Catalytic Properties of Phosphate-Coated CuFe$_2$O$_4$ Nanoparticles for Phenol Degradation

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Received 12 August 2018; Revised 10 November 2018; Accepted 28 November 2018; Published 3 March 2019

Copper ferrite (CuFe$_2$O$_4$) nanoparticles were prepared using the sol-gel auto-combustion method and then coated with phosphate using different treatments with H$_3$PO$_4$. The structural and chemical properties of the phosphate-coated CuFe$_2$O$_4$ nanoparticles were controlled by changing the concentration of H$_3$PO$_4$ during the coating process. The prepared nanoparticles were characterized using XRD, FTIR, SEM, and EDS which provided information about the catalysts’ structure, chemical composition, purity, and morphology. The catalytic and photocatalytic activities of the phosphate-coated CuFe$_2$O$_4$ samples were tested and evaluated for the degradation of phenol using HPLC. The prepared nanoparticles successfully emerged as excellent heterogeneous Fenton-type catalysts for phenol degradation. The phosphate-coated CuFe$_2$O$_4$ catalysts exhibited a higher catalytic activity compared with the uncoated CuFe$_2$O$_4$ ones. Such a higher catalytic performance can be attributed to enhanced morphological, electronic, and chemical properties of the phosphate-coated CuFe$_2$O$_4$ nanoparticles. Additionally, the phosphate-coated CuFe$_2$O$_4$ nanoparticles also revealed a higher catalytic activity compared with TiO$_2$ nanoparticles. Different experimental conditions were investigated, and complete removal of phenol was achieved under specific conditions.

1. Introduction

The rapid development in industries increased the amount of wastewater discharged into water bodies. The discharged wastewater contains different organic and inorganic pollutants which are highly toxic and harmful to the environment. These pollutants resist degradation and are environmentally persistent which required developing new approaches to tackle this problem [1, 2]. The discharged industrial waste contains chemicals like cyanides, mono- or polycyclic aromatics, mercaptans, phenols, ammonia, and sulfides, which are affecting the aquatic habitat via halting algae growth, oxygen depletion, and altering the properties of water [3]. Phenol is one of the abundant hazardous pollutants in wastewater. Phenol was found to be teratogenic, toxic, highly persistent in the environment, and non-biodegradable [4–6]. Once it is discharged into water bodies, it presents a threat to aquatic systems and its inhabitants as well as humans’ health [7]. Phenol in wastewater can be treated by various physical and chemical techniques, such as microwave [8, 9], membrane technology [10], electrochemical [11, 12], thermal [13], and physiochemical processes [14, 15]. One of the most adopted techniques in wastewater treatment is the chemical oxidation including the advanced oxidation processes [3, 16].

Advanced oxidation processes (AOP) include different systems like Fenton, photocatalysis, and UV/H$_2$O$_2$ processes, which mostly proceed via active nonselective radicals such as hydroxyl radicals (HO·). The radicals are produced through the decomposition of strong oxidants like hydrogen peroxide. In most of these processes, HO· oxidizes phenol and its derivatives to cyclic intermediates that are converted to organic acids which are then mineralized to CO$_2$ and H$_2$O [17]. Recent studies showed that heterogeneous catalysts combined with the advanced oxidation process (AOP) can be used for the degradation of aromatic organic compounds in wastewater [18, 19]. While zeolites, clays, and oxide materials were found to be some of the efficient systems...
for the AOP, the most used ones were mixed iron oxide nanoparticles [20–23].

Ferrites are iron oxides with the general formula MFe$_2$O$_4$ (M = Ni, Mn, Co, and so on). Spinel ferrites exhibit cubic close packing of oxide ions that form tetrahedral and octahedral coordination, where the divalent metal ions are incorporated. Ferrites have a large number of applications due to their being moderately cheap, highly efficient, recyclable, magnetic, and catalytic properties. They are often used in gas sensors, energy storage, semiconductors, magnetic-based separation, catalysis, and refractory materials. Reactions like decomposition of cyclic organic peroxides, oxidation of propane, oxidation of phenol, and decomposition of hydrogen peroxide are catalyzed by ferrites [13, 24]. Copper ferrites are thermally stable magnetic particles which are frequently employed in various environmental applications. CuFe$_2$O$_4$ nanoparticles are used as catalysts and gas sensors [19, 25, 26]. Ferrites tend to agglomerate due to van der Waals forces, high surface energy, and magnetic dipolar interaction. One of the solutions employed to overcome this problem is coating [27]. The organic coating includes polyamides, polyvinyl alcohol, epoxy, and silicone resins, while the inorganic coating includes oxides and phosphates. Among these coatings, phosphate stands out for its high electrical resistivity, the simplicity of preparation, and high adhesion to the substance surface [28]. The phosphate coating is often done through a phosphate bath or immersing the material in phosphoric acid to form phosphate layer on its surface.

Phosphate doping has improved the catalytic activities of oxide catalysts such as TiO$_2$ [29–31] and BiVO$_4$ [32], and, consequently, it is expected to improve the catalytic properties of ferrites. In our previous work [19], CuFe$_2$O$_4$ nanoparticles were utilized as efficient Fenton-like catalysts for phenol degradation. The main goal of the present work is to investigate the effect of phosphate coating on the structural, chemical, and catalytic properties of the CuFe$_2$O$_4$ nanoparticles. To our knowledge, there are no reports discussing the catalytic properties of phosphate-coated CuFe$_2$O$_4$ nanoparticles. The obtained results for the degradation of phenol demonstrated that the prepared nanoparticles exhibited a high Fenton catalytic performance with an almost complete degradation of phenol. The results also showed that phosphate-coated CuFe$_2$O$_4$ nanoparticles exhibited higher catalytic activities than pure uncoated CuFe$_2$O$_4$ ones. The influences of different coating treatments, solution pH, and reaction temperature on the degradation of phenol were investigated. The photocatalytic activity of the phosphate-coated CuFe$_2$O$_4$ nanoparticles was also examined.

2. Materials and Methods

2.1. Catalyst Preparation. Firstly, pure uncoated CuFe$_2$O$_4$ nanoparticles were prepared using the sol-gel autocombustion method as described previously [19]. In brief, predetermined amounts of ferric nitrate and the copper (II) nitrate were dissolved in distilled water. Citric acid was then added to the solution and stirred till the acid completely dissolved. The molar ratio of the ferric nitrate, copper (II) nitrate and citric acid was 2:1:3. After that, the solution was heated to 80°C, and then, ammonia was added until the pH of the solution was around 8. The solution was left to boil until a thick gel was formed, which was kept overnight at room temperature. The gel was then burned and an ash-like product was obtained. The catalyst was crushed and kept for the phosphate-coating step in which the obtained CuFe$_2$O$_4$ powder was treated with acetone for 15 minutes. After that, the powder was filtered and dried in the oven at 70°C. Then, 0.5 g of the dried CuFe$_2$O$_4$ powder was treated with 25 mL of 0.35 M, 0.60 M, 0.80 M, 1.20 M, or 1.50 M of H$_3$PO$_4$ for 30 minutes at room temperature. The separated powder was dried overnight in an oven at 100°C. Finally, the dried catalyst, phosphate-coated CuFe$_2$O$_4$, was gently grinded and stored for the study.

Additional comparative studies were carried out using TiO$_2$ nanoparticles (>99%) purchased from Sigma-Aldrich and used as received.

2.2. Catalyst Characterization. The crystal structures of the uncoated and coated catalysts were determined using X-ray diffraction PANalytical powder diffractometer (X’Pert PRO) which uses Cu-Kα radiation operating at 40 kV and 40 mA at 1.5406 Å, over the 2θ range of 10°-80° and a step size equal to 0.02°. The crystallite sizes were calculated by the Debye-Scherrer formula:

$$L = \frac{K\lambda}{B \cos \theta},$$

where $K$ is the Scherrer constant (0.89), $\lambda$ is the wavelength of the XRD instrument, $\theta$ is the diffraction angle, $B$ is the peak full width at half maximum of the intensity plotted against the 2θ profile, and $L$ is the crystallite size in nm [33].

The morphologies of the ferrites were analyzed through scanning electron microscopy FEG Quanta 250 provided with energy-dispersive spectrometer (EDS). The FTIR spectra were recorded using a Bruker ALPHA-Platinum ATR FTIR in the range of 400-4000 cm$^{-1}$.

2.3. Phenol Degradation Reaction. Degradation reactions were carried out in a 150 mL glass beaker containing 95.00 mL of 200 ppm phenol and 5 mL of 30% H$_2$O$_2$. The reaction started after adding 60 mg of catalyst to the solution with continuous stirring. At specific time intervals, samples were withdrawn and filtered using 0.2 μm nylon membrane filters. HPLC was used to analyze the samples in order to determine the remaining concentration of phenol. HPLC measurements were conducted using a Shimadzu machine equipped with a UV detector that was set at 280 nm. The HPLC method was previously developed to follow the phenol degradation process [19].

The following formula was used to calculate the degradation efficiency of phenol:

$$\text{Degradation\%} = \left(\frac{C_o - C_t}{C_o}\right) \times 100,$$
where \( C_0 \) is the initial concentration of phenol and \( C_t \) is the remaining concentration of phenol after a specific time of the reaction.

The degradation reactions were modeled using the following first-order expression:

\[
\ln \left( \frac{C_t}{C_0} \right) = -kt,
\]

where \( C_0 \) is the initial concentration of phenol, \( C_t \) is the residual concentration of phenol after a specific time of the reaction, and \( k \) is the rate contact which can be calculated from the slope of \( \ln \left( \frac{C_t}{C_0} \right) \) versus time.

In order to investigate the photocatalytic activities of the prepared catalysts, similar reactions were carried out using a photocatalytic reactor equipped with a metal halide lamp (OSRAM 400 W, 350-750 nm).

### 3. Results and Discussion

#### 3.1. Structural Analysis

3.1.1. XRD. XRD patterns of the sol-gel, as-prepared CuFe\(_2\)O\(_4\) sample, and the phosphate-coated CuFe\(_2\)O\(_4\) samples are presented in Figure 1. The observed XRD patterns are in agreement with the standard CuFe2O4 data (JCPDS card 77-0010) and with literature reports [19, 34]. The reflection planes (111), (220), (311), (222), (400), (422), (511), (440), and (533) confirm that the CuFe\(_2\)O\(_4\) samples were crystallites of spinel ferrite with a cubic phase [19]. The CuFe\(_2\)O\(_4\) nanoparticles maintained their cubic structure even after treatment with phosphoric acid. However, the diffraction peaks are less intense and broader for the sample treated with 1.5 M of phosphoric acid, which may have affected the CuFe\(_2\)O\(_4\) structure and reduced its crystallinity. Using Scherrer’s equation, the crystallite sizes of the samples were in the range of 24-31 nm.

3.1.2. FTIR. IR measurements are commonly conducted for ferrites in order to verify the presence of the spinel phase of the prepared samples. Ferrites exhibit two IR modes in the range of 400-600 cm\(^{-1}\) which are attributed to the vibrations of the cations with oxygen ions in the octahedral and tetrahedral sites in the unit cell. The FTIR spectra of the CuFe\(_2\)O\(_4\) samples are depicted in Figure 2 which clearly shows the typical frequency mode of ferrites at \( \sim \)600 cm\(^{-1}\) due to the stretching vibration of iron-oxygen ions in tetrahdral sites [19, 35]. Moreover, additional absorption peaks are observed in the region of 970–1120 cm\(^{-1}\) for the phosphate-coated CuFe\(_2\)O\(_4\) samples, which are attributed to phosphorus-oxygen stretching vibration [36]. The intensity of these peaks increased with the increase of phosphoric acid concentration from 0.35 to 1.5 M.

3.1.3. SEM. The SEM images of the phosphate-coated CuFe\(_2\)O\(_4\) samples are depicted in Figure 3. The images of the phosphate-coated CuFe\(_2\)O\(_4\) samples show sheet-like structures while those of the uncoated CuFe\(_2\)O\(_4\) samples exhibit a sponge-like structure. The size of these sheets increased with the increase of the concentration of phosphoric acid used for coating. It is also obvious that coating the CuFe\(_2\)O\(_4\) particles with phosphate increased the surface roughness. The EDS analysis confirmed the presence of phosphorus for each phosphate-coated CuFe\(_2\)O\(_4\) sample.

3.2. Phenol Degradation Reactions. Initially, the nonphotocatalytic performance of the prepared catalysts was investigated at room temperature. The obtained results, displayed in Figure 4, clearly show that phosphate-coated CuFe\(_2\)O\(_4\)
nanoparticles are more active than the pure uncoated 
CuFe$_2$O$_4$ nanoparticles toward phenol degradation. This 
result indicates that phosphate coating enhanced the cata-
ytic activity of the CuFe$_2$O$_4$ nanoparticles. The noticeable 
increase in the catalytic activity can be attributed to the 
changes in the surface morphology of the CuFe$_2$O$_4$ parti-
cles as observed in Figure 3. Based on Figure 4, the 

equation

\[
\text{H}_2\text{O}_2 + \text{catalyst} \rightarrow 2\text{HO}^-
\]

\[
\text{HO}^- + \text{PhOH} \rightarrow \text{PhO}^- + \text{H}_2\text{O}
\]

\[
\text{PhO}^- + \text{H}_2\text{O}_2 \rightarrow \text{intermediate products} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]
Figure 4 indicates that the catalytic performance of CuFe$_2$O$_4$ nanoparticles toward phenol degradation has significantly enhanced after the phosphate-coating process. Clearly, phosphate-coated CuFe$_2$O$_4$ nanoparticles promote a faster phenol degradation as compared to pure uncoated CuFe$_2$O$_4$ ones. The higher catalytic activity of the phosphate-coated CuFe$_2$O$_4$ nanoparticles is most likely due to a higher production of hydroxyl radicals, which in turn facilitates the degradation of phenol. Therefore, it can be suggested that the phosphate coating enhanced H$_2$O$_2$ decomposition to OH radicals. The rate of degradation reactions followed first-order kinetics (Equation 3) with respect to phenol concentration. The reaction rate constants are listed in Table 1.

3.2.1. Effect of Reaction Temperature. Figure 5 shows the effect of reaction temperature on the degradation of phenol using phosphate-coated CuFe$_2$O$_4$ catalysts. The reactions were investigated at three different temperatures which are 25°C, 35°C, and 45°C. The obtained results indicate that phenol degradation increased by increasing the reaction temperature. Reactions at 45°C and 35°C showed complete...
degradation of phenol less than 20 and 35 minutes, respectively. While at 25°C, the reaction consumed about 4 hours to achieve a complete degradation of phenol. High reaction temperatures activate the decomposition of H2O2 to OH radicals and, consequently, increase the degradation of phenol [37–40]. Table 2 presents the reaction rate constants calculated at the three reaction temperatures. Clearly, the reaction at 45°C exhibited the highest reaction rate constant value indicating the fastest degradation of phenol.

3.2.2. Effect of Initial pH. The role of solution pH on the degradation of phenol was investigated. The pH value of the reaction solution was adjusted using 0.1 M NaOH and 0.1 M HCl, and the results are presented in Figure 6. Clearly, the highest degradation of phenol was achieved at the acidic conditions (pH = 3), whereas the degradation at alkaline conditions (pH = 9) proceeded with a much lower extent. The high catalytic activity at acidic conditions can be due to metal leaching from the catalyst to the solution and, consequently, performing as a homogeneous catalyst. At alkaline conditions, H2O2 decomposition produces O2 and H2O, rather than OH radicals, which reduces the degradation extent of phenol [19, 41]. The rate constants for the reaction at different pH values are listed in Table 3.

Additionally, the photocatalytic activities of the CuFe2O4 catalysts were investigated, and the results are presented in Figure 7. The results reveal that the activity of the CuFe2O4 catalysts increased after the phosphate coating, which indicates that such coating also enhanced the photocatalytic performance of the CuFe2O4 nanoparticles. Moreover, comparing Figure 7 with Figure 4 clearly reveals that phenol degradation significantly increased for the photoinduced reaction. After 30 min, a complete phenol removal was achieved under photocatalytic conditions, whereas only about 25% of phenol removal was reached under nonphotocatalytic conditions. Such a difference in the phenol removal suggests that the phosphate-coated CuFe2O4 nanoparticles can be considered as efficient photocatalysts. The relevant photoinduced reactions at the catalyst surface causing the degradation of phenol can be expressed as follows:

\[ \text{catalyst} + hv \rightarrow e_{CB}^- + h_{VB}^+ \]  \hspace{1cm} (5)

\[ \text{H}_2\text{O}_2 + e_{CB}^- \rightarrow \text{OH}^- + \text{HO} \cdot \]  \hspace{1cm} (6)

\[ \text{PhOH} + h_{VB}^+ \rightarrow \text{intermediate products} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (7)

\[ \text{PhOH} + e_{CB}^- \rightarrow \text{intermediate products} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (8)

\[ \text{PhOH} + \text{HO}^- \rightarrow \text{intermediate products} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (9)

In equation 5, the photocatalytic reaction is initiated when the catalyst absorbs a photon which leads to the promotion of an electron in the conductive band (\(e_{CB}^-\)) and formation of a positive hole in the valence band (\(h_{VB}^+\)) [42]. The \(e_{CB}^-\) and \(h_{VB}^+\) exhibit powerful reducing and oxidizing properties, respectively. In addition to \(\text{HO}^-\), \(e_{CB}^-\) and \(h_{VB}^+\) facilitate the degrading of phenol as presented in equations 6, 7, 8, and 9.

TiO2 is considered one of the most used catalysts in many industrial processes. Therefore, the catalytic activities of phosphate-coated CuFe2O4 and TiO2 towards phenol degradation were compared. The results of photoinduced and nonphotoreactions are presented in Figure 8. Under nonphotoreaction conditions (Figure 8(a)), an almost complete phenol degradation was achieved after 4 hours using the phosphate-coated CuFe2O4 catalyst, while only 5% of phenol was removed by TiO2. This result clearly indicates that the coated CuFe2O4 catalyst is more active than the TiO2 catalyst. Compared to Figure 8(a), Figure 8(b) highlights the higher degradation of phenol by both catalysts, TiO2 and CuFe2O4, under photoinduced reaction conditions. However, the phosphate-coated CuFe2O4 catalyst is still significantly more active than TiO2 towards phenol.
4. Conclusions

The prepared sol-gel auto combustion CuFe₂O₄ nanoparticles were coated with phosphate after treatment with H₃PO₄ of different concentrations. The phosphate-coated CuFe₂O₄ catalysts’ purity, crystallinity, composition, and morphology were analyzed using SEM, EDS, FTIR, and XRD techniques. Their catalytic and photocatalytic activities were investigated for the degradation of phenol using HPLC. The obtained results showed that phosphate-coated CuFe₂O₄ catalysts are excellent heterogeneous Fenton-type catalysts for phenol degradation and exhibited higher catalytic activities compared with pure uncoated CuFe₂O₄ catalysts. The higher catalytic performance after phosphate coating can be due to improving the morphological, electronic, and chemical properties of pure uncoated CuFe₂O₄ catalysts. The phosphate-coated catalysts performed better in the acidic medium (pH = 3) and at high temperatures (e.g., T = 35 and 45°C) with complete removal of phenol. Moreover, the phosphate-coated CuFe₂O₄ catalyst showed higher activity compared to the TiO₂ catalyst which is one of the most used catalysts in industrial processes.

Data Availability

The XRD, SEM, and IR data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors are grateful to the Research Office at Khalifa University of Science and Technology, SAN campus, Abu Dhabi, UAE, for funding project # LTR14013.

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