Microwave-Assisted High-Efficiency Degradation of Methyl Orange by using CuFe₂O₄/CNTs Catalysts and Insight into Degradation Mechanism

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Research Article

Keywords: Microwave-assisted, Carbon nanotubes, CuFe₂O₄, Microwave absorption, Degradation mechanism

Posted Date: February 10th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-180386/v1>

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Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on April 5th, 2021. See the published version at <https://doi.org/10.1007/s11356-021-13694-z>.

1 **Microwave-assisted high-efficiency degradation of methyl orange by**
2 **using CuFe₂O₄/CNTs catalysts and insight into degradation**
3 **mechanism**

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1 **Abstract**

2 Microwave-assisted catalytic oxidation technology has become an effective
3 technology for rapid removal of organic pollutants in wastewater. In this research, the
4 removal of methyl orange from aqueous solution by CuFe_2O_4 loaded on carbon
5 nanotubes ($\text{CuFe}_2\text{O}_4/\text{CNTs}$) under microwave irradiation was studied. The effects of
6 different loadings (1:2, 1:4, 1:8) of CuFe_2O_4 on the dielectric loss, magnetic loss,
7 dielectric loss factor, magnetic loss factor and reflection loss of composite materials
8 were studied. The results showed that the microwave adsorption performance was
9 improved by loading CuFe_2O_4 on CNTs. These different composites were further
10 characterized by SEM, FTIR and XRD techniques. In addition, this article also
11 studied the effects of different microwave irradiation time, pH, and ionic factors on
12 the degradation of methyl orange. In particular, the mechanism of methyl orange
13 degradation by composite materials under different pH conditions was also studied in
14 detail. The results show that the removal rate reaches 97.16% with 5 min under the
15 best conditions, and the composite material has good anti-interference performance.
16 This study may provide a new option to degrade organic dye in wastewater treating.

17 **Keywords:** Microwave-assisted; Carbon nanotubes; CuFe_2O_4 ; Microwave absorption;

18 Degradation mechanism

1 **1. Introduction**

2 Nowadays, with development of some industries such as dyestuffs, textile,
3 printing, food, pulp, paper and paper-making, a large amount of dyes are discharged
4 into the natural environment (Liang et al. 2021, Shao et al. 2020a, Xiao et al. 2020a).
5 Particularly, azo dyes which have one or more azo groups, are about 50% in dye
6 wastewaters. Most of these dyes are considered to be toxic, non-biodegradable and
7 even carcinogenic. It may threaten human health and cause bad effects on the
8 environment (Chamjangali et al. 2015, Robati et al. 2016, Shao et al. 2019b, Tanhaei
9 et al. 2015). Therefore, the removal of dyes from effluents has received major
10 attention. Some common techniques and methods such as precipitation, adsorption,
11 coagulation/flocculation, microwave-assist, photochemical or electrochemical
12 oxidation and microbial degradation have been used to remove dyes from wastewater
13 (Liu et al. 2019a, Liu et al. 2018e, Liu et al. 2017, Shao et al. 2017). However, these
14 methods have more or less problems, such as expensive, low efficiency and technical
15 complexity, so further research and improvement are still necessary (Jiang et al. 2018,
16 Liang et al. 2020, Liu et al. 2016, Liu et al. 2018c).

17 Among these methods, microwave-assisted degradation process was considered
18 as a promising method due to the rapid reaction rate, high efficiency and

1 environment-friendly properties (Chen et al. 2016, Liu et al. 2018a, Liu et al. 2016,
2 Liu et al. 2018c). Under microwave irradiation, some special materials which called
3 as microwave adsorbents can adsorb microwave effectively, and “hot spots” are
4 generated on microwave adsorbents (Chen et al. 2016). Organic pollutants around
5 such regions with localized heat can be adsorbed and decomposed (Chen et al. 2016,
6 Liu et al. 2018a). In various azo dyes, MO is more stable due to the presence of
7 aromatic rings in its structure (Mohamed et al. 2020). Therefore, MO is often used as
8 a representative of azo dyes for microwave degradation.

9 Microwave adsorbents are essential in microwave assisted degradation process.
10 Common microwave adsorbents include carbon-based materials and magnetic
11 materials (Liu et al. 2018a). And there are two microwave loss mechanisms: dielectric
12 loss and magnetic loss accordingly. On the one hand, it is known that the effective
13 complementarities between two loss mechanisms are beneficial to improve the
14 microwave absorption performance of materials. On the other hand, single carbon
15 nanomaterials exhibit slow kinetics and poor selectivity while single magnetic
16 materials show strong adsorption strength and fast adsorption kinetics but have poor
17 dispersion and narrow adsorption frequency bandwidth. The combination of the two
18 kinds of microwave adsorption materials is beneficial to improve the microwave

1 adsorption performance (Li et al. 2018, Liu et al. 2018a, Liu et al. 2019b, Shen et al.
2 2018, Wu et al. 2020). Owing to the unique spinel structure and high catalytic activity,
3 CuFe_2O_4 has strong magnetic and can be used as microwave-adsorbing materials (Liu
4 et al. 2014, Taleshi et al. 2014). Carbon nanotubes (CNTs), as the promising
5 microwave-adsorbing materials, which can be applied to support the metal
6 nanoparticles for their nucleation and growth (Chen et al. 2016, Peng et al. 2020,
7 Taleshi et al. 2014, Zhang et al. 2020). Therefore, $\text{CuFe}_2\text{O}_4/\text{CNTs}$ composites with
8 two different loss mechanisms might be a promising candidate as
9 microwave-adsorbing materials.

10 In this research, the novel $\text{CuFe}_2\text{O}_4/\text{CNTs}$ composites were prepared and used for
11 microblog to assist in the degradation of MO. The effects of different loadings of
12 CuFe_2O_4 on the microwave absorption performance and catalytic degradation
13 performance of composite materials were studied. Meanwhile, the degradation
14 stability of composite materials in complex environments was studied. It is worth
15 noting that the mechanism of MO degradation of composite materials under different
16 pH conditions was studied in detail by using different quenchers.

2 Experimental

2.1 Materials

Multi-walled carbon nanotubes (95% purity) were purchased from Nanjing XFNANO Materials Tech Co. Ltd., China. Methyl orange, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, FeCl_3 , t-butanol (BU), benzoquinone (BQ), and potassium iodide (KI), nitric acid (HNO_3), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd., China. All of the chemical reagents were analytical reagent grade and the received reagents were without further treatment. The deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$) employed throughout the whole studies was purified by a Milli-Q water system (Millipore Company, USA).

2.2 Synthesis of $\text{CuFe}_2\text{O}_4/\text{CNTs}$

The preparation of $\text{CuFe}_2\text{O}_4/\text{CNTs}$ included two steps. The first step is that CNTs were oxidized by concentrated nitric acid. And then, the filtered oxidized-CNTs were washed with deionized water until the pH is neutral. The neutral CNTs were filtered and dried at 110°C in an oven for 6.0 h. The resulted CNTs powder were subjected to grinding (Chen et al. 2016, Liu et al. 2018a). To prepare the nanocomposites, 0.3g of oxidized CNTs powder were poured into 50 mL deionized water and dispersed by sonication for 10 minutes. Then, add a certain amount of FeCl_3 and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and

1 keep Fe:Cu (molar ratio) = 2:1. To get different mass ratios of CuFe₂O₄ to CNTs (1:2,
2 1:4, 1:8), the amount of CNTs increased with the decrease of proportion of CuFe₂O₄.
3 And the nanocomposites with different contents of CNTs were named as
4 CuFe₂O₄/CNTs_{1:2}, CuFe₂O₄/CNTs_{1:4}, CuFe₂O₄/CNTs_{1:8}. Furthermore, the CNTs
5 dispersion was adjusted to pH=12. Under stirring, according to the molar ratio of 1:2,
6 a certain amount of CuCl₂·2H₂O and FeCl₃ were added to the dispersion. After boiling
7 for one hour, the solution was filtered and rinsed several times with deionized water
8 until neutral. The obtained product was also dried in an oven and ground into powder.
9 In the end, the powder samples were calcined 3 h at 600 °C (Taleshi et al. 2014).

10 **2.3 Characterization**

11 A series of CuFe₂O₄/CNTs were analyzed by scanning electron microscope
12 (SEM, FEI,Quanta-F250) to observe the surface morphology and microstructure. The
13 crystal structure and crystallinity were identified by X-ray diffraction (XRD) analysis.
14 And it was performed with a Bruker AXS D8 advance diffractometer using Cu-Ka
15 source. The functional groups formed on the materials were identified by infrared
16 spectra recorded with a Fourier transform infrared (FTIR, NICOLET, 5700)
17 spectrometer within the range of 4000-400 cm⁻¹. The microwave-adsorbing
18 performance was measured by a microwave network vector. The range was between

2-18 GHz. All tested samples should be mixed with molten wax. And the proportion of materials was 20 wt%.

2.4 Degradation experiments

The MW-induced catalytic degradation of MO solutions was carried out in a microwave digestion instrument. Typically, in an experiment, 50 mg of CuFe₂O₄/CNTs was introduced into 100 mL flask-3-neck with 50 mL MO (20 mg·L⁻¹) solutions. After constant stirring, the suspension was put into MW instrument. The power of MW is 900W and the time is 5 minutes. The UV-vis spectra of MO solutions catalytic degradation by different materials (CuFe₂O₄/CNTs_{1:2}, CuFe₂O₄/CNTs_{1:4}, CuFe₂O₄/CNTs_{1:8}) was obtained using a UV-vis spectra (Cary 300, Varian Company, USA). MO solutions treated by MW only, CNTs only, CuFe₂O₄ only were obtained as controls. The degradation percentage was calculated according to the next equation:

$$Degradation \% = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where C₀ is the initial concentration of MO and C is concentration of MO at time t.

The total organic carbon (TOC) removal was measured by a TOC analyzer (TOC-5000A, Shimadzu, Japan.) And the TOC removal ratio can be calculated according to the equation:

$$TOC \% = \frac{T_0 - C}{T_0} \times 100\% \quad (2)$$

The meaning of T_0 and T are initial TOC and TOC at particular time, respectively. All experiments were repeated 2-3 times and the calculated experiment errors were less than 5%.

2.5 Evaluation the effects of pH on the degradation mechanism

In different pH condition, trapping experiments by using three scavengers (KI, BU, BQ) were conducted. These three scavengers can quench h^+ , $\bullet OH$ and $\bullet O_2^-$, respectively (Liu et al. 2018b, Shao et al. 2019a). In order to investigate the main active species in different pH, a series of concentration of scavengers (KI (6.02,9.04,12.05,15.06 mmol L⁻¹), BU(0.4,0.6,0.8,1,1.2 mol L⁻¹), BQ(3,6,9,12 mmol L⁻¹)) were added (Liu et al. 2018b). All of these experiments were repeated three times and the experiment errors were less than 15%.

3. Results and discussion

3.1 Characterization

The morphology and structural characteristics of the material were analyzed by SEM. SEM images of CNTs, CuFe₂O₄/CNTs_{1:2}, CuFe₂O₄/CNTs_{1:4}, CuFe₂O₄/CNTs_{1:8} were compared and the shape and composition were analyzed (Figure 1). The images showed that the size of CNTs with different content of CuFe₂O₄ was almost identical.

1 With the increase of CuFe_2O_4 content, the gaps between the materials were getting
2 smaller and smaller, and they were more closely combined, which showed that the
3 composite material is successfully prepared. In addition, the dispersibility of CuFe_2O_4
4 deteriorated and partially aggregated as the content increases, which might result in a
5 decrease in catalytic activity.

6 The chemical structure of the sample is judged by FTIR. [Figure 2a](#) showed some
7 differences in FTIR spectra among CNTs, $\text{CuFe}_2\text{O}_4/\text{CNTs}_{1:4}$ and CuFe_2O_4 samples.
8 The stretching band at 3412 cm^{-1} can be assigned to the stretching vibrations of O-H,
9 which may come from intramolecular crystal water. (Liu et al. 2014). Besides, the
10 band at $1600\text{--}1800\text{ cm}^{-1}$ belongs to stretching vibrations of C=O and the band around
11 1200 cm^{-1} belongs to the adsorption peaks of C-O (Chen et al. 2016, Liang et al. 2019,
12 Shao et al. 2020b). These oxygen-containing functional groups promote the
13 production of hydroxyl free radicals in MW/catalyst system. The band at 2363 cm^{-1} is
14 associated with CO_2 in environment. The band at 1632 cm^{-1} is assigned to C=C
15 skeleton vibration of CNTs (Chen et al. 2016). The bands at 563 cm^{-1} and 438 cm^{-1}
16 are the characteristic peaks of CuFe_2O_4 samples. After loaded CuFe_2O_4 nanoparticles
17 on CNTs, the bands attributed to the characteristic peaks of CuFe_2O_4 increase, the
18 adsorption bands at around 3412 cm^{-1} , 2363 cm^{-1} , 1632 cm^{-1} also increase. It indicated

1 an increase of related functional groups. And these changes are related to the
2 interaction between CNTs and CuFe₂O₄ (Liu et al. 2014). In summary, the composite
3 CuFe₂O₄/CNTs_{1:4} contains both CNTs and CuFe₂O₄ element characteristic peaks,
4 which are attributed to the interaction between CNT and CuFe₂O₄ (Liu et al. 2014).
5 Meanwhile, it also proved the successful construction of composite materials.

6 As shown in [Figure 2b](#), the crystal structure and the effect of different CNTs
7 content were analyzed by XRD spectra. The peaks at $2\theta = 26^\circ$ are characteristic peaks
8 of CNTs and are attributed to the presence of graphene sheets (Liu et al. 2018a,
9 Taleshi et al. 2014). The peaks at $2\theta = 30.1^\circ, 35.4^\circ, 38.8^\circ, 43.2^\circ, 53.5^\circ, 57^\circ, 62.7^\circ$ are
10 indexed to planes (220), (211), (200), (311), (222), (511), (224) of spinel-type
11 CuFe₂O₄ (JCPDS NO. 34-0425), respectively. The presence of these characteristic
12 peaks related to CuFe₂O₄ nanoparticles indicated that CuFe₂O₄ was successfully
13 loaded onto the surface of CNTs nanocomposites (Taleshi et al. 2014). Besides, with
14 the content of CNTs increasing, the intensity of peaks decreases except for peak at 2θ
15 $= 26^\circ$ and the width increases. The size of nanoparticles also decreases with the
16 decreased concentration of metal ions. According to Sharer equation 3, the sizes of
17 CuFe₂O₄ nanoparticles related to CuFe₂O₄/CNTs_{1:2}, CuFe₂O₄/CNTs_{1:4},
18 CuFe₂O₄/CNTs_{1:8} were determined as 48.93nm, 44.13nm and 36.69nm, respectively.

1
$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

2 **3.2 Evaluation of microwave-adsorbing properties**

3 The microwave absorption performance of the material is a very important
4 indicator for evaluating the microwave-assisted degradation performance. The
5 microwave adsorption properties are analyzed by four parameters: ϵ' , ϵ'' , μ' , μ'' . ϵ' is
6 real part and ϵ'' is imaginary part of relative complex permittivity (ϵ_r). μ' is real part
7 and μ'' is imaginary part of relative complex permeability (μ_r). The real part of relative
8 complex permittivity and permeability are related to the store ability of electric and
9 magnetic energy. The imaginary part of relative complex permittivity and
10 permeability are related to the dissipation ability of energy (Li et al. 2018, Liu et al.
11 2018a). As shown in [Figure 3](#), the ϵ' and ϵ'' values of CNTs and CuFe₂O₄/CNTs_{1:4}
12 exhibit descending trend as a whole. The ϵ' and ϵ'' values of CuFe₂O₄ have no
13 significant changes and values are around 0. The μ' and μ'' values of CuFe₂O₄/CNTs_{1:4}
14 and CuFe₂O₄ have minor fluctuation and stay around 1 and 0. However, the values of
15 CNTs change obviously from 2 to 18 GHz. It may be due to the particle size of CNTs
16 is nonuniform. Overall, it indicated that the main microwave loss mechanism of
17 CuFe₂O₄/CNTs_{1:4} nanocomposites was dielectric loss (Li et al. 2018). This can be
18 demonstrated by the higher values of dielectric loss factor ($\tan \delta_\epsilon = \epsilon''/\epsilon'$) than

1 magnetic loss factor ($\tan \delta_\mu = \mu''/\mu'$). The higher tangent loss means better microwave
2 adsorption performance. And in the high frequency range, the gap between the two
3 values narrowed. It indicates that high frequency is beneficial to achieve better
4 electromagnetic impedance matching. In this point, microwave-adsorbing materials
5 have better adsorption performance (Li et al. 2018, Liu et al. 2018a). Microwave
6 adsorption performance can be improved from several aspects. On the one hand, the
7 dielectric loss can be attributed to dipole polarizations, interfacial polarizations and
8 conductivity loss. On the other hand, the magnetic loss can be attributed to eddy
9 current effect as well as natural and exchange resonance (Jian et al. 2016, Pan et al.
10 2016). In our research, compared to CuFe_2O_4 , the improved microwave adsorption
11 performance was from interfacial polarizations between CuFe_2O_4 nanoparticles and
12 CNTs and the better impedance matching was achieved (Jian et al. 2016).

13 To evaluate the effect of different proportions of $\text{CuFe}_2\text{O}_4/\text{CNTs}$ on microwave
14 adsorption performance, the reflection loss (RL) was calculated according to the
15 following equations:

$$16 \quad RL \text{ dB} = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (4)$$

$$17 \quad Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[j \left(\frac{2\pi f d}{c} \right) \sqrt{\mu_r \epsilon_r} \right] \quad (5)$$

1 where Z_{in} represents the input impedance of the microwave absorber and Z_0
2 represents the impedance of the free space. Usually, Z_0 is treated as 1. f is frequency
3 of microwave, d represents the thickness of adsorber samples and c is the velocity of
4 light in free space (Li et al. 2018, Liu et al. 2018a). As shown in Figure 4a, the greater
5 absolute value of RL corresponds to weaker adsorption capacity of microwave. The
6 maximum RL followed a trend that: $CuFe_2O_4 > CNTs > CuFe_2O_4/CNTs_{1:8} >$
7 $CuFe_2O_4/CNTs_{1:4} > CuFe_2O_4/CNTs_{1:2}$, which indicated the construction of composite
8 materials effectively improves the microwave absorption performance of a single
9 material. This confirmed that effective impedance matching was the key to improve
10 microwave adsorption performance once again. In addition, the coating of $CuFe_2O_4$
11 and the small size of nanoparticles can facilitate the microwave transmitting into the
12 nanocomposites (Li et al. 2018).

13 3.3 Degradation of MO in various systems

14 Better microwave adsorption performance does not always mean higher removal
15 rate of MO in microwave induced catalytic oxidation process (Ju et al. 2013).
16 Therefore, the degradation rate of MO with several catalysts is compared. Figure 4b is
17 UV-vis spectra of MO solutions degraded in different conditions. The adsorption
18 peaks at 466 nm and 270 nm can be attributed to azo bonds and benzyl rings of MO,

1 respectively. The simultaneous decrease of these two adsorption peaks means that the
2 molecular structure of MO was destroyed in such systems (Chen et al. 2016).
3 Obviously, MO was barely degraded by microwave irradiation alone. Because the
4 energy of microwave irradiation is 2.45 GHz and it can't destroy covalent bonds,
5 hydrogen bonds etc. (Ju et al. 2013). CNTs are dominant in the removal of MO. With
6 the content of CNTs increased to 1:4 (CuFe₂O₄/CNTs), the absorbance decreased,
7 which indicated that the degradation rate was enhanced. However, the improvement
8 of removal effect was weakened when the content of CNTs further increased. And all
9 nanocomposites have higher removal rate of MO than single-component CuFe₂O₄.
10 This confirms that good impedance matching facilitates the adsorption of microwave
11 and later formation of "hot spots" (Liu et al. 2018a).

12 **3.4 Effects of pH on the degradation mechanism**

13 It was known that pH can affect the charge of contaminants and materials. Thus,
14 the adsorption of contaminants on materials would be changed by electrostatic
15 attraction or electrostatic repulsion (Shao et al. 2019a, Yu et al. 2015, Zhong et al.
16 2016a, Zhong et al. 2016b). In MW/catalyst systems, pH value has the same function.
17 It was determined that the isoelectric points (pH_{IEP}) of CNTs are about 5.5-6.5 (Chen
18 et al. 2016). As shown in [Figure 5](#), the maximum removal rate of MO was achieved at

1 pH=4, and the removal rate decreased with the pH value increased. This was
2 correlated with the change of electrostatic attraction between negatively charged MO
3 anions and CuFe₂O₄/CNTs nanocomposites. Moreover, active substances including
4 •O₂⁻, •OH and holes play a vital role in the degradation of pollutants in the
5 MW/catalyst system (Liu et al. 2019c, Pan et al. 2020, Xiao et al. 2020b). Therefore,
6 we studied the effect of active substances at different pH to further analyze and
7 explore the effect of pH on the degradation mechanism (Fang et al. 2013, Pan et al.
8 2018). As shown in Figure 5, the highest level of inhibition was achieved by BQ at
9 pH=4, indicating that •O₂⁻ would play a leading role for the degradation at this pH. At
10 pH=7, the main active species were still •O₂⁻. However, when pH value increased to
11 10, the •OH active species play a main role in the degradation process. It indicated
12 that the main active species had been changed. And all scavengers resulted in different
13 degrees of inhibition effects, indicating that all active species play a role in the
14 degradation of MO.

15 In summary, the possible degradation pathways of MO and the roles of active
16 species are depicted in Figure 6. Under MW irradiation, the electron (e⁻)/hole (h⁺)
17 pairs are separate. The oxygen molecules around catalysts can be reduced into •O₂⁻.
18 The donors were water molecules which adsorbed on the surface of catalysts, by

1 combination with $\bullet\text{O}_2^-$, the $\bullet\text{OH}$ radicals can be produced (Liu et al. 2014, Qiu et al.
2 2016). And the participation degree of the active species in degradation process can be
3 evaluated by addition of trapping agent. KI、BU and BQ are scavengers of h^+ , $\bullet\text{OH}$
4 and $\bullet\text{O}_2^-$, respectively (Liu et al. 2014, Shao et al. 2018, Shen et al. 2018).

5 **3.5 Effects of ions**

6 Various ions including inorganic anions (i.e. SO_4^{2-} , F^- , HCO_3^- , and Cl^-) and
7 cations (i.e. K^+ , Na^+ , Mg^{2+} , and Ca^{2+}) are common in real wastewater, especially
8 dyestuff and other industrial wastewater (Liu et al. 2016, Liu et al. 2018b). Therefore,
9 some ions are used at concentration of 0.05 M to investigate their effects on the
10 removal of MO. The anions had no significant effects on MO degradation. Most of
11 anions enhanced the degradation slightly while HCO_3^- showed a slight inhibition
12 effect (Figure 7a). The inhibition effect may be attributed to that HCO_3^- can serve as a
13 scavenger for $\bullet\text{OH}$ radicals. In addition, HCO_3^- can compete for adsorption sites on
14 catalysts (Liu et al. 2016). Interestingly, the cations had similar effect on MO
15 degradation. The removal rate of MO was increased in the order: $\text{Mg}^{2+} <$
16 $\text{Na}^+ < \text{K}^+ < \text{Ca}^{2+}$ (Figure 7b). The slight impediment of Mg^{2+} on the degradation of MO
17 in MW/catalyst system may be attributed to the high hydration free energy (-447.2
18 kcal/mol). When water molecules desorbed from the hydration shells of cations, a part

1 of microwave energy was consumed. Thus, it resulted in the reduced microwave
2 energy for formation of “hot spots” (He & Cheng 2016, Hu & Cheng 2013). However,
3 the addition of several other cations led to the increase of the removal rate of methyl
4 orange to varying degrees. Studies have shown that an increase in the density of
5 cations on the surface of mineral particles is beneficial to the microwave degradation
6 of nitrosodiphenylamine, and the lower the free energy of cation hydration, the higher
7 the degradation rate. This is due to the fact that hot spots can be formed by the
8 selective heating of polar substances in mineral particles, including surface cations,
9 hydroxide radicals, adsorbed water molecules and organic molecules (Liao et al.
10 2017). Overall, all ions had little effects on MO degradation. It may indicate that
11 CuFe₂O₄/CNTs nanocomposites had good selectivity and strong anti-interference
12 ability (He et al. 2019, Liu et al. 2018b).

13 **3.6 TOC removal test and effects of time on the degradation**

14 As shown in [Figure 7c](#), the removal rate of TOC and MO increased over time. In
15 the end, the TOC removal rate reached 91.16% while the removal rate analyzed by
16 UV-vis spectra was 83.44% after 5 min reaction. Such high TOC removal indicated
17 that MW catalytic degradation is an effective pathway to remove MO. And the main
18 removal mechanism is oxidation rather than adsorption. Under MW irradiation, MO

1 was oxidized into inorganic ions and carbon dioxide (Figure 6) (Zhang et al. 2012).

2 Besides, the degradation kinetic of MO in MW-CuFe₂O₄/CNTs 1:4 system was fitted

3 with pseudo first-order model:

4
$$\ln \frac{C_t}{C_0} = -kt \quad (6)$$

5 Where C₀ is the initial concentration of MO and C_t is concentration of MO at time t.

6 The linear equation is: Y=0.3446X+0.1331 (R²= 0.9722)(Figure 7c). It doesn't go

7 through the origin because of adsorption. According to the pseudo first-order model,

8 the rate constant k can be calculated as 0.3446 min⁻¹. Compared to previous studies,

9 the calculated rate constant of MO degradation by CNTs/MW with different diameter

10 (10–20 nm, 20–40 nm, 40–60 nm) was 0.375, 0.198 and 0.132 min⁻¹,

11 respectively(Chen et al. 2016). It seems that the MW catalytic degradation efficiency

12 of CNTs was improved by loading CuFe₂O₄ nanoparticles on the CNTs surface.

13 Moreover, the rate constants was only 0.00656 min⁻¹ for MO degradation by

14 photocatalysis using Pt/PtO/La₂O₃ hybrid as catalyst (Zhao et al. 2020). It may

15 indicate that CuFe₂O₄/CNTs nanocomposites could be a promising catalyst on MW

16 degradation of organic pollutants.

3.7 Influence of reuse time

The effects of reuse time of CuFe₂O₄/CNTs nanocomposites were investigated to evaluate the stability. The stability and reusability of catalysts are indicators of whether it is cost-effective (Shao et al. 2019c). In the actual wastewater treatment process, economic treatment of pollutants is necessary. Thus, the CuFe₂O₄/CNTs were reused for three times. Due to the magnetism, the used CuFe₂O₄/CNTs nanocomposites can be collected by external magnetic field and washed by diluted ethanol (H₂O:ethanol = 1:1). Then they were dried in an oven (Chen et al. 2016, Liu et al. 2018b, Pan et al. 2018, Shen et al. 2018). And the removal rate was shown in Figure 7d. The degradation rate of MO catalyzed by CuFe₂O₄/CNTs under MW was decreased gradually when the reused time increased. The removal rate was 40.09% for reusing two times and about 36.78% reduced efficiency compared to the first degradation. The decreased catalytic activity of CuFe₂O₄/CNTs can be attributed to two reasons. One is that the adsorption capacity of CuFe₂O₄/CNTs may be decreased. Another is that metal may be leached from CuFe₂O₄/CNTs (Liu et al. 2018d). Therefore, some appropriate regeneration method should be applied to maintain the activity of catalysts (Chen et al. 2016).

1 **4. Conclusion**

2 The novel CuFe₂O₄/CNTs nanocomposites were proved effective in removing
3 MO. Under MW irradiation, active species including h⁺, •OH and •O₂⁻ were formed
4 on the surface of nanocomposites. With combined action of all active species, the
5 removal rate reached 83.44% and the TOC removal rate was 91.16% within 5 min
6 (initial concentration of MO=20mg/L, concentration of CuFe₂O₄/CNTs_{1:4}=1g/L). And
7 the efficiency increased with the content of CNTs increased. The high removal
8 efficiency of CuFe₂O₄/CNTs nanocomposites may be attributed to the improved
9 microwave adsorption performance. In addition, the effect of pH on the degradation
10 mechanism of MO was discussed in detail. The prepared CuFe₂O₄/CNTs
11 nanocomposites had strong anti-interference ability and it was less affected by some
12 common anion and cations. High catalytic efficiency, easy separation and less
13 by-products made CuFe₂O₄/CNTs catalytic degradation organic pollutants under MW
14 irradiation become a promising approach. Although the performance of currently
15 prepared composite materials needs to be further improved and poor reusability may
16 affect the wide use of catalysts in actual wastewater treatment, it is clear that
17 microwave-assisted degradation is an efficient and rapid degradation technology.
18 Therefore, in the future, some research should be conducted to construct

1 high-performance materials and improve the reusability of catalysts, and to test the
2 influence of different synthesis pathways on the catalytic effect.

3 **Author's contribution Zhifeng Liu:** Conceptualization, Resources, Project
4 administration, Funding acquisition. **Wei Zhang:** Conceptualization, Methodology,
5 Investigation, Validation, Writing-original draft. **Qinghua Liang:** Investigation,
6 Validation, Writing-original draft. **Jinhui Huang:** Investigation, Data curation. **Binbin**
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8 Data curation. Min Cheng: Data curation. **Yujie Liu:** Resources, Project administration.
9 **Qingyun He:** Writing-review & editing. **Ting Wu:** Investigation, Data curation. **Jilai**
10 **Gong:** Data curation. **Ming Yan:** Writing-review & editing. **Wangwang Tang:**
11 Software, Writing-review & editing.

12 **Funding** The study was financially supported by the Program for Changjiang
13 Scholars and Innovative Research Team in University (IRT-13R17), the National
14 Natural Science Foundation of China (51979103, 51679085), the Fundamental
15 Research Funds for the Central Universities of China (531107050930, 531107051205),
16 the Funds of Hunan Science and Technology Innovation Project (2018RS3115), the
17 Key Research and Development Project of Hunan Province of China (2017SK2241).

18 **Competing interests** The authors declare that they have no competing

1 of interests.

2 **Availability of data and materials** Not applicable

3 **Compliance with ethical standards**

4 **Ethical approvals** Since this study did not recruit any human and/or animal subjects,

5 this section does not apply.

6 **Consent to participate** Since this study did not recruit any human subjects, this

7 section does not apply.

8 **Consent to publish** Since this study is not attempting to re-publish/publish any third

9 party or author's previously published material, this section does not apply.

10 **Competing interests** Zhifeng Liu declares that he had no financial and other conflicts

11 that could have affected the conclusions arrived at in this communication.

12

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Figure 1. SEM images of : (a) CNTs; (b) CuFe₂O₄/CNTs_{1:2}; (c) CuFe₂O₄/CNTs_{1:4}; (d) CuFe₂O₄/CNTs_{1:8}

Figure 2. FTIR spectra (a) and XRD pattern (b) of samples prepared

Figure 3. Frequency dependence of relative (a, b) complex permittivity, (d, e) complex permeability, and (c) dielectric and (f) magnetic loss values

Figure 4. Calculated reflection loss (a) and absorption spectra of MO solution (b) for different materials .

Figure 5. Effects of three scavenger (potassium iodide (KI), t-butanol (BU), benzoquinone (BQ)) on MO degradation under pH=4 (a); pH=7 (b); pH=10 (c) (20 mg/L MO, 900W, 5 min MW, 1.0 g/L $\text{CuFe}_2\text{O}_4/\text{CNTs}_{1:4}$)

Methyl Orange + h^+ + $\bullet\text{O}_2^-$ + $\bullet\text{OH}$ = degradation products

Figure 6. Possible degradation pathways of MO solutions.

Figure 7. Effects of different anions (a) and cations (b) on MO degradation, effects of contact time on the TOC removal ratio, MO removal ratio and the reaction kinetic (c), and effects of recycle times on MO degradation (d).

Graphical abstract:

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Figures

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