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Ciprofloxacin oxidation by magnetic Fe_3O_4/Multi Walled Carbon Nano tubes composite as an effective heterogeneous Fenton catalysts

Mohammad Taghi Samadi[1], Reza Shokoohi[1], Ali Poormohammadi [1,2], Behnam Salmani[3], Roya Harati[1*]

[1]Department of Environmental Health Engineering, Faculty of Health and Research Center for Health sciences, Hamadan University of Medical Sciences, Hamadan, Iran
[2]Social Development & Health Promotion Research Center, Kermanshah University of Medical Sciences, Kermanshah, Iran
[3]Department of Environmental Health, School of Public Health, Yazd University of Medical Sciences, Yazd, Iran

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ABSTRACT

Ciprofloxacin (CIP) is one of the most common antibiotics for treating bacterial infection. The presence of ciprofloxacin in water environment has adverse effects on human health. Multi-walled carbon nanotube (MWCNT) is a promising technology for water and wastewater treatment. However, the lake of suitable catalysts limits its efficiency in the removal of pollutants. In this study, magnetic Fe_3O_4/MWCNTs composite were prepared and then the effect of magnetic Fe_3O_4/MWCNT composite as a heterogeneous Fenton catalyst in ciprofloxacin removal from synthetic wastewater was studied. Results showed that the heterogeneous Fenton process (HFP) efficiency decreased significantly with increasing pH. Moreover, by increasing CIF concentration the process efficiency decreased. The maximum removal efficiency of CIP was equal to 94% and was achieved at 2 g/L of magnetic Fe_3O_4/MWCNT composite. These findings suggested that magnetic Fe_3O_4/MWCNTs composite acts an effective catalyst in HFP for removing CIF from wastewater.

Keywords: Ciprofloxacin, oxidation, multi walled carbon Nano tube, Fenton

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INTRODUCTION

In recent years, the intensive use of pharmaceutical compounds in human and veterinary medicine has become a major public health concern [1]. The detection of antibiotics in sediments as well as sewage, surface water, groundwater and drinking water has been taken into huge consideration, due to its adverse effects [2]. Ciprofloxacin is one of the most important fluoroquinolone antibiotics for treating bacterial infections in both human and veterinary medicine [3]. Ciprofloxacin is also used worldwide in aquaculture and agricultural applications [4]. Their widespread application can lead to release of a high amount of this antibiotic into water bodies. This could also transported into the environment through discharge of wastewater and direct runoff. In addition, pharmaceutical wastewater usually contains a high concentration of antibiotics. Ciprofloxacin have been found in wastewater effluents and surface water in the range ngL^{-1} to mgL^{-1} [5]. The presence of ciprofloxacin in water environment could leads to increasing antibiotics resistant bacteria. Moreover, chlorination and ozonation processes may increase the toxicity of antibiotics and cause the formation of undesirable by-products [2,6]. It has been reported that

ciprofloxacin are not removed by conventional wastewater treatment plants [7,8]. Therefore, the development of novel and cheap technologies is necessary to remove these antibiotics before their discharge into the environment. Nowadays, nanotechnology has been considered as a promising technology to treat wastewater. Multi-walled carbon nanotubes (MWCNTs) have shown an ability to remove a wide range of pollutants such as heavy metals, organics and biological impurities from aqueous environments [9]. Major problems in the use of MWCNTs include costly regeneration, secondary contamination and difficult separation from liquid phase due to their small size. A combination between MWCNTs and iron oxide nanoparticles can create a new magnetically compound, which can be easily recovered from treated wastewaters by using a magnetic separation method [10].

In recent years, various magnetic materials such as activated carbon/Fe_3O_4 [10], activated carbon supported Fe_3O_4 [11] and polymer encapsulated Fe_3O_4 [12] have been studied as effective heterogeneous Fenton catalysts for the removal of organic pollutants. These compounds could lead to a significant promotion of H_2O_2 decomposition in Fenton process.

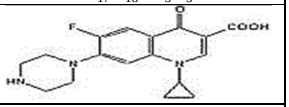
In this study, magnetic Fe_3O_4/MWCNTs composite were prepared and characterized by X-ray diffraction. The effect of magnetic Fe_3O_4/MWCNT composite as a heterogeneous Fenton catalyst in ciprofloxacin removal from wastewater synthetic was also studied. Moreover, the effect of some parameters such as pH, ciprofloxacin concentration, magnetic Fe_3O_4/MWCNT composite concentration, contact time and H_2O_2 concentration was studied in relation to the performance of heterogeneous Fenton catalyst in ciprofloxacin removal.

MATERIALS AND METHODS

Chemicals

Ciprofloxacin (99.5%) was purchased from Sigma Aldrich (Germany), acetonitrile and methanol (HPLC grade) were purchased from Merck (Germany), and MWCNTs were obtained from Nutrieno Co. (Tehran, Iran, http://parscenter.com/Company/CMP645327). All chemicals were used without further purification. The characteristics of ciprofloxacin were summarized in Table 1.

Table 1. Characteristics of ciprofloxacin

Formula	$C_{17}H_{18}FN_3O_3$
Molecular structure	
Molecular mass	331.346 g/mol
State	Milky powder
Other name	Neofloxin
Length	30 µm
External diameter	20-30 nm
Specific surface area	110 m^2/g
Density	2.1 g/cm^2
C.I. number	85721-33-1

The preparation of magnetic Fe_3O_4/MWCNTs composite

Magnetic Fe_3O_4/MWCNTs composite was synthesized based on the method by Hu et al [13]. First, the quantities of MWCNT (100 mg) were added to a flask which already contains 120 ml of H_2SO_4/HNO_3 (3:1, v/v). The flask was placed into the ultrasonic bath for 3h (60˚C). Then, the synthetic MWCNTs were dried at 80 ˚C for 8 h under vacuum conditions. Nitrogen gas was blown into the solution for removing oxygen from the solution, and 2 g $FeSO_4 \cdot 7H_2O$ was added. In the next step, the solution containing 1.8 g NaOH and 0.9 g $NaNO_3$ was heated at 95 °C and added into the heating MWCNTs-$FeSO_4$ suspension while kept vigorous stirring. The final solution was also heated at 95 °C for 2 h, the Fe_3O_4/MWCNTs composites formed. The precipitate then was separate by a magnet and washed with distilled water and methanol and, finally dried in the oven at 100 °C for 24 h under vacuum conditions. The preparation of MWCNTs was accomplished by stirring them in nitric acid for 12 h (70˚C). Next, they were filtered off, washed with distilled water and then dried at 110˚ C for 6 h. Then, MWCNTs were refluxed with 50% nitric acid for 12 h under stirring conditions. The product was then filtered and washed with doubly distilled water and finally dried in the oven [9,13]. The characteristics of MWCNTs were summarized in Table 2.

Table 2. Characteristics of MWCNTs

Appearance	Black powder
External diameter	20-30 nm
Length	30 µm
Purity carbon	95%
specific surface area	110 m^2/g
Density	2.1 g/cm^3

Batch experiments

In the present study, experiments were carried out in a batch reactor. The effect of some operational parameters such as pH (4-10), ciprofloxacin concentration (30, 50, 80, 100, 120, 150 and 200 mg/L), magnetic Fe_3O_4/MWCNT composite concentration (1, 2 and 3 g/L), contact time (15, 30, 60, 120, 180, 240 and 300 min) and H_2O_2 concentration (5, 10, 15, 25, 30 mmol/L) on the process efficiency was investigated. All samples were placed on the shaker (model sigma 301) with a speed of 150 rpm. Next, the samples were shaken with a speed of 2500 rpm for 15 min. Then, they were filtered using a cellulose acetate membrane filter, and finally the concentration of residual ciprofloxacin was measured.

RESULTS AND DISCUSSION

FTIR analysis

Fig.1 shows the FTIR spectra of MWCNT and modified magnetic Fe_3O_4/MWCNTs composite. The FTIR photograph of MWCNT presents two peaks at 3434 and 2919.57 cm^{-1}, which corresponded to the O-H and -COO- stretching, respectively. As shown, there were various functional groups detected on the surface of modified magnetic Fe_3O_4/MWCNT composite. Moreover, several peaks are observed on the FTIR photograph of modified magnetic Fe_3O_4/MWCNTs composite. The peak around 3438 cm^{-1} indicated the presence of OH compounds and the peak around 1384 cm^{-1}correspond to the presence of N-O nitrate compounds. The change in FTIR photograph of modified magnetic Fe_3O_4/MWCNT composite indicated the presence of sulfate and nitrate compounds in the structure of magnetic Fe_3O_4/MWCNT composite. Moreover, the peak around 579 indicated the presence of Fe_3O_4 in the magnetic Fe_3O_4/MWCNT composite.

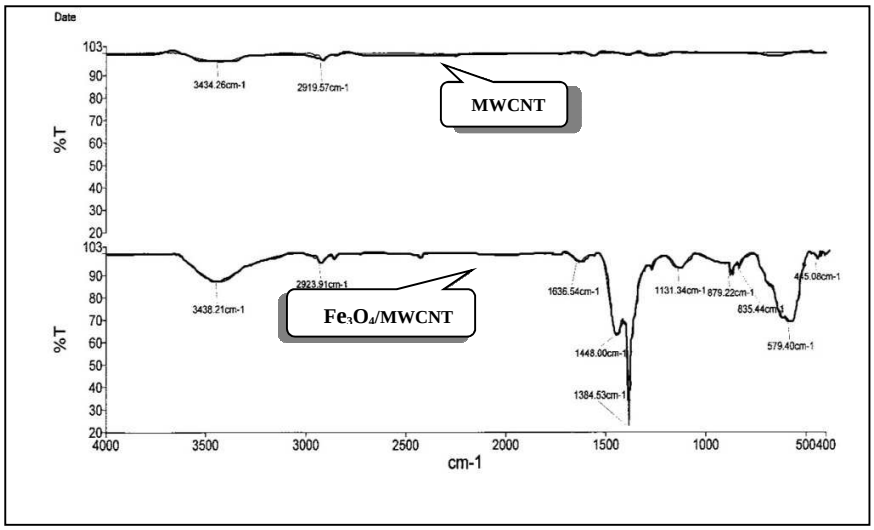


Fig.1 FTIR spectra of MWCNTs and magnetic Fe_3O_4/MWCNTs composite

XRD analysis

Fig.2 shows X-ray diffraction (XRD) patterns of (a) fresh and (b) used magnetic Fe_3O_4/MWCNTs composite catalyst at 2θ=15-65˚. As revealed, modified magnetic Fe_3O_4/MWCNT composite have a higher diffraction peaks than that of MWCNT. The increase of the diffraction peaks in magnetic Fe_3O_4/MWCNT composite may be due to the presence of crystalline phase and a high percentage of Iron. A broad peak was observed at 27˚ and 37˚ for fresh

and used magnetic Fe_3O_4/MWCNT composite catalyst, respectively, which may be related to the presence of Iron (III) sulfate heptahydrate. In addition, wedding of the bands indicated that ciprofloxacin has been hydrated.

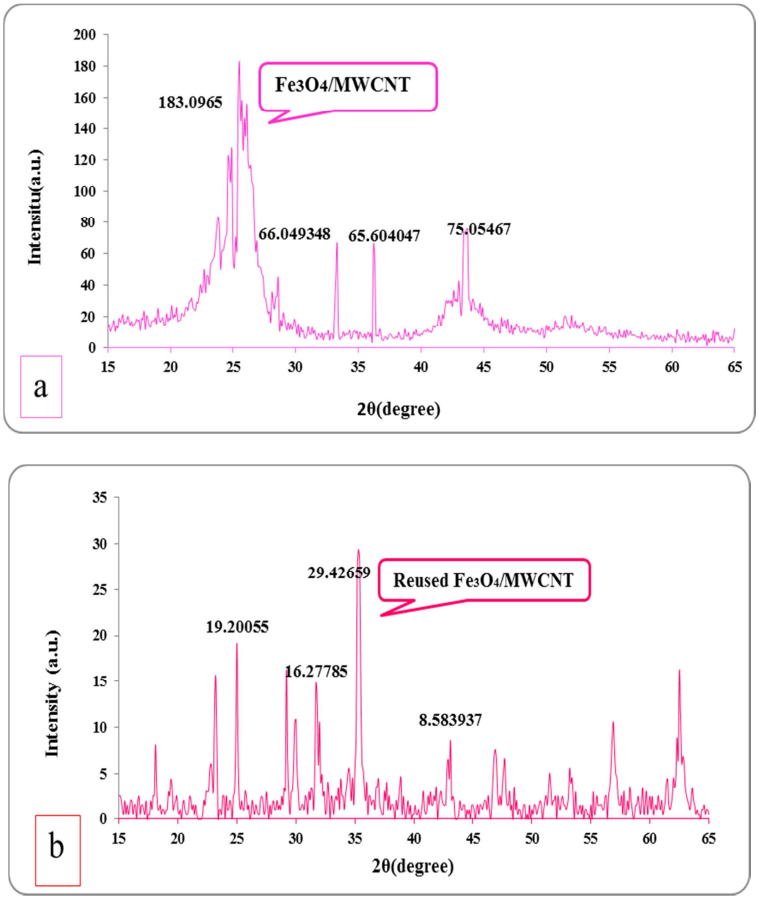


Fig.2 XRD pattern of (a) fresh and (b) used magnetic Fe_3O_4/MWCNTs composite

Effect of contact time

Fig. 3 shows the effect of contact time in the range 15-300 min on the heterogeneous Fenton process (HFP) efficiency in CIF removal. As shown here, the process efficiency increased with the increase of contact time from 15 to 180 min. The removal efficiency of CIF was 94% in 180 min of contact time. Then, after 180 min the process efficiency in CIF removal decreased sharply and became almost constant. Therefore, 180 min of contact time was chosen as the optimum contact time for following experiments.

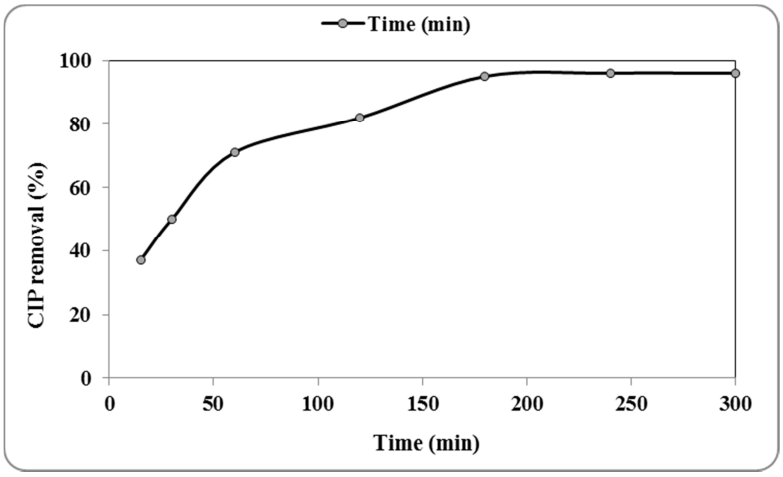


Fig. 3 The effect of contact time on the HFP efficiency (CIF concentration: 30 mg/L, catalyst dosage: 2 g/L and pH: 4)

Effect of pH

In order to investigate the effect of pH in HFP on CIF removal was studied in the range of 4-10. As shown in Fig. 4, the process efficiency decreased obviously with increasing pH. The maximum removal efficiency was observed at pH 4 and was equal to 94%. On the other hand, the minimum CIP removal (36%) was observed at pH 10 after 180 min. This can be attributed to the fact that the CIP solubility is very high at low pH values. Previous studies have also reported that the use of magnetic composite have a better efficiency at acidic pH values. A similar trend of pH effect was observed by Hu X et al. on methyl testosterone 17α removal using HFP [13].

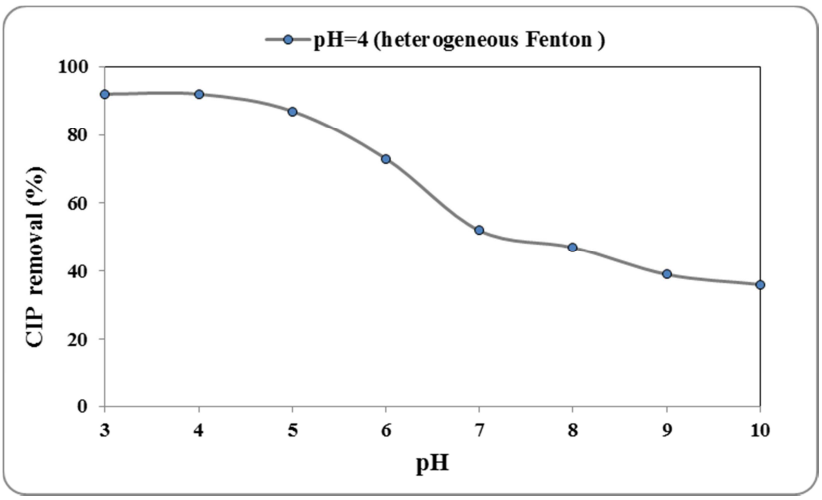


Fig. 4 The effect of pH solution on the HFP efficiency (CIF concentration: 30 mg/L, catalyst dosage 2 g/L and contact time: 180 min)

Effect of CIF concentration

In this part of the study, the effect of CIF concentration in the range 30 to 200 mg/L on HFP was studied. As shown in Fig. 5, the HFP efficiency decreased with increasing CIF. So, the maximum removal efficiency of CIP was achieved at 30 mg/L of initial CIF concentration. On the contrary, the minimum efficiency was seen at 200 mg/L of initial CIF concentration that was equal to 25%, after 180 min. This can be attributed to the fact that HFP produced only a limited amount of oxidant (e.g. hydroxyl radical). Therefore, by increasing CIF concentration, the process efficiency decreased under constant experimental conditions. Similar results were also obtained by Xing Zha et al [14].

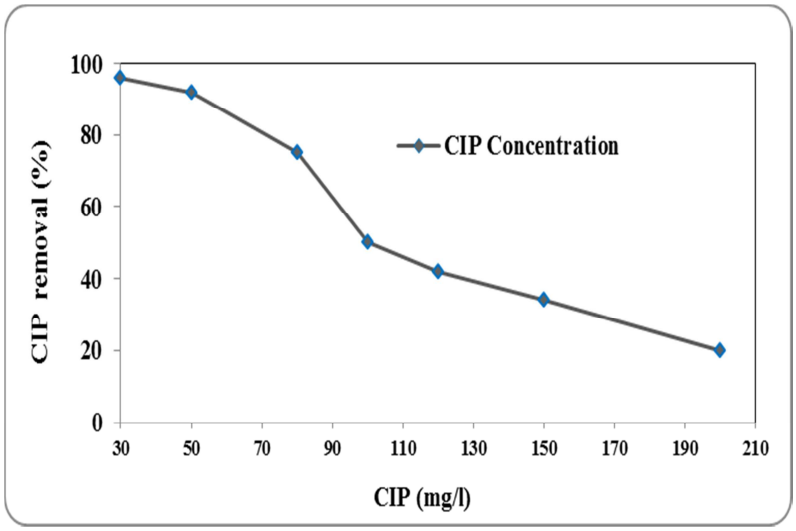


Fig. 5 The effect of initial CIF concentration on the HFP efficiency (CIF concentration: 30 mg/L, catalyst dosage 2 g/L, pH: 4, H_2O_2 dosage: 1 mmol/L and contact time: 180 min)

Effect of magnetic Fe_3O_4/MWCNT composite

One of the most important factors in HFP is the catalyst concentration. In this research the effect of magnetic Fe_3O_4/MWCNT composite as a catalyst in HFP on CIF removal was studied in the range 1 to 3 g/L. When 1 to 2 g/L of magnetic Fe_3O_4/MWCNT composite were used, the HFP efficiency proceeded in a sharp manner (from 60.42% to 94%). The increase of CIF removal with increasing catalyst dosage is due to the increase of catalyst surface area. On the other hand, by increasing the dosage of magnetic Fe_3O_4/MWCNT composite from 2 to 3 g/L, the HFP efficiency increased slightly. Therefore, 2 g/L of magnetic Fe_3O_4/MWCNT composite was chosen as the optimum catalyst concentration (Fig.6).

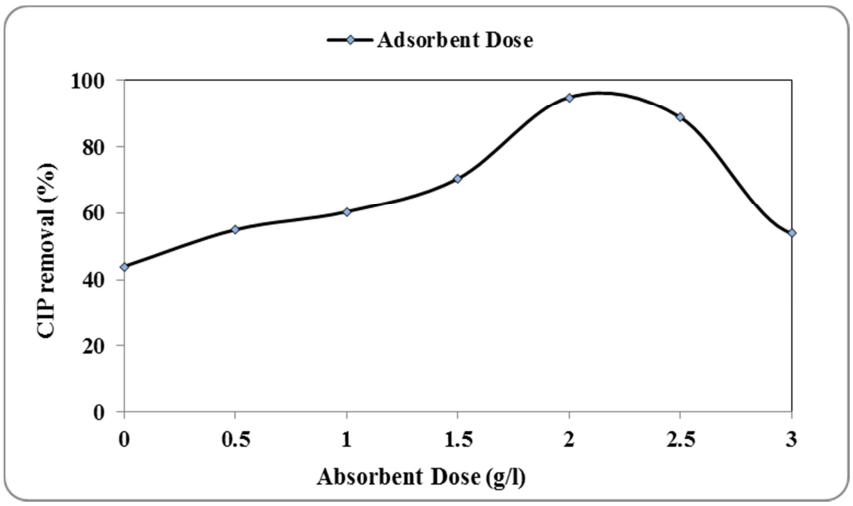


Fig.6 The effect of catalyst dosage on the HFP efficiency (CIF concentration: 30 mg/L, pH: 4 contact time: 180 min)

Effect of H_2O_2 dosage

In this part of the study, the effect of hydrogen peroxide dosage in the range 5 to 25 mL/L on HFP was investigated. As revealed in Fig. 7, in HFP the removal efficiency of CIF increased with the increase of hydrogen peroxide dosage from 5 to 20 mL/L. On the contrary, as hydrogen peroxide dosage increased from 20 to 25 mL/L, CIF removal efficiency decreased. This result is due to over-dosage of hydrogen peroxide in the reactor. High dosage of hydrogen peroxide can lead to the faster hydrogen peroxide consumption. Finally, the hydroperoxyl radical generated from the

hydrogen peroxide decomposition (according to Eq. 6), is a weak oxidant compared with the hydroxyl radical [15,16].

$OH° + H_2O_2 \rightarrow H_2O + HO_2°$

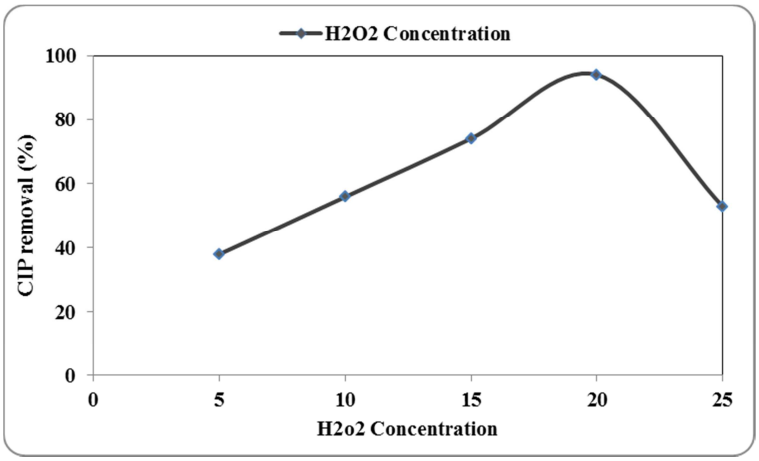


Fig.7 The effect of H_2O_2 dosage on the HFP efficiency (CIF concentration: 30 mg/L, catalyst concentration: 2 g/L, pH: 4 and contact time: 180 min)

CONCLUSION

In this study, magnetic Fe_3O_4/MWCNT composite were prepared and characterized by X-ray diffraction. The effect of magnetic Fe_3O_4/MWCNT composite as a heterogeneous Fenton catalyst in ciprofloxacin removal from synthetic wastewater was studied. Moreover, the effect of some parameters such as pH, ciprofloxacin concentration, magnetic Fe_3O_4/MWCNT composite concentration, contact time and H_2O_2 concentration on HFP was studied. Results showed that the HFC efficiency decreased significantly with increasing pH. Moreover, by increasing CIF concentration the process efficiency decreased. The maximum removal efficiency of CIF was equal to 94% and was achieved at 2 g/L of magnetic Fe_3O_4/MWCNT composite. These findings suggested that magnetic Fe_3O_4/MWCNT composite acts an effective catalyst in HFP for removing CIF from wastewater.

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