Preparation of magnetic imprinted graphene oxide composite for catalytic degradation of Congo red under dark ambient conditions
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ABSTRACT
Magnetic imprinted N-doped P25/Fe3O4-graphene oxide (MIGNT) was prepared with methyl orange as the dummy template and pyrrole as functional monomer for catalytic degradation of Congo red (CR). Hummers method and the hydrothermal method were used to synthesize Fe3O4-GO and N-doped P25, respectively. The results of adsorption and degradation experiments showed that the adsorption capacity and catalytic degradation ability of the imprinted composite for CR were obviously higher than those of a non-imprinted one. Moreover, the effect factors on degradation efficiency of CR, such as the initial concentration of CR, catalysis time, pH of the solution and temperature, were investigated. The MIGNT was characterized by X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, a physical property measurement system and a thermal gravimetric analyzer. The degradation products of CR were detected with high performance liquid chromatography and a mass spectrometer. The MIGNT was a brand-new imprinted composite and had high degradation efficiency for CR under dark ambient conditions. The MIGNT could be recycled conveniently, due to its magnetic property, and could be used as an effective, environmentally friendly and low-cost catalytic degradation material for the treatment of water contaminated by CR.

Key words | catalytic degradation, Congo red, dark ambient conditions, imprinted, magnetic property

INTRODUCTION
Environmental pollution caused by dyes has become a global challenge faced by human beings. Owing to their large and complex molecular structures, the high recalcitrance to degradation of dyes has been a severe problem for color removal (Anliker 1977). Among these dyes, azo dyes are highly toxic and even carcinogenic to animals and humans. Since Congo red (CR) is one of the well-known azo dyes that are not readily degraded, it was used as the dye model (Bagheri et al. 2017). Efficient and reliable methods are clearly indispensable for the removal and degradation of CR from wastewater.

Some methods have been developed and used for the removal of dye contaminants, including coagulation/flocculation (Huang et al. 2016), advanced oxidation processes, ozonation, membrane filtration and biological treatment (Walker et al. 2005). However, the remarkable results obtained from these treatment methods required high operation and maintenance cost (Forgacs et al. 2004). Recently, the removal of dyes from wastewater through heterogeneous photocatalysis has drawn increasing attention (Senthilraja et al. 2014).

Titanium dioxide (TiO2) is usually used to remove the dyes through heterogeneous photocatalysis. However, TiO2 has a large band gap of 3.2 eV, which severely limits absorption of visible light (Linsebigler et al. 1998). To develop a highly efficient and low-cost catalyst system with activity extended in the visible region, approaches like sensitization and/or doping with cations or anions have been attempted (Chen & Mao 2007; Wang et al. 2009). Among these approaches, N-doped TiO2 (N-doped P25) exhibited the highest photocatalytic activity in the visible range (Chen et al. 2008; Kuvarega et al. 2011).

In recent years, research into graphene oxide (GO) as an adsorbent has attracted intense interest (Sitko et al. 2015).
However, it is hard to separate GO from aqueous solution (Yazici et al. 2017). To overcome this drawback, GO was modified with Fe₃O₄ nanoparticles. The prepared magnetic GO combined the magnetic property of Fe₃O₄ with the huge specific surface area of GO (Gao et al. 2009). Moreover, the magnetic property could solve the recycling problem of the catalytic degradation materials.

In addition, molecular imprinting has been proven to be an effective strategy for improving the catalytic selectivity of materials in complex systems (Gupta et al. 2014). Due to the capabilities of efficiently donating electrons and transporting cavities under visible light excitation, the conductive polymer, polypyrrole (PPy), could not only be used as the structure material for molecular imprinting (Huang et al. 2015), but also as a stable photo-sensitizer to modify TiO₂. Thus, a molecularly imprinted coating, PPy, could be used for enhancing the catalytic degradation activity of TiO₂ under visible light and its catalytic selectivity (Wei et al. 2015). However, the main limitation of this method lies in the demand for a greater amount of light.

Dark catalytic oxidation methods have aroused people’s attention (Lafaye et al. 2015). However, some of them require additional chemicals, high electrical power or other extreme conditions. Compared with other methods, catalytic wet air oxidation (CWAO) is a very promising advanced oxidation process to efficiently degrade the dyes under relatively mild conditions. In experiments, CWAO has provided enough free oxygen for the catalytic process of TiO₂ and significantly improved the oxidation rate of the target molecules under dark ambient conditions. Moreover, due to the low price of the oxidant and great availability everywhere in the world, CWAO was adopted to solve the light problem of the TiO₂ catalyst (Anushree et al. 2015).

In this paper, magnetic imprinted N-doped P25/Fe₃O₄ graphene oxide composite (MIGNT) was prepared for the catalytic degradation of CR. The magnetic GO was used to solve the recycling and separation problem of the MIGNT. In addition, the method of CWAO was adopted to solve the light problem of the TiO₂ catalyst. CR could be degraded when used as the template molecule in the imprinting process. Thus, methyl orange (MO), a structural analogue of CR that was stable in the imprinting procedure was necessary as the dummy template. A series of characterizations of MIGNT were investigated. Moreover, the degradation products of CR were detected with high performance liquid chromatography (HPLC) and a mass spectrometer (MS).

## METHODS

### Materials

Natural flake graphite powder (99.0% purity) was purchased from Sigma–Aldrich. Titanium dioxide (P25, 20% rutile and 80% anatase) was purchased from Degussa (Frankfurt, Germany). Iron (II) chloride tetrahydrate (FeCl₂·4H₂O, 98%), iron (III) chloride hexahydrate (FeCl₃·6H₂O, 97%), ammonium hydroxide (28%), (NH₄)₂Fe(SO₄)₂·6H₂O and NH₄Fe(SO₄)₂·12H₂O were all of analytical grade supplied by Tianjin Institute of Fine Chemicals (Tianjin, China). Pyrrole (98%), methyl orange (MO, 98%) and Congo red (CR, 98%) were all purchased from J&K Scientific (Shanghai, China). All other substances were of analytical grade from Yong Chang Reagent (Harbin, China).

### Preparation of Fe₃O₄-GO

GO was prepared with a modified Hummers method. Natural flake graphite powder (2 g), H₂SO₄ (50 mL), NaNO₃ (2 g) and KMnO₄ (6 g) were sequentially added into a 500 mL three-necked flask immersed in an ice water bath, then the mixture was stirred for 10 min. After that, the flask was transferred to a water bath at 28 °C, and the mixture was stirred for 20 h. After successively mixed dropwise with 80 mL distilled water and 20 mL H₂O₂, the mixture was incubated for 30 min. Then the obtained solid was washed with 0.1 mol L⁻¹ HCl aqueous solution, distilled water and absolute ethyl alcohol, respectively. Finally, the desirable solid (GO) was dried for 8 h at room temperature under static air.

After dissolution of (NH₄)₂Fe(SO₄)₂·6H₂O (5.8 g) and NH₄Fe(SO₄)₂·12H₂O (10.7 g) into 50 mL distilled water with stirring for 10 min, the solution was adjusted with 20 mL of 28% ammonium hydroxide to obtain Solution A. In the meantime, GO (1 g) was dispersed into 50 mL distilled water under ultrasound for 50 min to obtain GO suspensions. After that, GO suspensions were slowly added into Solution A at 80 °C, accompanied with stirring for 30 min. The product (Fe₃O₄-GO) was washed with distilled water and absolute ethyl alcohol, respectively, then dried in an oven at 70 °C for 12 h.

### Preparation of N-doped P25

N-doped P25 (NT) was synthesized by a hydrothermal method according to previous reports (Chen et al. 2008;
Preparation of MIGNT

NT (0.5 g), Fe$_3$O$_4$-GO (0.1 g), 45 mL distilled water and 25 mL ethyl alcohol were mixed in a 100 mL beaker. The suspensions were stirred for 30 min and then dispersed under ultrasound evenly. After hydrothermal reaction for 12 h at 130 °C, the composite object (NT/Fe$_3$O$_4$-GO) was washed with 0.01 mol L$^{-1}$ HCl aqueous solution, distilled water and absolute ethyl alcohol, respectively. Then, NT was dried for 8 h at 70 °C under static air.

Moreover, the magnetic non-imprinted NT/Fe$_3$O$_4$-GO graphene oxide (MNGNT) was prepared and processed similarly as above, except that MO was not added.

Instruments

X-ray diffraction (XRD) patterns of the prepared materials were taken by a DX-2600 X-ray diffractometer (Dandong, China) with Cu Kα radiation ($\lambda$=0.154 nm) operated at 30 mA and 40 kV. Transmission electron microscope (TEM) images were acquired on a Hitachi H-7650 transmission electron microscope (Matsudo, Japan). Fourier transform infrared spectroscopy (FTIR) analysis of the samples was recorded on a Nicolet Avatar 360 spectrophotometer (Nicolet, Madison, WI, USA) using conventional KBr pellets. The element contents of materials were measured by an elemental analyzer (vario EL, Elementar Analysensysteme GmbH, Germany). The absorbancy of the CR aqueous solution at 496 nm was recorded on a TU-1901 ultraviolet and visible spectrophotometer (UV-vis, Shanghai, China) equipped with an integrating sphere using water as reference. Thermal gravimetric analysis (TGA) was performed by an STA 6000-SQ8 analytical instrument with a heating rate of 10 °C min$^{-1}$ and a flow rate of 60 mL min$^{-1}$ under N$_2$ environment (PE Analytical Instruments Inc., USA). The magnetic property was determined with a Model 6000 physical property measurement system (PPMS, American Quantum Design Inc., USA).

Catalytic degradation experiments

The catalytic degradation experiments of MIGNT and MNGNT for CR aqueous solution were carried out as follows.

For degradation kinetics, MIGNT or MNGNT (15 mg) was added into 15 mL CR aqueous solutions with different initial concentrations ranging from 150 mg L$^{-1}$ to 200 mg L$^{-1}$, and then the obtained suspensions were continuously shaken at the rate of 300 rpm in the dark which was created with a shading cloth at 25 °C for 45 min. Finally, the adsorbent was separated by an external permanent magnet. The remaining CR on MIGNT was eluted with methanol and the eluent together with the residual CR in the supernatant was detected by UV-vis at a wavelength of 496 nm. According to the calibration curve, the total residual concentration of CR was calculated for instant time. The concentration of CR degraded by MIGNT could be calculated by subtracting its total residual concentration from the initial concentration of CR. According to the first-order reaction equation, the concentrations of CR degraded by MIGNT were used for degradation kinetics of CR on MIGNT.

The primary liquid was diluted before measurement. The degradation efficiency ($\eta$%) was calculated as follows:

$$\eta \% = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\%$$

where $C_0$, $A_0$ and $C_t$, $A_t$ represent the concentration and absorbency of CR in the catalytic reaction solution before and after irradiation, respectively.
RESULTS AND DISCUSSION

Preparation of MIGNT

MIGNT was prepared for the catalytic degradation of CR. Hummers method and the hydrothermal method were used to synthesize Fe3O4-GO and NT, respectively. The molecular imprinting technique is notable in endowing the surface sites catalytic activity and selectivity concurrently by creating specific molecular recognition sites in MIGNT with the use of target substances as template molecules during the growth of the PPy. As a result, abundant recognition sites were retained on the surface of the MIGNT after the template was removed. However, the MNGNT was prepared similarly to the MIGNT, except that the template molecule was not added. Thus, there were no recognition sites on the surface of the MNGNT. Furthermore, the MIGNT had higher adsorption capacity than MNGNT. Because CR could be degraded when used as the template molecule in the imprinting process, MO, a structural analogue of CR that was stable in the imprinting procedure, was used as the dummy template. Since the catalytic reactions predominantly occurred on the surface of MIGNT, the adsorption of pollutants on MIGNT played an important role in the catalytic degradation process (Liu et al. 2017).

Characterization

Figure 1 shows the FTIR spectra of NT, NT/Fe3O4-GO, Fe3O4-GO, GO and MIGNT. In the spectrum of Figure 1(a), various oxygenated functional groups, such as –OH group (broad peak at ∼3,400 cm⁻¹), C=O group (at ∼1,700 cm⁻¹) and C-O-C group (at ∼1,050 cm⁻¹) were found on GO surfaces (Liu et al. 2015). In the spectrum of Figure 1(c), the peak at 632 cm⁻¹ was a characteristic adsorption peak of the N-Ti-O group, which indicates the formation of NT. In addition, the strong adsorption peak at 580 cm⁻¹ of Fe-O indicates the successful synthesis of Fe3O4. And in the spectrum of Figure 1(e), the weak peak at 2,925 cm⁻¹ demonstrates the formation of the PPy shell.

An elemental analysis of the NT was performed. The quality percentage of nitrogen was 1.12%, which is evidence of the successful preparation of N-doped P25.

The XRD patterns of NT, Fe3O4-GO, GO, NT/Fe3O4-GO and MIGNT are illustrated in Figure 2. The intensified diffraction peaks of NT at 2θ = 25.31°, 37.87°, 41.44°, 48.21°, 54.21°, 55.11°, 62.71° and 69.86° reveal a pure anatase phase with tetragonal structure (Wang et al. 2013). A series of characteristic peaks of pure Fe3O4 at around 2θ of 30.21°, 35.51°, 43.31°, 53.21°, 57.21° and 63.11° are related to the reflection of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of magnetite Fe3O4, which are well indexed to the typical cubic inverse spinel structure (JCPDS card no. 19-629) (Akhavan & Azimirad 2013). The intensified diffraction peak of GO at 2θ of 9.98° is related to the reflection of (002) plane. It should be noted that some maghemite occurred in the magnetic cores due to the partial oxidation of Fe3O4 to γ-Fe2O3 during the coprecipitation and catalytic oxidation process, which was in accordance with a previous report (Jing et al. 2013). Because the magnetic property of maghemite is similar to magnetite, the separation of MIGNT was not affected.

Figure 3 illustrates the TGA curves of NT/Fe3O4-GO and MIGNT. The samples underwent a multistep decomposition process in the temperature range of 50–800 °C. Compared with NT/Fe3O4-GO, the MIGNT had an obvious weight loss (about 6%) in the temperature range of 500–800 °C, which further proved the formation of organic polymer coating on the surface of NT/Fe3O4-GO.
The TEM images of GO, Fe$_3$O$_4$-GO, NT/Fe$_3$O$_4$-GO and MIGNT are shown in Figure 4, where it can be observed that the GO nanosheets had a well-defined layer structure and high ratio of surface to thickness. By contrast, Fe$_3$O$_4$ particles can be observed to be deposited uniformly on the surface of GO in Figure 4(b). Figure 4(c) reveals a well-separated and homogeneous distribution of the NT on the surface of Fe$_3$O$_4$-GO. Moreover, Figure 4(d) shows that Fe$_3$O$_4$-GO served as the core, then with an NT layer and the imprinted layer as the outermost layer.

Figure 5 shows the magnetic hysteresis loops of Fe$_3$O$_4$, Fe$_3$O$_4$-GO, NT/Fe$_3$O$_4$-GO and MIGNT measured at 300 K. The magnetic saturation values of the Fe$_3$O$_4$, Fe$_3$O$_4$-GO, NT/Fe$_3$O$_4$-GO and MIGNT were 63.88 emu g$^{-1}$, 31.8 emu g$^{-1}$, 22.51 emu g$^{-1}$ and 11.5 emu g$^{-1}$, respectively. By contrast, the decrease of magnetic saturation values proved the existence of GO, NT and PPy coating. Moreover, the inset of Figure 5 shows that the MIGNT still had good magnetic property. The magnetic property would favor the separation and recovery of the MIGNT from the aqueous solution.

**Binding experiments of MO and CR**

The adsorption performance results of the MIGNT and MNGNT (13 mg) for MO (15 mL) are shown in Figure 6(a). The amounts of MO bound to the MIGNT and MNGNT
increased rapidly at the beginning of the initial concentration range of 120–220 mg L$^{-1}$, then had a little change at the concentration of 130 mg L$^{-1}$, which indicated that the binding amount of MO almost reached saturation.

A binding experiment for CR as a control experiment is shown in Figure 6(b). It was also observed that the adsorption phenomenon of CR was similar to MO and the binding amount of MIGNT toward CR was higher than that of the MNGNT at the initial concentration range of 120–220 mg L$^{-1}$. Furthermore, the MIGNT has a higher adsorption capacity and catalytic degradation ability toward CR than the MNGNT.

### Effect factors for the catalytic degradation ability of MIGNT

#### The initial concentration of CR

The MIGNT was applied to degradation of CR with different concentrations. Figure 7(a) shows that the degradation efficiency of CR was smooth and steady at 99.2% at the concentration range of 30–150 mg L$^{-1}$ and dropped to 89.3% at 160 mg L$^{-1}$, which indicates that much higher concentration of CR would make degradation efficiency decline.

The quantification of MIGNT had the maximum value of adsorption and degradation, therefore, different concentrations of CR determined that different amounts of MIGNT had different catalytic degradation abilities. According to a previous report (Muthirulan et al. 2014), this may be due to: (i) higher dye concentration might serve as inner filter shunting the photons away from the catalyst surface; (ii) non availability of oxidative free radicals; and (iii) a greater number of dye molecules get adsorbed on the catalyst surface thus blocking the surface active sites to participate in the degradation reaction.

#### Catalysis time

The catalysis time could also affect the degradation efficiency of CR. In Figure 7(b), the catalysis time was segmented into 20, 30, 40, 45, 50 and 60 min to carry out a test. It can be seen that the degradation efficiency of the MIGNT and MNGNT increased rapidly in the range of 20–45 min and the MIGNT turned steady at 99.3%, but the MNGNT changed to 40.6% after 45 min. The results prove that the MIGNT had a better catalytic degradation ability in a short time.

#### The pH of solution

The pH (2–10) of solution had a significant effect on the degradation of CR. The degradation efficiency first increased rapidly from 47.3% to 71.2% at pH = 2–3, then rose steadily at pH = 3–6 with the maximum value of 99.3% at pH = 6,
and at last declined gradually at pH = 7–10 in Figure 8(a). At low pH values (pH < 5), a lot of protons existing in the solution reacted with hydroxyl ions, which held back the formation of hydroxyl radicals, thus resulting in low degradation efficiency. Due to the effect of pH on surface ionic speciation of TiO$_2$, the NT would show different electronegativity. The point of zero charge (pHpzc) of TiO$_2$ was 6.5 (Kong et al. 2015). Therefore, repulsion of the positively charged MIGNT at pH < pHpzc made low pH values not beneficial for the degradation of CR. Moreover, because of the negatively charged surface of MIGNT and large amount of hydroxyl ions at pH > pHpzc, the transfer of electrons was prevented (Rincón & Pulgarin 2004). Therefore, the higher catalytic degradation ability could be obtained in water.

**Temperature**

The effect of temperature on degradation of CR was also studied. Different common temperatures of water (15, 20, 25 and 30 °C) were investigated as depicted in Figure 8(b). The degradation efficiency of CR increased obviously with the increase of temperature and then reached a maximum, which agreed well with the theoretical trend of the influence of temperature on degradation efficiency.

**Repeatability of the MIGNT**

The repeatability of MIGNT for CR was proved by the results of repetitive use experiments shown in Figure 9. After the degradation of CR, the MIGNT was separated,
washed, dried and reused for the next cycle by making reaction conditions fixed. After five cycles, the degradation efficiency of MIGNT dropped from 99.3% to 92.1%, which may result from the generated by-products of MIGNT during the degradation reaction. The results proved the good repeatability of MIGNT.

Degradation kinetics of CR on MIGNT

The kinetics data in Figure 10 indicate that the MIGNT degraded CR more quickly than the MNGNT. Moreover, the degradation efficiency of MIGNT and MNGNT reached maximum after 45 min. The kinetics data were analyzed according to the first-order reaction equation:

\[
\ln \left( \frac{C_0}{C} \right) = Kt
\]

where \( C \) (mg L\(^{-1}\)) is the concentration of CR at instant \( t \) (min), \( C_0 \) (mg L\(^{-1}\)) is the initial concentration of CR, and \( K \) (min\(^{-1}\)) is the reaction rate constant. The results of kinetics in Table 1 show that the MIGNT had a higher catalytic degradation activity than MNGNT for CR. The reason could be that the MIGNT showed a higher binding capacity toward CR than the MNGNT in the binding test. The higher binding capacity of the MIGNT could directly result in its higher catalytic degradation activity.

Degradation pathway and identification of degradation products

To further identify the degradation products, HPLC and MS analysis were employed. As shown in Figure 11(a) and 11(b), the chromatograms of CR solutions before and after degradation were different, especially a new peak at 4.3 min which appeared after degradation. Based on the results and a previous study (Kong et al. 2012), a plausible degradation pathway was proposed in Figure 12. In Figure 12(a), the peak (m/z) of 696 decreased to 673 after reducing by Na\(^+\). Moreover, it was shown that the peak changed to 658, 644, 621, 573, 550, 471, 377 and 235 after intermediate degradation products reduced some materials, gradually; see Figure 12(b)–12(i). These results agreed well with previous reports that CR was degraded to many substances.

Postulated mechanism

The charge transfer mechanism in MIGNT during degradation of CR is shown in Figure 13. Electrons transferred from \( \gamma \)-Fe\(_2\)O\(_3\) into the conduction band of P25, leaving cavities in \( \gamma \)-Fe\(_2\)O\(_3\). The GO sheet accelerated the
**Figure 11** | HPLC chromatograms of CR methanol aqueous solutions (a) before and (b) after degradation.

**Figure 12** | Possible pathway for degradation of CR by MIGNT in the dark.
charge separation of electrons and cavities. The trapped electrons on the GO and P25 surface reacted with the dissolved oxygen to form a reactive oxygen species, which reacted with water to give hydroxyl radicals. Therefore, the electron-cavity recombination rate decreased. Moreover, these electrons probably reacted with O₂ and H₂O on the surface of PPy to generate ·OH and O₂. All the generated cavities could react with OH⁻ or H₂O to produce ·OH. And subsequently, CR molecules adsorbed on the surface of MIGNT reacted with ·OH to produce degradation products. The degradation mechanism of the MIGNT could be described as Equations (3)–(10):

\[
\begin{align*}
\text{Fe}_2\text{O}_3 & \rightarrow \text{Fe}_2\text{O}_3(h^+ + e^-) & (3) \\
\text{GO}(e^-) + \text{O}_2 & \rightarrow \text{O}_2^- + \text{GO} & (4) \\
\text{H}_2\text{O} + h^+ & \rightarrow \text{OH} + \text{H}^+ & (5) \\
\text{TiO}_2^+ & \rightarrow \text{TiO}_2 + \text{H}^+ & (6) \\
\text{OH}^- + h^+ & \rightarrow \text{OH} & (7) \\
\text{O}_2 + e^- & \rightarrow \text{O}_2^- & (8) \\
\text{O}_2^- + \text{H}_2\text{O} & \rightarrow \text{OH} + \text{O}_2 & (9) \\
\text{OH} + \text{CR} & \rightarrow \text{degradation products} & (10)
\end{align*}
\]

**CONCLUSION**

An easy and effective route was adopted for the fabrication of MIGNT which was an environmentally friendly hybrid nanocomposite and prepared with a novel molecularly imprinting and hydrothermal method. Microscopy studies revealed that magnetic P25 was incorporated on the GO surface and molecularly imprinted material was in the outer layer. Spectroscopic studies showed that the optimal assembly and interfacial coupling were between the GO and P25. Thermodynamic analysis evinced that the molecularly imprinted material showed stable adhesion at normal temperature. The dummy imprinting technique effectively alleviated the decomposition of the template molecule in the synthesis process of MIGNT. Moreover, the MIGNT was easy to recycle and capable of rapid degradation of CR without light illumination and additional chemicals. This type of environmentally friendly, low-cost and efficient material could promote environmental protection and material recycling.

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