Method Article

Photocatalytic degradation of ciprofloxacin using CuFe$_2$O$_4$@methyl cellulose based magnetic nanobiocomposite

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**A B S T R A C T**

Herein, magnetically separable CuFe$_2$O$_4$@methyl cellulose (MC) as a novel magnetic nanobiocomposite photocatalyst was synthesized with a facile, rapid, green, and new microwave-assisted method. After that, CuFe$_2$O$_4$@MC was characterized with FESEM, EDS, FT-IR, XRD, TGA, and VSM techniques. To measure CuFe$_2$O$_4$@MC photocatalytic activity, ciprofloxacin (CIP) removal ability of CuFe$_2$O$_4$@MC was investigated under the conditions such as initial CIP concentrations (3, 5, 7, and 9 mg/L), pHs (3, 7, and 11), photocatalyst loadings (0.025, 0.05, 0.1, 0.2, 0.3, and 0.4 g), and irradiation time (15, 30, 45, 60, 75, and 90 min). Kinetic process was evaluated with the pseudo-first order and the Langmuir-Hinshelwood models. CIP concentration was measured with high performance liquid chromatography (HPLC). The maximum CIP removal efficiency in the optimal conditions which contained pH = 7, CIP initial concentration of 3 mg/L, photocatalyst loading of 0.2 g, and at irradiation time 90 min was achieved 72.87 % and 80.74 % from real and synthetic samples, respectively. Also, COD removal efficiency in the optimal conditions was achieved 68.26 %. Furthermore, the CuFe$_2$O$_4$@MC reusability and chemical stability were examined and 73.78 % of CIP was degraded after the fourth cycle.

**Advantages of this technique were as follows:**

- CuFe$_2$O$_4$@MC as a new nanobiomagnetic photocatalyst was synthesized with a facile, fast, and green method and were characterized with FESEM, EDS, FT-IR, XRD, TGA, and VSM techniques.
- Ferromagnetic property and pure-phase spinel ferrites of CuFe$_2$O$_4$@MC were confirmed and significant photocatalytic activity of CuFe$_2$O$_4$@MC was observed.
- Easily gathering, reusability and good chemical stability were interests of this nanobiomagnetic photocatalyst.

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Photocatalytic method to ciprofloxacin degradation with CuFe2O4@MC synthesised as a novel nanobiomagnetic photocatalyst

Keywords: Ciprofloxacin, Methyl cellulose, Copper ferrite, Photocatalytic degradation, Nanobiomagnetic photocatalyst

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Method details

Pharmaceutical pollutants could enter to the aquatic environment from residual part of pharmaceutical industry, hospital wastewater, and human waste disposal. Antibiotics are one of these pollutants, which metabolize imperfectly and enter to various sources of water [1]. Ciprofloxacin (CIP) is the most applied antimicrobial and anti-inflammatory antibiotics that uses in infection diseases treatment. Due to the high–dose usage of CIP and other antibiotics, serious environmental damages were occurred by accumulation of these antibiotics in wastewater, plants, and animal cells [2,3]. Because of the low biodegradability, the conventional volatilization, adsorption, sedimentation, coagulation, and biological methods are not effective ways for removal of CIP and other antibiotics from the aquatic environment [4–7]. Thus, new efficient methods for CIP removal are desirable. Recently, the advanced oxidation processes (AOPs) with heterogeneous photocatalysts has been regarded as a promising option for CIP-containing wastewaters treatment [8]. The AOPs with photocatalysts involves generation of the highly reactive hydroxyl radical to eliminate of the organic pollutants with oxidative degradation. In the heterogeneous AOPs, the UV-irradiation as energy source excites photoactive semiconductors [9] which causes electron transfer from the valence band to the conductive band, electron-hole (h+) pairs production, and hydroxyl radical (OH•) or other oxidizing radicals were generated for oxidation of hazardous materials [10]. Moreover, hydroxyl radical (OH•) production, photocatalysis efficiency, response to light, and photocatalytic activity of photocatalysts increase using nanophotocatalysts, due to the smaller size, greater surface area, the higher diffusion power, and superior behavior of nanomaterials [11].

Photocatalytic degradation by using metal oxides and metal spinel ferrites such as CoFe2O4, ZnFe2O4, and CuFe2O4 as photocatalyst is one of the effective methods for antibiotic removal from aqueous solutions [12–21]. The photocatalytic removal process with nanophotocatalysts, which has been reported in some studies, was pH-sensitive. Also for increase degradation efficiency a chemical oxidant such as H2O2 has been used [22,23]. To prevent damage to the environment, using green processes for photocatalysts synthesis is preferred. Recently, bio-polymers as cellulose, carboxy methyl cellulose, chitosan, natural gums, agar, gelatin, chitin, collagen etc. for many reasons such as abundance in nature and multi-functionality have attracted attention [24]. These polysaccharides due to numerous properties such as non-toxicity, biocompatibility, flexibility, high functionality and ease of processing have many applications in the water
treatment [25,26]. Due to, previous studies literature review, there is no research about the CIP removal using CuFe$_2$O$_4$@methylcellulose as a magnetic nanobiocomposite photocatalyst from aqueous solutions. CuFe$_2$O$_4$@methylcellulose is a new class of biocomposites, which built from organic linkers and inorganic metal nodes through coordination bonds [21]. Therefore, a magnetically separable CuFe$_2$O$_4$@methyl cellulose (MC) photocatalyst was designed with a facile, fast, and green microwave-assisted method.

The research steps were as follows: at first, CuFe$_2$O$_4$@MC was prepared with a new microwave-assisted method and characterized. After that, the photolysis, adsorption, and photocatalytic processes were compared with each other. Then the operational parameters effects on the CIP removal efficiency were evaluated and optimized. In the next step, comparison of the photocatalytic performance of CuFe$_2$O$_4$@MC and CuFe$_2$O$_4$ was done. Also, in the optimal conditions, the CIP degradation from hospital wastewater and the COD removal were investigated. Finally, the CIP photocatalytic removal kinetics were evaluated and CuFe$_2$O$_4$@MC reusability and chemical stability were obtained. The study stages have been shown in the Fig. 1.

![Fig. 1. Research steps.](image-url)
Chemicals

FeCl₃·6H₂O, CuCl₂·2H₂O, NaOH, and methyl cellulose (MC) were purchased from Merck Company (Germany) and used without more purification. Also, CIP (99 % purification) was purchased from Tamad Pharmaceutical Company (Tehran, Iran). All the materials were in analytical grade and used without further purification. Deionized water was used during the tests.

Synthesis and characterization of CuFe₂O₄@MC

In the first step, FeCl₃·6H₂O (20 mmol; 5.4 g), plus CuCl₂·2H₂O (10 mmol; 1.7 g), were dissolved in the 50 mL deionized water (DW). Then, MC (1 g) was added to the gained solution, and the mixture was stirred at the room temperature (25 °C). After that, sodium hydroxide was added to the suspension during 1 h. Dark brown solution was transferred to microwave oven (3 × 5 min at 450 W) (Samsung Microwave ME201, 20 L). Afterwards, CuFe₂O₄@MC as a lightweight sediment powder was observed. In the next step, the obtained nanobiomagnetics were separated by using an external magnet and was washed several times with DW. The final product was dried in an oven vacuum at 100 °C for 24 h [21]. The Fourier transform infrared spectroscopy (FT-IR) of the samples was measured using a FT-IR 6300 Brucker, and the X-ray powder diffraction (XRD) of CuFe₂O₄@MC was reported in the diffraction angle range of 2θ = 15°–70° by an X′Pert PRO MPD PA nalytical using Ni-FILTERED Cu Kα radiation. Thermal gravimetric analysis (TGA) was carried out using an STA (PC Luxx 409-NETZSCH) instrument at the rate of 10 °C min⁻¹ in air. The CuFe₂O₄@MC magnetic properties were characterized with a vibrating sample magnetometer (VSM) (LakeShore Cryotronics-7404) at the room temperature (25 °C). The CuFe₂O₄@MC chemical composition, microstructure, and morphology were evaluated with field emission scanning electron microscope-energy dispersive spectroscopy (FESEM-EDS) (MIRA3TESCANXMU) (Fig. 2).

The dissolved Fe and Cu ions quantity in leachate was estimated with flame atomic absorption spectrometer (PG Instruments, model PG 990, England) at the wavelength of 248.30 nm and 324.70 nm, respectively. The CIP concentration was specified with HPLC device (Waters E600, USA) using column with the properties of C₈; 259 × 4.6 × 5 mm with UV detector at wavelength of 272 nm with a hybrid mobile phase 10 micro molar HCl and acetonitrile (80:20 v/v), and input flow rate of 1 mL/min (Table 1). Chemical oxygen demand (COD) was determined by spectrophotometer (Shimadzu, Japan).

Comparison of the photolysis, adsorption, and photocatalytic processes

In the researches which are about photocatalysis processes, comparison of the adsorption, photolysis results, and the photocatalytic mechanisms are valuable so, the mentioned processes were compared at irradiation time = 90 min, at pH = 7, CuFe₂O₄@MC = 0.2 g, and CIP concentration =3 mg/L [21]. The results indicated that the photocatalytic processes, adsorption, and photolysis are effective methods in the CIP removal process. The removal efficiency in the photolysis process with UV, the adsorption with CuFe₂O₄@MC, and the photocatalytic process was obtained 10.11 %, 17.6 % and 80.77 %, respectively. It means that the higher CIP removal efficiency is depends on the photocatalytic mechanism against photolysis and adsorption processes.

Optimization of effective parameters on the CIP degradation

Effects of initial CIP concentrations (3, 5, 7, and 9 mg/L), pHs (3, 7, 11), nanocatalyst loadings (0.025, 0.05, 0.1, 0.2, 0.3, and 0.4 g), and UV-C irradiation time (15, 30, 45, 60, 75, and 90 min) were optimized in a batch photoreactor. A plexiglas rectangular cubic shape photoreactor with internal dimensions of 25 cm (length), 10 cm (width), and 5 cm (height), an applicable volume of 300 mL was used in this study which had three UV-C lamps (low pressure, 6 W, Philips). The lamps were installed on the top of the reactor. To generate more hydroxyl radicals, a reactor was designed which could supply the minimum distance between the light supplier and the catalyst. To mix the reactor contents a peristaltic pump with a flow of 1 mL/s was used. The designed photoreactor is shown in Fig. 3. The
samples were collected at the specific times during the irradiation. The samples were examined by HPLC when the CuFe₂O₄@MC was separated with an external magnet. After that, the degradation efficiency (η) was obtained by Eq. (1):

\[ \eta\% = 100 \left( \frac{C_0 - C_t}{C_0} \right) \]  

(1)

Where \( C_t \) and \( C_0 \) show the obtained CIP concentration at different periods of irradiation time (t) and at nil min, respectively, indicated by HPLC.

**Comparison between the CuFe₂O₄@MC and CuFe₂O₄ photocatalytic performance**

The CuFe₂O₄@MC and CuFe₂O₄ photocatalytic performance in the CIP degradation was compared in the optimal conditions such as pH of 7, irradiation time of 90 min, CIP concentration of 3 mg/L, and photocatalyst loading of 0.2 g. The CIP degradation efficiency with these photocatalysts was obtained 80.77 % and 51.03 %, respectively.
The CIP degradation kinetics were evaluated with the pseudo-first order (Eq. 2) and the Langmuir-Hinshelwood (Eq. 3) kinetic models (Table 2).

The kinetic linear models indicate that the CIP degradation, following the pseudo-first order kinetic model and the Langmuir-Hinshelwood equations. In accordance with the pseudo-first order kinetic model, the correlation coefficient ($R^2$) for concentrations of 3, 5, 7, and 9 mg/L was 0.902, 0.923, 0.922, and 0.929, respectively. The Langmuir-Hinshelwood equilibrium adsorption coefficient and the superficial reaction rate constant were gained 0.202 L/mg and 0.141 mg/L min, respectively. The high correlation coefficient ($R^2 = 0.930$) indicated that the CIP photocatalytic degradation followed the Langmuir-Hinshelwood kinetic model.

Investigation of the reusability and chemical stability of CuFe$_2$O$_4$@MC

Considering the importance of the photocatalyst reusability in practical applications, the recycled CuFe$_2$O$_4$@MC photoactivity was examined. At first, The CuFe$_2$O$_4$@MC was separated with a magnet,
and after that, was washed with ethanol/water and dried at 100 °C for 2 h. The recycled photocatalyst in each run was added to a fresh solution of CIP the under UV-irradiation condition. In the first cycle, the CIP removal efficiency was gained 80.77%. The results demonstrated that the CuFe$_2$O$_4$@MC photocatalytic activity had significant reduction in the second cycle (75.25%) and maintained relative stability. Adsorption of intermediate products on the photocatalytic active sites can reduce the percentage of the CIP degradation. However, the CIP removal efficiency was obtained 73.78% in the fourth cycle. Moreover, the Fe and Cu metal ions leaching in the photocatalytic process and loss of them could cause the CIP degradation efficiency reduction. Due to this reason, after the fourth cycle, copper and iron ion concentrations were determined in the solution. However, the mentioned ions were not detected in the solution. The CuFe$_2$O$_4$@MC chemical stability was determined with the XRD analysis, which showed the XRD peaks intensity after the fourth cycle, did not have an obvious change. This result cause to understand that this photocatalyst has good chemical stability and could be recycled.

**Conclusion**

Briefly, a strong, magnetically separable photocatalyst was prepared by a simple, fast, green, and new microwave-assisted method and by using iron and copper salts on MC in an alkali medium. The magnetic nanobiocomposite characterization showed pure phase spinel ferrites, spherical particle morphology with smaller agglomeration, and the ferromagnetic nature of CuFe$_2$O$_4$@MC. The maximum CIP removal efficiency occurred in the optimum conditions at pH 7, CIP concentration 3 mg/L, photocatalyst loading 0.2 g, and irradiation time 90 min. Then, after being used in the fourth cycle CuFe$_2$O$_4$@MC was separated with a magnet and recycled without loss considerable photocatalytic activity. CuFe$_2$O$_4$@MC has a lot of advantages such as high reusability, stability, environmentally-friendly and great photocatalyst activity. As well as, it can be applied for the contaminated water treatment.

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**Declaration of Competing Interest**

The authors declare that they have no competing financial interests.

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