A new effective way to degrade methylene blue by introducing negative ions powder into \( \text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2 \) system to accelerate \( \text{Fe}^{\text{III}}/\text{Fe}^{\text{II}} \) transformation

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ABSTRACT

Negative ions powders (NIP) have been widely applied in many fields because of their natural electric field and far infrared radiation, especially in wastewater treatment. In this study, the NIP was first introduced into \( \text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2 \) system to degrade methylene blue (MB). The MB removal was completely achieved at 5 h via a non-photochemical pathway and the degradation rate constant of this system is about 0.565 h\(^{-1}\), which is about 16 times higher than in \( \text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2 \) Fenton-like system (0.035 h\(^{-1}\)). In addition, the results of quenching experiments indicate that the electron (e\(^-\)) and negative oxygen ion (\( \cdot\text{O}_2\)) are the main reactive species. It was determined that \( \text{Fe}_3\text{O}_4@\text{NIP} \) is the effective component that leads to the activation of \( \text{H}_2\text{O}_2 \) to produce \( \cdot\text{OH} \), which derive from the pathway: NIP acts as an electron donor to reduce \( \text{Fe}^{\text{III}} \) into \( \text{Fe}^{\text{II}} \). Moreover, NIP can produce negative ions, which is also conductive to degradation. This study suggests a promising direction for the practical application of NIP based catalysis by integrating it with the \( \text{Fe}^{\text{III}}/\text{Fe}^{\text{II}} \) transformation process.

Key words | degradation, dye, isomorphic replacement, negative ions powder

HIGHLIGHTS

- The FTIR, XRD, and XPS spectra indicate that the chemical properties of NIP change after the precipitation-hydrothermal process.
- The SEM revealed that \( \text{Fe}_3\text{O}_4 \) was uniformly dispersed in the composite.
- The catalytic activity performance of the Fenton-like system was investigated to remove MB.

INTRODUCTION

To date, dyes are widely used in textile, leather, paper, rubber, plastics, cosmetics, pharmaceutical and food industries and approximately 15% of the world’s total production of dyes is lost during the dyeing process and released with the textile effluents (Wang et al. 2013a). Hence, from both human and environmental health aspects, the places of the world put more and more emphasis on environmental issues. It is very important to remove dyes from industrial wastewater before they are discharged into the natural environment (Dai et al. 2019). Therefore, there is an urgent need to develop a novel environment-friendly catalyst with an excellent activity against organic contaminants in wastewater (Changqiang Yu et al. 2020).

Advanced oxidation processes (AOPs) (Cai et al. 2014a) based on the generation of highly reactive hydroxyl radicals that present a high redox potential of 2.80 eV (Enric Brillas & Oturan 2009) are generally regarded as a potential...
alternative technologies for the degradation of recalcitrant contaminants (Cai et al. 2014b). In terms of AOPs, the Fenton process is simple, cheap, and easy to perform under moderate conditions of temperature and pressure. But during the Fenton reaction, on the one hand, hydrogen peroxide (H$_2$O$_2$) is activated by Fe$^{2+}$ under acidic solution (pH = 3) to produce ·OH, so the pH value of the solution can closely affect ·OH formation; one the other hand, Fe(II)/H$_2$O$_2$ system has some innate shortcomings: active Fe(II) will be rapidly consumed by H$_2$O$_2$, which leads to a quick accumulation of inactive Fe(III) because the reaction rate of Fe(II) and H$_2$O$_2$ is much higher than that of Fe(III) and H$_2$O$_2$ (Equations (1) and (2)) (Wang et al. 2015b).

\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \cdot\text{OH} + \text{OH}^- + \text{Fe}^{3+} \quad k_1 = 70\text{M}^{-1}\text{s}^{-1} \quad (1) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \cdot\text{OOH} + \text{Fe}^{2+} + \text{H}^+ \quad k_2 = 0.002 - 0.01\text{M}^{-1}\text{s}^{-1} \quad (2)
\end{align*}

To steer clear of this defect, previous researchers have tried to introduce UV or visible radiation to the Fenton system, which would increase the energy in the system and add chelating agents or reducing agents to the Fenton system (Bernd Ensing & Baerends 2003). As for the reducing agents, hydroxylamine (HA) was proposed to relieve the drawbacks of Fe$_3$O$_4$@NIP composite catalyst by a facile precipitation. Thereby, NIP may perform well in Fenton-like system to degrade dye.

Herein, we have successfully synthesized the catalyst of Fe$_3$O$_4$@NIP composite catalyst by a facile precipitation–hydrothermal process. This work firstly put forward an easy method to improve the catalytic activity of Fe$_3$O$_4$ by coupling with the polar mineral NIP, and provide a perfect example for the development of easily synthesized and low-cost NIP-based catalysts. The degradation properties, morphology, pore structure, electron spectrum, magnetism and durability of the samples are characterized and discussed. The abilities of NIP for degrading other dyes have not been extensively studied, and its catalytic activity and mechanisms are not well understood. Therefore, the current research focuses on the catalytic degradation performance of the Fe$_3$O$_4$@NIP composite, and a plausible mechanism has been proposed.
MATERIALS AND METHODS

Materials and reagents

Negative ions powder was acquired from Hebei province, China. Ferric chloride (FeCl₃·6H₂O, analytical reagent) was obtained from Fuchen Chemical Reagent Co, Ltd (Tianjin, China), Ferrous sulfate (FeSO₄·7H₂O) and sodium hydroxide (NaOH) was obtained from Guangzhou Chemical Reagent Co., Ltd (Guangzhou, China), methylene blue was supplied by Guangzhou Chemical Reagent Co., Ltd (Guangzhou City, China). The Yellow label tea was purchased from Lipton.

Preparation of Fe₃O₄@NIP composite

All reagents were used without further purification or other treatments. Fe₃O₄@NIP composite catalytic materials were prepared by precipitation–hydrothermal method, then were dried (Dai et al. 2019) for further use. The preparation of Fe₃O₄ was conducted according to the above method in the case of negative ions powder absence. By using different amounts of Fe₃O₄ (0.5, 1, 2, 3, 4, and 5 mmol, respectively) while keeping the same amount of negative ions powder (4 g), we obtained the composite samples Fₓ@NIP with different ratios of Fe₃O₄ (x = 0.5, 1, 2, 3, 4, and 5 mmol).

Batch experiment studies

Deionized distilled water was used to prepare all solutions and suspensions. Stock solutions of MB (25 mg/L) were prepared by dissolving measured amounts of the dyes in deionized distilled water. Degradation experiments were conducted using 100 mL of MB solution with a fixed amount of catalyst (0.1 g) and H₂O₂ (30%, v/v). In order to evaluate any real catalytic activity, the adsorption should be excluded. The catalyst-containing solution was maintained in the dark for 0.5 h (Wang et al. 2020b) under stirring to achieve adsorption-desorption equilibrium between the pollutant molecules (Yu et al. 2019) and the catalyst surface and then added H₂O₂ in the solution. Batch experiments included catalyst type, concentration of H₂O₂, effects of ion species. Further, solution pH variation and the types of reactive species were studied. The purpose was to investigate the catalytic activity and degradation mechanism of dyes by Fe₃O₄@NIP.

Characterization

The catalysts were characterized by FTIR (LEO 1530VP), and their crystallographic nature was analyzed by X-ray diffraction (X’Pert PRO X-ray diffractometer). Their surface morphology was examined by Fifield emission scanning electron microscopy (FE-SEM) with Nova NanoSEM430, while the surface areas were analyzed on the basis of N₂ adsorption-desorption isotherms obtained using a surface area and porosity analyzer (BET, Flowsorb3 2310). The Zeta potential of the catalyst was evaluated using a Zeta potential analyzer. X-ray photoelectron spectroscopy (XPS) was performed on an axis Ultra DLD X-ray Photoelectron Spectroscopy/ESCA. The residual concentrations of the MB were monitored, at its characteristic absorption band (generally 664 nm for MB) using a UV–vis spectrophotometer.

RESULTS AND DISCUSSION

Fourier transform infrared (FTIR) study

It is easy to find the chemical bonds in complex materials by FTIR spectroscopy. As shown in Figure 1, two bands appeared at 3,406 cm⁻¹ resulting from the vibration of the —OH groups in NIP (Yu et al. 2019). The bending vibration of the Si–O group was detected at 462 cm⁻¹. The band at 400 cm⁻¹ – 650 cm⁻¹ was due to the M–O( M = Al, Fe, Ti, Si) stretching vibration. A band at 1,027 cm⁻¹ stemmed from the C–O stretching vibration (Jastrzębska et al. 2019) and Fe–O vibration at 983 cm⁻¹ (Liu et al. 2016). A well-resolved band at 605 cm⁻¹ originated from the Al–O stretching vibration, and was shifted to 612 cm⁻¹ with a blue-shift of 7 cm⁻¹ for the Fe₃O₄@NIP composite compared with that of the pure NIP. This result implied that NIP could chemically interact with Fe₃O₄ via Al–O–Fe bonds. The

Figure 1 | FTIR spectra of the Fe₃O₄, NIP, and F₂@NIP composite.
presence of water be proved by the absorption peak at 1,627 cm\(^{-1}\), which corresponded to the bending H–O–H (Ghalamchi & Rasoulifard 2019) and the absorption peak at 2,360 cm\(^{-1}\) should belong to O = C = O.

**CATALYTIC PERFORMANCE**

**NIP enhanced MB removal in Fe\(_3\)O\(_4\)/H\(_2\)O\(_2\) system**

Figure 2(a) shows different degradation rates of MB in various experimental systems at the 3 ml of H\(_2\)O\(_2\). It is widely known that a typical organic degradation reaction can be simplified as a pseudo-first order reaction when the initial concentration of reactant is at a low value (Wang et al. 2011): \(-\ln\left(C_t/C_0\right) = kt\), where \(k\) is the apparent first-order rate constant (h\(^{-1}\)), \(C_t\) is the concentration of MB at a certain time (t), and \(C_0\) is the initial concentration of MB. The apparent rate constant (k) can be confirmed by linear regression of the value \(\ln\left(C_t/C_0\right)\) versus the degradation time (t). The experimental results showed that the activity of F\(_2@NIP\) was higher than that of either NIP or Fe\(_3\)O\(_4\) as shown in Figure 2(a). It should also be noted that there is only about 1% of MB degradation in the NIP/H\(_2\)O\(_2\) system, implying that NIP cannot obviously activate H\(_2\)O\(_2\) and generate sufficient active radicals to degrade MB under dark conditions; meanwhile, in Fe\(_3\)O\(_4\)/H\(_2\)O\(_2\) Fenton-like system, there is less than 3% of MB degradation in 5 h. This result in Figure 2(b) depicts that Fe(II) is more active than NIP when reacting with H\(_2\)O\(_2\). By contrast, over 99% MB degraded in 5 h in the NIP@Fe\(_3\)O\(_4\)/H\(_2\)O\(_2\) system. As we all know (Xu et al. 2020) that the low degradation efficiency is induced by the low conversion of Fe(III) to Fe(II), so the results implied that NIP is favourable to Fe(III)/H\(_2\)O\(_2\) oxidation-reduction process. It has also verified that the introduction of Fe\(_3\)O\(_4@NIP\) can decompose H\(_2\)O\(_2\) faster, not only due to the standard Fenton reaction but also due to NIP, which is beneficial to the process of reducing Fe(III) by excluding possible dominant contribution by Fe(III)/Fe(II)-induced H\(_2\)O\(_2\) decomposition. As the degradation time increased, the intensity of the absorption peak at approximately 664 nm gradually became weaker and finally disappeared and the results are shown in Figure 2(c), which meant that the chromophore and benzene ring structure of MB were ruined.

**Effect of catalyst composition**

The degradation of MB was conducted to assess the properties of the different catalyst sample. Figure 2(d) displays the concentration variations of MB (initial concentration: 25 mg/L) under the degradation of catalyst F\(_x@NIP\) (x = 0.5, 1, 2, 3, 4, 5 mmol) with 3 ml H\(_2\)O\(_2\) which is in line with the pseudo-first order reaction (Figure 2(e)). The results
support the fact that the F2@NIP perform the highest degradation activity (Figure 2(f)). With the increasement dosage of Fe3O4, the tendency of degradation efficiency first showed an upward trend and then decreased. This phenomenon can be explained thus: when Fe3O4 was less than 2 mmol, the more active points appear on the surface of NIP with the increased molarity of Fe3O4; when it is larger than 2 mmol, the number of active points will decrease due to agglomeration, which will lead to smaller special surface area. And the number of active points can directly affect the degradation rate. In comparison with the different catalyst Fx@NIP (x = 0.5, 1, 2, 3, 4, 5 mmol), the F2@NIP exhibited the highest apparent rate constant (0.565 h⁻¹), which proved that the Fe3O4@NIP composite is successfully prepared and show higher catalytic organic oxidation ability with the use of H2O2.

**Effect of the H2O2 concentration**

The Fenton system generates free radicals based on decomposition of H2O2 catalyzed by Fe(II) (Wang et al. 2020c), which indicated that MB degradation depended mainly on the effective decomposition of H2O2. As shown in Figure 2(e), H2O2 could be decomposed more efficiently even with lower molarity of Fe3O4 with the presence of NIP. The higher [H2O2] determine faster MB decomposition, which agreed with the faster MB degradation rate in Figure 3(a). However, the rate increment decreased gradually with the increasing dosage of [H2O2], as displayed in Figure 3(b). This may be ascribed to the excess H2O2 concentration resulting in the reduction of catalytic efficiency by reacting with OH• radicals to produce OOH• radicals (Equation (3)), which is a weaker oxidant agent compared with the much stronger OH• radicals (Mohammadzadeh et al. 2020).

\[
\text{H}_2\text{O}_2 + \text{OH}• \rightarrow \text{H}_2\text{O} + \text{OOH}•
\]  

(3)

Based on the results, 3 ml of H2O2 was used in all experiments.

**Effects of inorganic ions on the degradation of MB**

Various inorganic ions may co-exist with dye wastewater. Thus, examining the effects of co-existing ions on MB degradation is very important and beneficial for a realistic dye treatment process. Previous researches have confirmed that the presence of some inorganic ions in the catalytic system could affect the adsorption or degradation of dye (Zhou et al. 2019). Cations can interact with negatively charged mineral surfaces by purely electrostatic attraction. Such reactions are

![Figure 3](https://iwaponline.com/wst/article-pdf/83/8/1834/880435/wst083081834.pdf)
well-known for cation interactions with permanently charged mineral surfaces. The usually weak electrostatic nature of cation attachment to permanently charged surfaces renders this interaction readily reversible and strong competition with other cations takes place (Geckes et al. 2013). Considering that natural water does not contain buffer solution, and that the introduction of buffer solution will make the degradation system more complicated, the influence of inorganic ions was not investigated in buffer solution (Luo et al. 2020).

The influence of inorganic cations on the degradation of MB in the NIP@Fe3O4/H2O2 heterogeneous Fenton-like system was investigated at the cation concentration of 40 Mm. As shown in Figure 5(c), inorganic cations, including Na+, Ba2+ and Mg2+, exhibited an inhibitory effect on the degradation of MB, and it was determined that the adsorption affinities of different alkaline earth ions at the Fe3O4@NIP surfaces decline in the order of Ba2+ > Mg2+ > Na+. The greater the adsorption of inorganic cations, the less of MB, which leads to a decrease in the degradation rate. We all know how important it is to consider not only the effect of the ions interacting with the mineral surface, but also the bulk solvent phase (Underwood et al. 2016). So the ionic dipole interaction and hydration need to consider when the cations were added into solution. The ionic dipole interaction of different metal ions in bulk solutions depends on the ionic radius. So the studied inorganic ions are known to decline in the order of Ba2+ > Na+ > Mg2+, and the greater the dipole interaction between ions and mineral surface, the greater the adsorption. Meanwhile the hydration effects of different metal ions in bulk solutions are known to decline in the order of Na+ > Mg2+ > Ba2+ and the greater the hydration, the less ions are adsorbed on the mineral surface. Hydration will play a major role in a low electric field and ionic dipole interaction will take the lead in a high electric field (Jia et al. 2018). Hence, the preliminary results indicated that the surface of NIP has a low electric field. The varied absorption of cations depends on different hydration, which leads to poor adsorption and weak degradation of MB. At the same time, the accompanying shielding effect, with reduction in the number of active sites, also caused the low catalytic efficiency (Qian et al. 2018).

Degradation efficiency of F2@NIP at different pH values

The solution pH plays an important part in heterogeneous Fenton-like systems because it can influence the electrostatic interactions between reactant molecules and the catalyst surface, metal leaching and H2O2 decomposition (Hanna et al. 2008). When Zeta potential of the mineral surface is 0, the pH value of the solution is called the isoelectric point (pH_{iep}). The isoelectric point is the dividing point to confirm whether a mineral surface is negatively or positively charged. When the solution’s pH > pH_{iep}, it shows the mineral surface is negatively charged; in the reverse, it is positively charged. Different pH of solution resulted in different degradation effects of MB and surface potential of catalyst (Figure 3(d) and 3(e)). The isoelectric point of the F2@NIP composite was determined to be pH = 6.67. When the pH value of the solution was less than 6.67, the adsorption between the positively charged composite and the positively charged MB was weakened by electrostatic repulsion, and the acidic condition may decelerate the ionization of H2O and H2O2, so fewer OH− exist near the active sites of the catalyst, which causes reduction of hydroxyl radicals derived from OH− oxidation (Bian & Ji 2013). However, at the same time, as the pH of the solution decreased, a few [Fe2+] that can be released from Fe3O4 showed a faster catalytic reactivity. Generally, the degradation rate of MB decreased under acidic conditions. Judging from the experiment, it showed that pH values of the solution larger than 6.67 were more conducive to degradation. The reason for this result was probably that the adsorption between the negatively charged composite and the positively charged MB is strengthened by electrostatic attraction in an alkaline environment; moreover, the possibility of isomorphic replacement is greater, which will produce more negative charge on the surface of the NIP. For example (Equation (4)), NIP crystals have Al3+ replaced by Fe2+, which will create one negative charge.

\[
\text{NIP(Al}^{3+}) + \text{Fe}^{2+} \rightarrow \text{NIP(Fe}^{2+})_{(\text{surface})}\text{e}^- + \text{Al}^{3+}
\]  

(4)

Negative zeta potential increases with pH (Figure 3(e)). This was not only because the material has stronger adsorption to the outside, which promotes the electrolysis of a higher number of H2O2 and H2O, thus increasing the number of negative ions (Wang et al. 2020a), but also because the more isomorphous replacements occurs, the more electrons are produced, thus increasing the number of free radicals. F2@NIP Fenton-like catalyst has an advantage of working over a wider pH range compared with the traditional one, which is limited to pH < 4 (Bernd Ensing & Baerends 2003). Under natural conditions, the pH of the MB solution was 6.89 and according to the zeta potential of the Fx@NIP composites at various pH values, it was easy to judge that the surface of F2@NIP is negatively charged, so F2@NIP composites can efficiently adsorb MB, which can improve degradation rate.
Study of active species

The types of reactive species produced in the Fe₃O₄@NIP/ H₂O₂ system were determined using isopropanol (IPA) as hydroxyl radical (·OH) scavenger, benzoquinone (BQ) as a superoxide radicals (·O₂⁻) scavenger, and AgNO₃ as electron (e⁻) scavenger (Kaveh et al. 2020). It was found that IPA had little effect on MB removal in this system. However, AgNO₃ and BQ showed a significant inhibitory effect on MB degradation as shown in Figure 3(f). These results indicated that e⁻ and ·O₂⁻ was the predominant reactive species in the process of the MB degradation, while a mild reduction in MB degradation was observed by hindering hydroxyl radical reactive species. In this work, the degradation system was maintained under constant air-equilibrated conditions, indicating that the abundant O₂ from air promoted the formation of ·O₂⁻, resulting in its high catalytic efficiency (Chen & Liu 2017). The results also confirmed that NIP could promote the reduction of Fe(III) as an electron donor, thus accelerating H₂O₂ decomposition and MB degradation. The mechanisms will be discussed later (Equation (10)).

Morphological and structural characterizations of catalyst

Figure 4(a) and 4(b) demonstrate SEM images of the F₂@NIP particles with different parts, and the agglomeration of the sample is observed. Moreover, with the EDS spectrum in Figure 4(c), the purpose was to further explore the dispersion of Fe₃O₄ in NIP. A certain area was intercepted arbitrarily in the SEM image, there was an apparent oxygen element peak in the elemental composition map, and the area was about 6 μm². Representative elements of Fe₃O₄ and NIP were presented in such a small range and it indicated to some extent that Fe₃O₄ can be relatively uniformly dispersed in NIP under this preparation process (Luo et al. 2019). The EDS spectrum also showed the presence of C, O, P, Fe, Al, Si, Ti and Th elements in the sample. The Cu and Au signals were owing to the SEM grid used for the imaging.

The XRD patterns of Fe₃O₄, NIP and Fₓ@NIP (x = 0.5, 1, 2, 3, 4, 5 mmol) are shown in Figure 5. The diffraction peaks at 2θ = 30.1, 35.4, 43.2, 54.0, 56.8 and 62.5
correspond to the (220), (311), (400), (422), (511), and (440) planes of Fe$_3$O$_4$ (Tan et al. 2019) (JCPDS No.19-0629), respectively. As for NIP, the diffraction peaks were sharp and intensive, indicating a highly crystalline phase in the sample. The XRD patterns of F$_x$@NIP could be perfectly indexed as the inverse spinal structure of magnetite Fe$_3$O$_4$. And the peaks in the XRD patterns of the F$_x$@NIP coincided almost completely with those of the Fe$_3$O$_4$ and NIP raw materials (Figure 5(a)), which indicted that F$_x$@NIP has been successfully synthesized. We also noticed that with increasing mass of Fe$_3$O$_4$, the diffraction peak intensity for Fe$_3$O$_4$ at $2\theta = 62.5$ enhanced (Figure 5(b)), the diffraction peak narrowed and the grain size increased. This demonstrated that the lesser mass of Fe$_3$O$_4$ of the composite materials result in grain refinement; in turn, this resulted in a larger specific surface area that maximized the effect of the raw materials. The XRD patterns revealed that the diffraction peaks of the composite materials had shifted slightly to the left; moreover, the d-spacing increased or decreased to varying degrees compared with the original materials (Wang et al. 2020a). This indicated that Fe$_3$O$_4$ caused slight crystal defects or crystal doping of raw materials.

**BET, XPS and VSM analysis**

The BET surface areas of NIP, F$_2$@NIP composites and pure Fe$_3$O$_4$ are given in Figure 6(a). The BET surface area of the F$_2$@NIP sample was much higher than that of NIP and the pure Fe$_3$O$_4$. According to the IUPAC classification, the isotherm of F$_2$@NIP composite material showed that it is a typical mesoporous material with H3 hysteresis loop type IV isotherm (Inagaki et al. 1993). This indicated that the catalyst is composed of aggregates of cubic particles, forming pores of uneven size and shape (Bakre et al. 2016). This conclusion is in agreement with the SEM image. The F$_2$@NIP composites showed larger average pore size and pore volume than NIP (Table 1). The pore size distribution (Figure 6(b)) implied that F$_2$@NIP presented a relatively narrow distribution with an average pore diameter close to 2.049 nm. The experimental results showed that Fe$_3$O$_4$-doped NIP possesses a larger BET specific surface area and pore volume compared with pure NIP. Moreover, it was confirmed that F$_2$@NIP composite owns an incremental number of active sites.

Based on the data in Figure 2(a), the active constituent in the Fe$_3$O$_4$/H$_2$O$_2$ system increased greatly after the addition of NIP. There may be some interaction between NIP and Fe$_3$O$_4$, which increases the production of Fe(II) in the system, resulting in acceleration of active constituent generation. The surface element component and valence state of the as-synthesized catalysts were investigated with XPS. The Fe $2p_{3/2}$ presents two peaks: Fe$^{2+}$ at 709.3 eV and Fe$^{3+}$ at 711.2 eV, and Fe $2p_{1/2}$ also presents two peaks: Fe$^{2+}$ at 718.5 eV and Fe$^{3+}$ at 723.5 eV in pure Fe$_3$O$_4$ (Crisan et al. 2018). From the deconvolution result of the Fe peaks in the spectrum (Figure 6(c)), in comparison with pure Fe$_3$O$_4$, the binding energy of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ for the Fe$_3$O$_4$@NIP composite was shifted to 711.60 eV and 724.55 eV, respectively. The evidence of the chemical interaction between Fe$_3$O$_4$ and NIP accords with the results of XRD analysis.

Figure 6(d) demonstrates the hysteresis loop of F$_2$@NIP and F$_5$@NIP at room temperature. The saturation
magnetizations were 2.67 emu/g and 19.51 emu/g for F2@NIP and F5@NIP, respectively. Obviously, a much stronger Hall effect could be obtained in F5@NIP than in F2@NIP (Tan et al. 2019), resulting in the different catalytic performances as have been discussed above. For the good magnetic property, the F2@NIP could be easily separated from the mixture using a magnet, as shown in the Figure 6(e).

The reusability of Fe3O4@NIP

Stability of the catalyst in the successive applications is critical for practical usage. The reusability of Fe3O4@NIP was also researched, and the results are presented in Figure 7.

It can be seen that catalysts slowly deactivated with time. After four repetitions, the degradation efficiency was still high, as shown in Figure 7(a), implying that Fe3O4@NIP had good stability and reusability. As shown in Figure 7(b), the well-resolved band at 612 cm⁻¹ originated from the Al–O stretching vibration, which was shifted to 622 cm⁻¹ with a blue-shift of 10 cm⁻¹, and the band at 1,027 cm⁻¹ originated from the C–O stretching vibration, which was shifted to 1,039 cm⁻¹ with a blue-shift of 12 cm⁻¹ for the F2@NIP composite that had degraded four times compared with that of the untouched F2@NIP. The infrared absorption intensity of the used catalyst was slightly lower than that of the untouched catalyst. The shift of peak position and the change of peak absorption intensity in the fingerprint region provided evidence for isomorphism replacement. It was also found that the amount of MB desorbed from catalyst decreased gradually after each process of degradation and ethanol washing. That might be related to the loss of surface area; in addition, as the number of catalyst reuses increased, isomorphous replacement of NIP is likely to become less and variable charge decreases. That all could

Table 1

| Sample     | Total pore area (cm² g⁻¹) | Average pore size (nm) |
|------------|---------------------------|------------------------|
| NIP        | 0.104                     | 1.848                  |
| F2@NIP     | 0.122                     | 2.049                  |
| Fe3O4      | 0.324                     | 16.142                 |

Figure 6 | (a) (b) N₂ adsorption/desorption isotherm and pore size distribution of the NIP, the Fe3O4@NIP composites and Fe3O4, (c) high-resolution Fe 2p XPS spectra of the Fe3O4 and F2@NIP composite, (d) magnetization curves of F2@NIP and F5@NIP at room temperature, (e) the suspension of F2@NIP solution before and after applied with an external magnet.
lead to a gradual deterioration in the catalytic performance of the catalyst. But the efficiency of degradation was still higher than the Fe₃O₄/TiO₂ system (Ghalamchi & Rasoulifard 2019) and Fe-tourmaline system (Wang et al. 2013a). The NIP contains a certain amount of thorium dioxide and it appears likely, though not entirely verified, that the stable catalysts may be attributed to thorium, the solids that kept the surface area during the reaction (João Lúís Rangel Costa & Rangel 2002). After each repetition of the test, the F₂@NIP sample was washed with deionized water and ethanol 3 times, and heated at 80°C for 3 h.

**EFFECT MECHANISM OF NIP ON THE CATALYTIC ACTIVITY OF Fe₃O₄/H₂O₂**

**Far infrared radiation of NIP**

Far infrared rays serve the purpose, by being absorbed in water clusters. If the radiation wavelength of far infrared rays accords with the absorption wavelength of an object to be irradiated, molecules in the object absorb the radiations at that wavelength, causing stretching and deformation due to the resonance, and the molecules are brought to a place where it becomes easier to react (Feng & Shang 2015). We have studied the effects of Fe₃O₄@NIP on the infrared emissivity. Tea leaves of the same mass were added to the Fe₃O₄@NIP treated deionized water and ordinary deionized water, and the tea leaves soaking conditions were observed at different times (Figure S1, ESIf). From the experimental results, it can be seen that the color of treated water is darker (Figure S1a,c, ESIf), indicating that the activity of treated water molecules is higher than that of ordinary deionized water, so this will be favorable for tea soaking. An implication of this is the possibility that Fe₃O₄@NIP will reduce the van der Waals forces and destroy the hydrogen bonding force between the water molecules, which may lead the clusters of liquid water to change from large to small (Equations (5) and (6)) compared with ordinary deionized water.

**Natural electric field of NIP**

Fine NIP just has a natural peculiarity that can offer a spontaneous and permanent polarity to produce an electrostatic field and can generate negative oxygen ion (O₂⁻) (Equation (9)), which is a big advantage in enhancing the catalytic activity of catalysts containing NIP. For one thing, the resulting electrostatic interaction between NIP and molecules or ions plays an important role in the process of degradation; for another, the electric field of the NIP can impel charges to move in a certain range when the surface of the Fe₃O₄@NIP releases charges from isomorphous replacement (the ion being replaced could be Al³⁺, shown as Equation (4)). Based on an increase in the electron density compared with pure Fe₃O₄, the electric field generated on the surface of NIP led directional transportation of the generated electron (e⁻) (Yu et al. 2019), thus enhancing the catalytic activity. Due to the ability to release electrons (e⁻) (Equation (10)), NIP could rapidly reduce Fe(III) in the presence of H₂O₂. The fast transformation of Fe(III)/Fe(II) is the key factor to induce the generation of ·OH (Equation (12)). The spontaneous electric field would promote the electron...
transfer process and minimize the resistance of the transfer from Fe(III) to Fe(II), although further research is required regarding the mechanism responsible (Yu et al. 2014). The half-life of thorium is 7,340 years. During the process of radioactive decay, the α-particles collide with the atoms and molecules in the solution. This may be beneficial to the effects of the degradation though it has not been entirely verified (Alam et al. 2020). Therefore, NIP can increase the catalytic activity of the Fe3O4/H2O2 system.

\[
\begin{align*}
\text{NIP} + (\text{H}_2\text{O})_m & \rightarrow \text{NIP} + m \text{H}_2\text{O} \\
\text{NIP} + (\text{H}_2\text{O}_2)_n & \rightarrow \text{NIP} + n \text{H}_2\text{O}_2 \\
\text{NIP}^{(\text{surface})} \text{e}^- + \text{H}_2\text{O} & \rightarrow \text{NIP} + \bullet \text{OH} + \text{H}^+ \\
\text{NIP}^{(\text{surface})} \text{e}^- + \text{H}_2\text{O}_2 & \rightarrow \text{NIP} + \bullet \text{OOH} + \text{H}^+ \\
\text{NIP}^{(\text{surface})} \text{e}^- + \text{O}_2 & \rightarrow \text{NIP} + \bullet \text{O}_2^- \\
\text{NIP}^{(\text{surface})} \text{e}^- + \text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{NIP} + \text{Fe}^{2+} + \bullet \text{OH} + \text{H}^+ \\
\text{Fe}^{3+} + \bullet \text{OOH} & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \bullet \text{OH}
\end{align*}
\]

Hence, the addition of NIP can speed up the transformation of Fe(III)/Fe(II) by non-photochemical pathways and activate H2O2, which will all generate ·OH and ·O2 to remove MB. With a combination of the analyses carried out above, a plausible mechanism for strengthening the catalytic degradation activity of Fe3O4/H2O2 with NIP is proposed and shown in Figure 8.

**CONCLUSIONS**

Taken together, these findings indicated that under dark conditions, the addition of NIP to the Fe3O4/H2O2 system could greatly promote the degradation of MB. This study is the first comprehensive investigation of how the NIP works in the system. In this work, we found that the surface of NIP has a low electric field that could mildly activate H2O and H2O2; moreover, electrons (e−) can be generated by isomorphous replacement in the system of Fe3O4@NIP/H2O2. The released electrons not only favor the production of ·O2 but also the production of Fe(II). A large amount of Fe(II) formed in the system contributed to the production of ·OH and boosted the degradation of the system. The application of Fe3O4@NIP composites in engineering has not been studied. In the future, the pyroelectric effect and piezoelectric effect of Fe3O4@NIP composites will be further explored to broaden their application.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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