O_4$

Reaction time was determined to be a key factor affecting the crystal structure development and catalytic performance of

$CoFe_2O_4$ materials. XRD spectra (Figure 3a) showed that when the reaction time increased from 6 hour to 15 hours, the crystallinity of the material improved significantly (Table 3), as shown by the sharpness and increasing intensity of the diffraction peaks. At 6 hour, the material was still in the early stages of crystallization, with weak peaks and high background noise, reflecting an incomplete structure. When the time was extended to 9 hour and 12 hours, the crystallization process was stronger, especially at 12 hours, the clear XRD peaks proved that the spinel structure had fully formed. Although the 15 hour sample had the highest crystallinity, the performance results showed that the TC removal efficiency only increased to a maximum at 12 hours (66.1%), then slightly decreased to 61.5% at 15 hours (Figure 3b).

The results in Table 3 show that 12 hours is the optimal reaction time to achieve an ideal balance between crystallinity and nanoparticle size. During that reaction time, the material not only achieved a stable crystal structure but also maintained a small particle size, thereby retaining a large surface area – an important factor in increasing the number of Co^{2+}-sites accessible to persulfate activation process [21]. In contrast, when the reaction time was extended to 15 hours, the Ostwald ripening phenomenon could strongly occur [22], causing the particles to grow larger and reducing the specific surface area (9.35 nm at 15 hours compared to 6.72 at 12 hours), leading to a decrease in treatment efficiency. In summary, a reaction time of 12 hours was the optimal condition for synthesizing $CoFe_2O_4$ with excellent catalytic activity.

Tables 2. Parameters calculated using XRD experimental data

Samples (conditions)	Crystallinity (%)	Crystal size (nm)
160 °C	81.8	3.35
180 °C	100	6.72
200 °C	100	10.01
220 °C	100	13.33

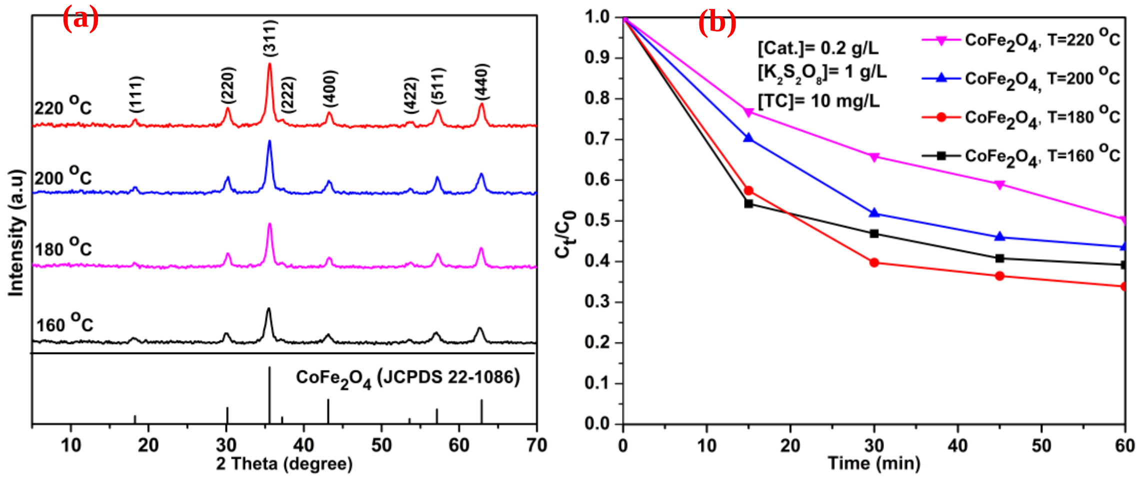


Figure 2. XRD (a), Comparison of TC decomposition efficiency between different temperature samples (b).

Tables 3. Parameters calculated using XRD experimental data

Samples (conditions)	Crystallinity (%)	Crystal size (nm)
6 hour	52.4	1.44
9 hour	78.6	4.37
12 hour	100	6.72
15 hour	100	9.35

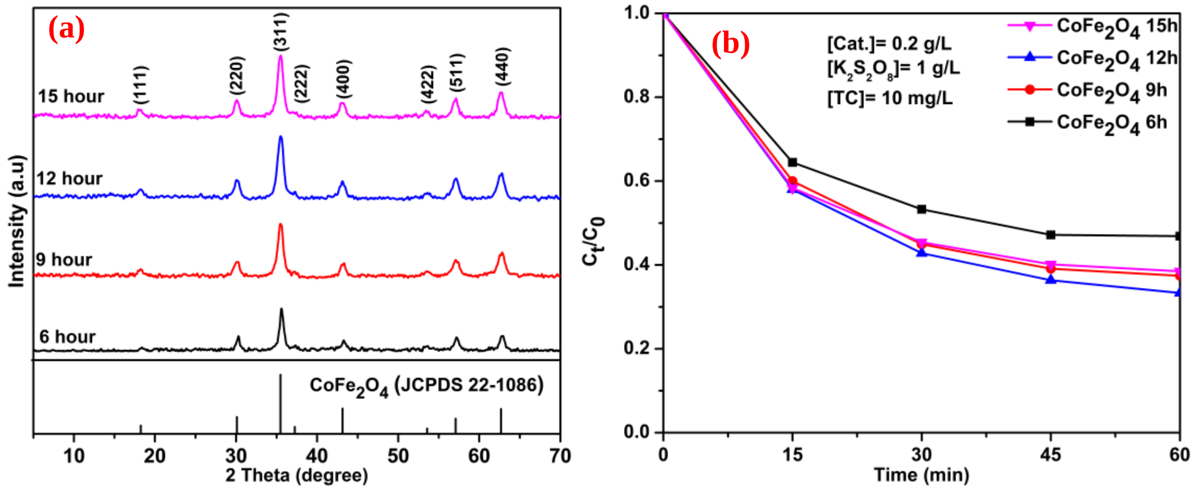


Figure 3. XRD (a), Comparison of TC decomposition efficiency between samples of different time (b).

3.4. Properties and Catalytic Performance of $CoFe_2O_4$ Nanoparticles Obtained under Optimal Conditions

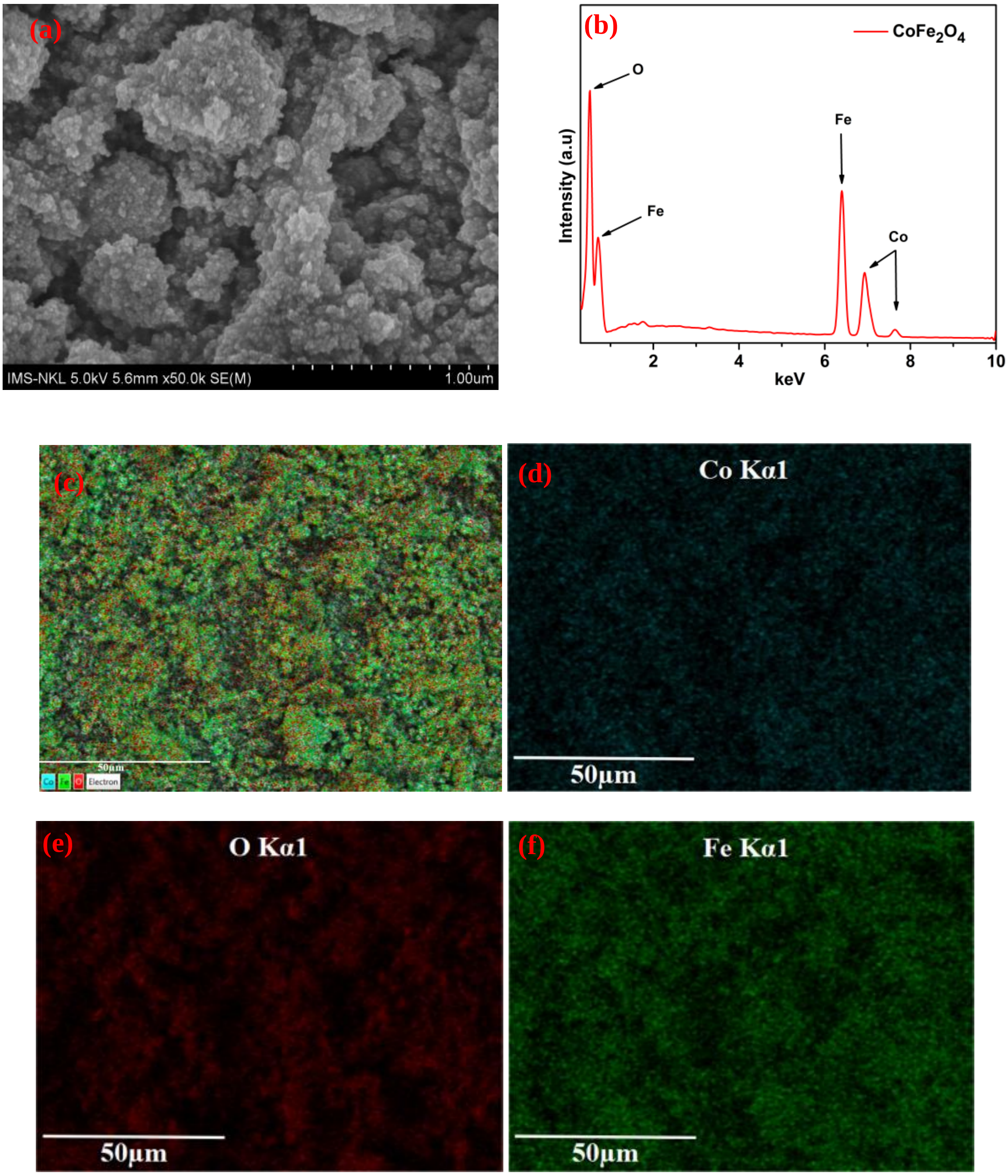
3.4.1. Morphology, Particle Size and Chemical Composition of $CoFe_2O_4$ Nanoparticles

Observation of the surface morphology from Figure 4a shows that $CoFe_2O_4$ exhibited typical spherical particles, which tended to aggregate due to strong magnetic interactions. The elemental composition of $CoFe_2O_4$ was analyzed by EDX spectroscopy (Figure 4b). The results showed that $CoFe_2O_4$ was composed of Co, Fe and O elements, with mass proportions of 27.35%, 50.55% and 22.1% (wt./wt.), respectively. Furthermore, the EDX mapping (Figure 4c-f) showed a relatively uniform distribution of these elements on the material surface. These results confirm the successful synthesis of the composite material without detecting any impurities. Dynamic light scattering (DLS) measurements by using a Zetasizer, model ZS-90 (Mervern, UK) revealed an average diameter of 50.75 nm which was significantly larger than crystal size of $CoFe_2O_4$ nanoparticles, implying the formation of agglomerations.

The characteristic vibrational bonds of $CoFe_2O_4$ were determined by FT-IR spectrum (Figure 4g). The absorption bands appearing at 419 cm^{-1} and 588 cm^{-1} corresponded to the stretching vibrations of Co–O and Fe–O bonds, respectively. From these results, the successful synthesis of $CoFe_2O_4$ was confirmed, which could exhibit promising properties for catalytic and environmental treatment applications.

3.4.2. Kinetics of TC Degradation Process

Kinetics of TC degradation using persulfate activation process were evaluated for a concentration range of 5 – 20 mg/L. As shown in Figure 5a, there was a gradual decrease in the degradation efficiency as the pollutant concentration increased. The maximum removal efficiency of 74.34% was achieved after 60 min at the lowest TC concentration (5 mg/L).



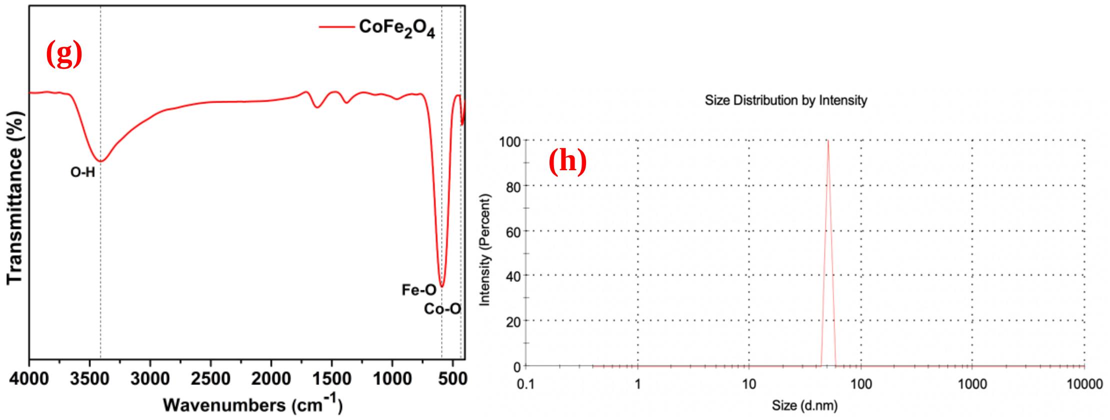


Figure 4. SEM of $CoFe_2O_4$ (a), EDX- Mapping of $CoFe_2O_4$ (b), EDX (c) and FT-IR (d) of $CoFe_2O_4$.

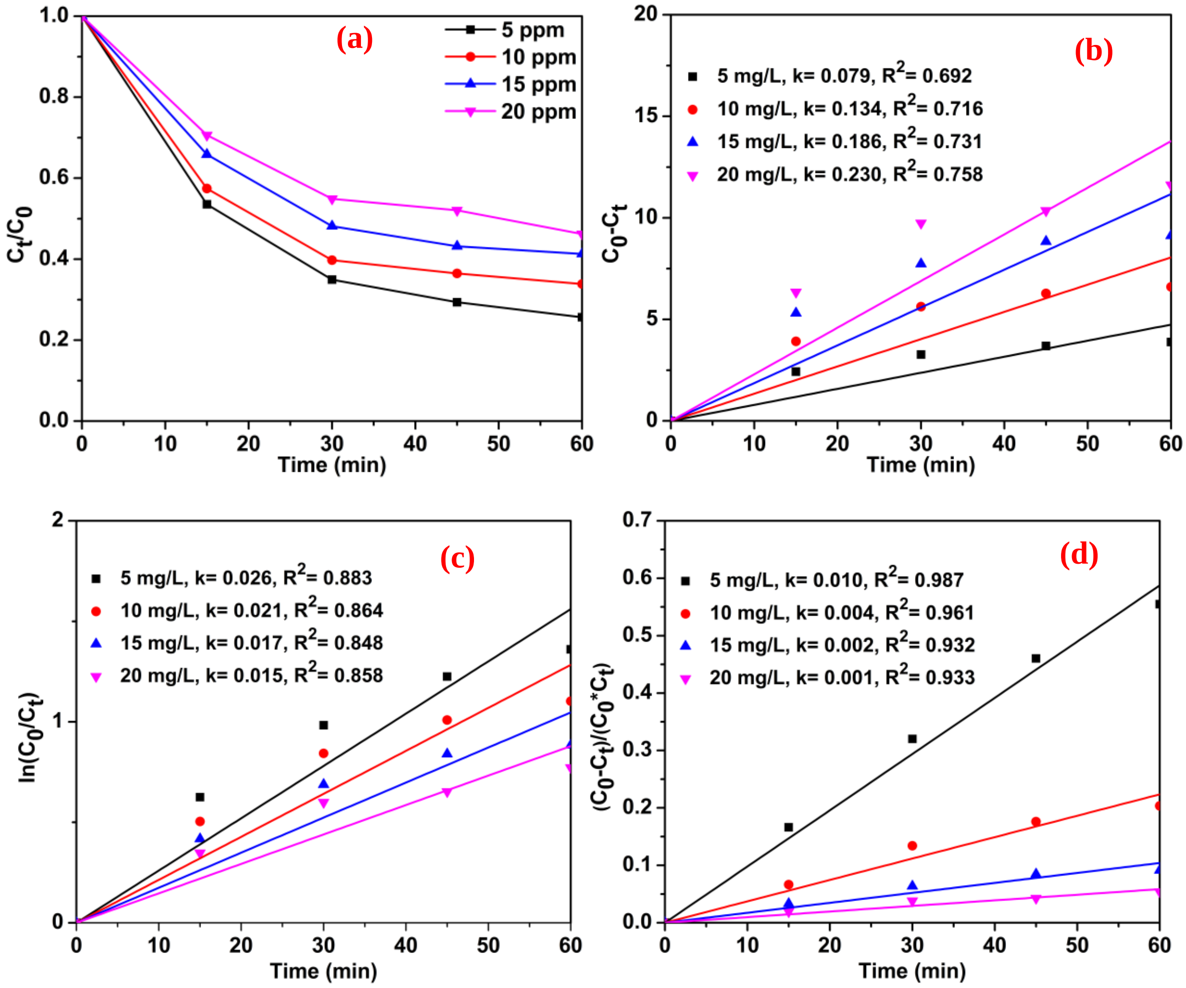


Figure 5. Effect of TC concentration on decomposition efficiency at [Cat.] = 0.2 g/L, [PS] = 1 g/L, pH 7.0 (a), the pseudo-zero-order (b), pseudo-first-order (c), and pseudo-second-order kinetic models (d) of TC photodegradation process.

In contrast, increasing the TC concentration to 20 mg/L would decrease the efficiency to 53.79%. This decrease might be due to the higher initial TC concentration, which resulted in more TC molecules adsorbing onto the $CoFe_2O_4$ surface. This adsorption reduced the number of active sites available for persulfate activation, thereby limiting the formation of important reactive radicals. Furthermore, at a constant catalyst dosage and a PS concentration, high TC concentrations would result in a shortage of both active sites and free radicals, ultimately reducing the removal efficiency.

The degradation of tetracycline (TC) was evaluated based on three kinetics models: zero-order, first-order, and pseudo-second-order. Based on Figure 5b–d, the pseudo-second-order model showed the best fit for the TC degradation using persulfate activation process, with correlation coefficients (R^2) ranging from 0.933 to 0.987. The reaction rate constant (k) gradually decreased with increasing TC initial concentration, from 0.01 $mg \cdot L^{-1} \cdot min^{-1}$ for 5 mg/L solution to 0.001 $mg \cdot L^{-1} \cdot min^{-1}$ for 20 mg/L solution. Therefore, a TC concentration of 5 mg/L was selected as the optimal condition for the degradation process.

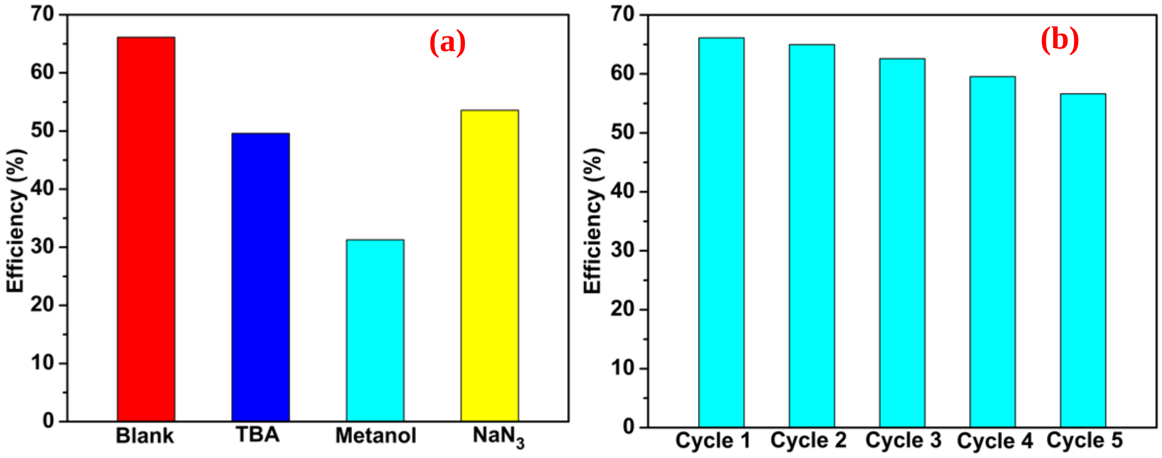


Figure 6. Impact of radical scavengers on catalytic performance (a), and stability of the catalyst (b).

3.5. Proposed Mechanism

Tert-butanol (TBA), Methanol (MeOH), and sodium azide (NaN_3) 1.0 M solution each [23] were added to the reaction mixture containing 10 mg/L TC, [Cat.] = 0.2 g/L, [PS] = 1 g/L, pH 7.0 for respectively trapping $HO^{\bullet}$, $SO_4^{\bullet -}$, and $^1O_2$. Efficiencies calculated by Eq. 1 when TBA, MeOH, or NaN_3 were added allow to evaluate the impact of radicals formed during the reaction on the TC degradation process. The outcomes in Figure 6a show that in the presence of NaN_3 the efficiency decreased from 66.12% to 53.56%, while these figures for MeOH and TBA declined to 31.28% and 49.59%, respectively. These imply that, $SO_4^{\bullet -}$ is the most predominant radicals responsible for TC degradation followed by $HO^{\bullet}$ which can be formed by the reaction of $SO_4^{\bullet -}$ with H_2O molecules according to Eq. 6. $^1O_2$ can contribute to a small portion to the TC degradation process.

$$Fe^{3+} + S_2O_8^{2-} \rightarrow Fe^{2+} + S_2O_8^{\bullet -} \quad (2)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\bullet -} + SO_4^{2-} \quad (3)$$

$$Co^{2+} + S_2O_8^{2-} \rightarrow Co^{3+} + SO_4^{\bullet -} + SO_4^{2-} \quad (4)$$

$$Me^{3+} (Co, Fe) + H_2O \rightarrow Me^{2+} + HO^{\bullet} + H^{+} \quad (5)$$

$$H_2O + SO_4^{\bullet -} \rightarrow H^{+} + HO^{\bullet} + SO_4^{2-} \quad (6)$$

$$SO_4^{\bullet -} + O_2 \longrightarrow SO_4^{2-} + O_2^{\bullet -} \quad (7)$$

$$2O_2^{\bullet -} + 2H^{+} \rightarrow {}^1O_2 + H_2O \quad (8)$$

$$Co^{3+} + Fe^{2+} \leftrightarrow Co^{2+} + Fe^{3+} \quad (9)$$

$$TC + SO_4^{\bullet -}, HO^{\bullet}, {}^1O_2, O_2^{\bullet -} \rightarrow Intermediates \rightarrow CO_2 + H_2O$$

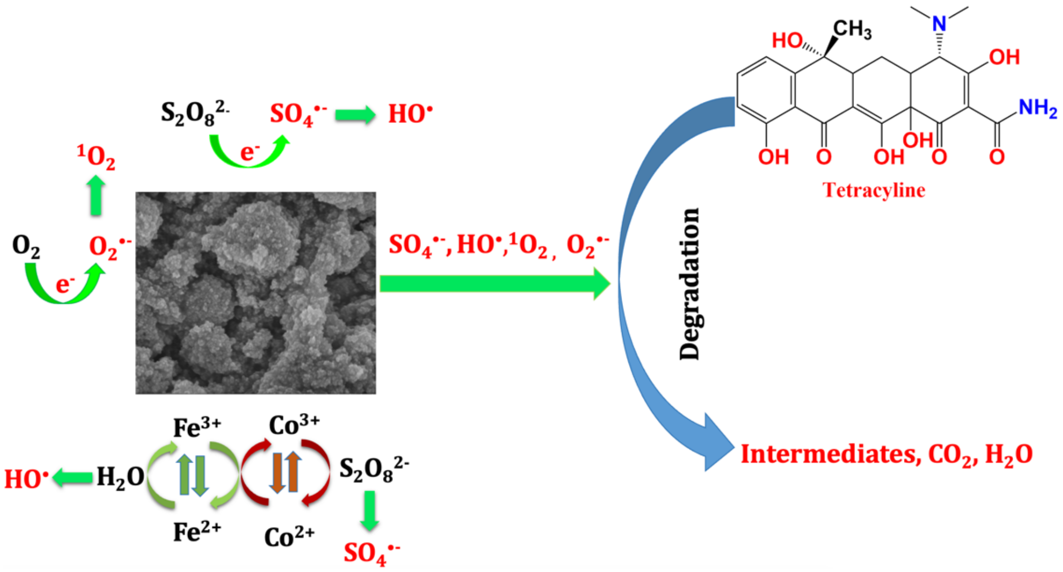


Figure 7. Proposed mechanism of the TC degradation catalyzed by $CoFe_2O_4$.

3.6. Stability of the Catalyst and Comparison of the Catalytic Performance

The stability of the catalyst was evaluated by conducting five consecutive cycle of TC degradation and regenerating the catalyst with the aid of DI water and absolute ethanol (washing 3 times each). The outcomes in Figure 6b revealed that the catalytic performance slightly decreased after each cycle, from 66.12% to 56.51% after five cycles, implying high potential of application of the as-synthesized catalyst.

4. Conclusion

In this study, $CoFe_2O_4$ nanoparticles were successfully synthesized by hydrothermal method. The resulting materials were characterized by means of XRD, SEM, EDX, and presented high purity, single-phase spinel structure, spherical particle, and no significant impurities. The investigation into the synthesis conditions showed that pH 11.0, temperature of 180 °C and reaction time of 12 hours were the optimal parameters, resulting in the material with the highest catalytic activity. The optimized $CoFe_2O_4$ material showed very good ability to degrade TC antibiotic by persulfate activation process. The treatment efficiency decreased with increasing TC initial concentration. Under optimal conditions (pH 11.0, 180 °C, 12 hours of reaction time), the degradation process followed a second-pseudo order kinetics, with R^2 ranged from 0.933 to 0.987, and k values within the range of 0.001 – 0.01 $mg \cdot L^{-1} \cdot min^{-1}$. These results confirm that hydrothermally synthesized $CoFe_2O_4$ is a promising, efficient, and potential catalyst material for wastewater treatment applications.

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