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Highly efficient and recyclable graphene oxide-magnetite composites for isatin mineralization

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1	Highly Efficient and Recyclable Graphene Oxide-Magnetite Composites for			
2	Isatin Mineralization			
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10				
11	ABSTRACT: A series of graphene oxide-magnetite (GO-Fe ₃ O ₄) composites with			
12	various GO/Fe ₃ O ₄ weight ratios (i.e., GO/Fe ₃ O ₄ = $1/20$, $2/20$, $3/20$ and $4/20$) was			
13	successfully synthesized via chemical precipitation of Fe ₃ O ₄ nanoparticles on GO			
14	sheets. The chemical and physical properties of as-synthesized GO-Fe ₃ O ₄ composites			
15	were characterized by XRD, TEM and FT-IR. Results from XRD and TEM revealed			
16	that cubic-phase Fe ₃ O ₄ was in situ deposited on the surface of GO resulting in			
17	GO-Fe ₃ O ₄ composites. The C-O-Fe bridging coordination mode was determined by			
18	FT-IR, demonstrating the Fe ₃ O ₄ nanoparticles were well coupled with GO sheets by			
19	coordination bond. TEM images revealed that two types of geometrical structures of			
20	GO-Fe ₃ O ₄ composites were formed by loading different amounts of GO. With low			
21	GO loadings (i.e., GO/Fe ₃ O ₄ = $1/20$, $2/20$ and $3/20$), a single layer structure			
22	GO-Fe ₃ O ₄ composite was obtained. At a high GO loading (i.e., GO/Fe ₃ O ₄ = $4/20$),			
23	stacking structure of GO-Fe $_3O_4$ composite was formed. The as-prepared GO-Fe $_3O_4$			
24	nanocomposites exhibited an excellent catalytic performance in the degradation of			
25	isatin in the presence of H_2O_2 . With GO/Fe ₃ O ₄ weight ratio of 3/20, GO-Fe ₃ O ₄			
26	composites showed superior degradation efficiency of isatin, mainly due to the			
27	effective functional combination between GO and Fe ₃ O ₄ .			

28 Keywords: Graphene oxide; Magnetite; Catalytic; Isatin; Mineralization

29 1. Introduction

Over the past few years, more than 10,000 types of commercial dyes with an annual 30 production of 7×10^5 tons per year are globally produced [1]. Annually, over 50% of 31 these dyes are consumed in textile industry all over the world [2,3]. After used, 10-20% 32 33 of textile dyes are directly discharged as aqueous effluents, leading to a pressing 34 environmental issue [4-7]. Dye is known to be a class of reluctant pollutant and 35 dyeing wastewater is one of the most refractory industrial wastewater. Therefore, it is 36 difficult to degrade dye via conventional wastewater treatment methods [8]. Effective removing dye from the wastewater stream has been considered as a huge challenge in 37 38 the field of wastewater treatment [9].

39

40 A number of wastewater treatment technologies, including physical (adsorption [10] and membrane [11]), chemical (coagulation [12], oxidation [13,14] and photocatalysis 41 42 [15]), biological (aerobic [16] and anaerobic [17,18] degradation) and electrochemical 43 [19] methods, have been developed and adopted for dyeing wastewater treatment. Because of its high efficiency, Fenton/Fenton-like process, which used Fenton's 44 reagents (i.e., Fe^{2+} and H_2O_2) at low pH, has been widely applied in dyeing 45 wastewater treatment [20]. However, homogeneous Fenton process will inevitably 46 47 produce a large amount of iron-rich sludge. In recent years, recyclable heterogeneous Fenton-like catalysts such as hematite (α -Fe₂O₃) [21,22], magnetite (Fe₃O₄) [23] and 48 49 goethite (δ -FeOOH) [24,25] have attracted a great attention since iron-rich sludge will 50 be remarkably reduced in the case of using magnetically recyclable catalysts. Within 51 these iron-based catalysts, magnetite (Fe₃O₄) is a promising catalyst due to its recyclability and superior catalytic performance [25-28]. Only using Fe₃O₄ in 52 53 Fenton-like process, the removal efficiency of organics is often unsatisfactory [29,30]. 54 Coupling with materials could generally enhance the catalytic properties of Fe_3O_4 55 based catalysts [29,30]. It has been reported that carbon coating (humic acid [29], polyhydroquinone [30], sodium carboxymethyl cellulose-graft-poly(acrylic acid) [31] 56

57 and multiwall carbon nanotubes [32-35]) could serve as an electron shuttle in 58 Fenton-like reaction, which could remarkably increase the catalytic performance of 59 magnetite nanoparticles [36]. Zubir et al. [37] coupled magnetite nanoparticle with 60 graphene oxide and applied this composite in the degradation of Acid Orange 7 (AO7) 61 via a Fenton-like process. Although the catalytic performance of GO-magnetite 62 composite has been experimentally documented in a number of studies [37-40], the formation mechanism of GO-magnetite composite has not been fully revealed yet. As 63 a new Fenton-like catalyst, the knowledge of its chemical and physical properties, 64 65 catalytic behavior and practical application is timely needed.

66

Isatin and its derivatives were commonly used in textile industry [41], resulting in high COD value, colority and biotoxity in dyeing wastewater [42]. Isatin cannot be efficiently removed by traditional biodegradation processes (e.g., aerobic and anaerobic degradation) due to its particular chemical structure [43]. In this study, isatin (2,3-indolinedione) is therefore used as an organic pollutant for the evaluation of the catalytic property of as-prepared GO-magnetite composites.

73

74 This work synthesized a series of GO- Fe₃O₄ composites with different GO and Fe₃O₄ 75 loading ratios. The influences of GO loading ratio on the morphology, crystallization and catalytic property of GO-Fe₃O₄ nanocomposites were investigated. FT-IR 76 77 technique was employed to reveal the coordination behavior of C-O-Fe in the as-synthesized nanocomposite. 78 The formation mechanism for GO-Fe₃O₄ 79 nanocomposites proposed. The catalytic performance GO-Fe₃O₄ was of 80 nanocomposites in the degradation of isatin is studied.

- 81
- 82 **2. Experimental**
- 83 2.1 Materials
- 84 Ammonia solution ($NH_3 \cdot H_2O$, 30-33 wt.%) was purchased from E. Merck, LTD.

85 Concentrated sulfuric acid (H₂SO₄, 95 wt.%), di-phosphorus pentaoxide (P₂O₅), ferric 86 chloride hydrate (FeCl₃·6H₂O) and hydrochloric acid (HCl, 35.4 wt.%) were 87 purchased from BDH Merck Chemical Co.. Ferrous chloride hydrate (FeCl₂·6H₂O), 88 potassium permanganate (KMnO₄) and potassium persulfate ($K_2S_2O_8$) were purchased from Sigma-Aldrich. Graphite (325 mesh) and manganese dioxide (MnO₂, 75 wt.%) 89 90 was purchased from Beijing HWRK Chem Co., LTD. Hydrogen peroxide (H₂O₂ 33 wt.%) was purchased from Riedel-de Haen AG. Isatin (C₈H₅NO₂) was purchased 91 from ACROS Organics. GD120 glass fiber was purchased from Toyo Roshi Kaisha, 92 93 Ltd..

94

95 2.2 Preparation of Graphene Oxide (GO) Sheets

96 Graphene oxide (GO) was prepared via a modified two-step Hummers method [44]. At the first pre-oxidation step, 20 ml 95 wt.% H₂SO₄, 3.0 g K₂S₂O₈, 3.0 g P₂O₅ and 97 3.0 g graphite were mixed in a 100 mL Erlenmeyer flask. The mixture was 98 99 homogenized by magnetic stirring. The reaction system was maintained at 80 °C for 6 100 h through a water bath. Next, the mixture was diluted by adding 500 ml deionized 101 water and this as obtained was statically aged at ambient temperature for 12 h. Black 102 precipitate was collected by vacuum filtration with glass fiber filter paper and dried at 103 105 °C in an oven for 24 h. For the second oxidation step, 3.6 g preoxidized sample (black precipitate from the first step), 120 ml 95% H₂SO₄ and 15 g KMnO₄ were 104 105 slowly added into a 250 mL Bunsen flask under magnetic stirring in an ice-bath to 10 °C. After the reaction was kept at 35 °C for 6 h, 500 ml deionized water with 20ml 106 107 35 wt.% H₂O₂ was slowly added into the reaction mixture. The resulting solution was centrifuged by centrifuge (Eppendorf 5810R) at 4,000 rpm for 10 min and washed 108 109 with 3wt. % HCl aqueous solution and deionized water for several times. The final 110 product was diluted in deionized water and exfoliated by ultrasonic treatment for 2 h 111 to form GO solution (0.08 g/L).

113 2.3 Preparation of Graphene Oxide-Magnetite (GO-Fe₃O₄) Composites

114 For the synthesis of GO-Fe₃O₄ composites, 0.041 g FeCl₂·6H₂O and 0.0932 g 115 $FeCl_3 \cdot 6H_2O$ were added to 100 ml GO solutions (0, 0.02, 0.04, 0.06 and 0.08 g/L) 116 with magnetic stirring under Ar atmosphere in a three-necked flask. 20 ml NH₃·H₂O 117 (30-33 wt.%) was dropwise added into FeCl₂-FeCl₃-GO solution to keep the pH at 118 10.0. The reactive system was maintained at 50 °C by water bath. After 2 h reaction, black product was collected by magnetite and washed with deionized water for 119 120 several times. Final products were ultrasonically dispersed in deionized water to form 121 a homogeneous solution. The concentration of Fe_3O_4 in all as-obtained homogeneous 122 solution is estimated to be 3 g/L. Fe_3O_4 without coupling with GO was denoted as 123 Catalyst 1 and the as-prepared GO-Fe₃O₄ composites were denoted as Catalyst 2-5 for GO/Fe₃O₄ weight ratios of 1/20, 2/20, 3/20 and 4/20, respectively. The as obtained 124 Catalysts were characterized by XRD (D8, Bruker AXS, Germany), SEM (Hitachi 125 126 S-4800 field emission scanning electron microscope, Japan), TEM (FEI Tecnai G2 20 Scanning Transmission Electron Microscope, USA) and FI-TR (Perkin-Elmer 127 Spectrum One FT-IR spectrometer, USA). The XRD patterns were recorded over a 2θ 128 129 range from 5 to 80° with a step width of 0.02° and a sampling time of 0.3 s per step. 130 The FT-IR measurement used a potassium bromide (KBr) pellet method.

131

132 **2.4 Catalytic Study**

133 To examine the catalytic activities of the as-prepared catalysts (i.e., Fe₃O₄ and 134 GO-Fe₃O₄ composites), 2 ml of as-prepared homogeneous solution with catalyst was 135 added into 8 ml of 50 ppm isatin aqueous solution, then 4 ml of 0.125 M H₂O₂ was 136 added into 25 ml Erlenmeyer flasks. Then, the reaction solutions were diluted with 137 deionized water to 20 ml. The pH in the reaction system was adjusted to 2.5, 3.5 and 138 5.0 by 0.1 M sulfuric acid. The reaction system was magnetically stirred in water bath at different reaction temperature (25 °C, 35 °C, 45 °C and 55 °C). At different reaction 139 140 time (15, 30, 45, 60, 120 and 180 min), MnO₂ powders (0.05 g) were added to

- 141 reaction solutions to terminate the reaction. The final reaction solutions were filtered
- 142 by nylon syringe filter (0.45 μ m, Filtrex) for UV-vis and TOC measurement.
- 143

144 **3. Results and Discussion**

145 **3.1 Characterization of GO-Fe₃O₄**

146 The particle size and combination behavior of newly generated Fe_3O_4 in the as-prepared GO-Fe₃O₄ composites were revealed by TEM and SAED. In the SAED 147 patterns (Fig. S1e, S1h, S1k, S1n and 1q) of the as-obtained products, various distinct 148 electron diffraction rings of the GO-Fe₃O₄ composites were observed. These 149 150 diffraction rings are corresponding to the (220), (311), (400), (511) and (440) lattice 151 plane of cubic-phase Fe₃O₄ [45], respectively, confirming the black particles (Fig. 1a-1e) were Fe_3O_4 . The particle sizes of the newly generated Fe_3O_4 were approximate 152 10 nm (Fig. S1d, Fig. S1g, Fig. S1j, Fig. S1m and Fig. S1p), as revealed by TEM. 153 With an increase of GO loading, the trend of distribution density of Fe_3O_4 in the 154 GO-Fe₃O₄ composites tends to decrease (Fig. S1f, Fig. S1i, Fig. S1i and Fig. S1o). 155 156 For instance, with a great GO/Fe_3O_4 ratio (i.e., 4/20), GO sheets overlapped 157 significantly with Fe₃O₄ (Fig. 1e). In Fig. 2a and Fig. 2b, the GO boundaries were 158 able to be clearly observed and these boundaries were overlapped. We inferred that 159 the GO-Fe₃O₄-GO bedded layer structure might be formed [37].

160

161 XRD pattern of the unexfoliated GO is shown in Fig. 3. It can be seen that GO without ultrasonic exfoliation had a single broad diffraction peak at 2θ of 10°. This 162 163 (001) diffraction peak corresponded to an interlayer spacing of 0.88 nm, indicating the 164 presence of oxygen functionalities in the product [46]. With an ultrasonic treatment, 165 GO sheets were well exfoliated and become a few-layer structure. Consequently, in XRD pattern of as-synthesized GO-Fe₃O₄ products (Fig. S1b), the (011) diffraction 166 peak of GO disappeared. A series of diffraction peaks at 30.0°, 35.5°, 43.0°, 53.5°, 167 57.0° and 63.0° was observed in the XRD pattern of GO-Fe₃O₄ composites (Fig. 3). 168

169 These diffraction peaks were indexed to be (220), (311), (400), (422), (511) and (400) 170 diffraction planes of cubic Fe₃O₄ [47], respectively. The intensity of these Fe₃O₄ peaks progressively became weakened when the GO loading ratio increased, which 171 172 indicated GO may render the crystallization of Fe₃O₄ during the process of forming GO-Fe₃O₄ composites. When dried same amount of GO-Fe₃O₄ samples at 105 °C for 173 174 24 h, the dried products exhibited different appearance at various GO loadings (Fig. 175 S2). For the samples with low GO loadings (e.g., GO/Fe_3O_4 of 1/20), their appearance are very similar to the product which only composed of Fe₃O₄ nanoparticles. With GO 176 loading increased, the appearance of GO-Fe₃O₄ is different, for instance, folding fan. 177 178 fishbone and paper dust for GO/Fe₃O₄ of 2/20, 3/20 and 4/20, respectively (Fig. 179 S2a-2e).

180

FT-IR is a powerful tool to verify the vibrational stretching frequency of GO, Fe₃O₄ 181 and GO-Fe₃O₄ composites. Fig. 4 showed the collated FT-IR spectra of GO, Fe₃O₄ 182 and GO-Fe₃O₄ composites. The strong peak at 3401 cm⁻¹ was attributed the O-H 183 stretching vibration in GO [48]. Due to the O-H stretching vibration of hydrogen 184 bonded carboxyl groups, peak broadening effect was commonly observed in all FT-IR 185 spectra. In the FT-IR spectra of GO sample, two peaks at 1720 and 1620 cm⁻¹ were 186 observed, which are derived from the C=O stretching vibration of carboxylate and 187 conjugated carbonyls [48,49]. A peak at 1231 cm⁻¹ suggested the C-O stretching 188 vibration of epoxy ring in the as-prepared GO. Note that the characteristic peak at 189 1091 cm⁻¹ was often attributed to the C-O stretching of alcohols. The peak at 618 cm⁻¹ 190 was in-plane deformation vibrations of C-CHO for aromatic aldehydes. The peak at 191 585 cm⁻¹ was the typical Fe-O stretching vibration of Fe₃O₄. Two significant 192 193 vibrations were observed in the FT-IR spectra of GO-Fe₃O₄ composites, most likely due to the carboxyl groups, such as an antisymmetric stretching ($v_a(\text{COO}^-)$) at 1540 194 cm⁻¹ and a symmetric stretching ($v_s(COO^-)$) at 1407 cm⁻¹. The observation of the 195 196 signals of these two vibrations further indicated that carboxyl groups of GO sheets

were deprotonated [50]. The Δ values of both $v_a(\text{COO}^-)$ and $v_s(\text{COO}^-)$ was 133 cm⁻¹ 197 which were close to the ionic values [51], implying that the carboxyl group 198 coordinated with Fe^{2+} or Fe^{3+} ions in bridging coordination mode (Fig. S3). Notice 199 that the as above FT-IR results gave a strong evidence for the formation of C-O-Fe 200 201 coordination bond between GO sheets and Fe_3O_4 nanoparticles. The coordination 202 behavior between GO and Fe₃O₄ was derived from the chemical bond. Notably, in a 203 Fenton process, C-O-Fe coordination bond played a pivotal role for electron shuttle, 204 achieving a higher efficiency for the removal of organics [36]. Higher GO loading would provide more carboxylate group for the nucleation and growth of Fe₃O₄ 205 206 crystallites, thus resulting in smaller Fe₃O₄ nanoparticles. As a consequent, the 207 diffraction intensities of Fe₃O₄ decreased as GO loadings increased. Based on the observation from our devised synthesis scheme and the results of FT-IR, a possible 208 formation mechanism for GO-Fe₃O₄ composites was illustrated in Fig. S3. First, iron 209 210 (II, III) ions were absorbed on the surface of GO nano-sheets, forming C-O-Fe 211 coordination bonds. Then, the nuclei of Fe₃O₄ crystallization were generated. With further addition of ammonia solution, Fe₃O₄ crystallites rapidly grew on the surface of 212 213 GO. The pH for the synthesis system was maintained at 11.0 to ensure the complete 214 precipitation of iron (II, III) ions (eq. 1).

215

$$Fe^{2+} + 2Fe^{3+} + 8NH_3 \cdot H_2O = Fe_3O_4 + 8NH_4^+ + 4H_2O$$
(1)

217

As previously indicated, the amount of GO loading tends to alter the quantity of carboxyl groups for Fe_3O_4 crystallization. Higher loading of GO will produce smaller Fe₃O₄ nanoparticles in GO-Fe₃O₄ composites. When GO loading is as higher to 4/20 of GO/Fe₃O₄, the free carboxyl group on GO surface will form C-O-Fe coordination bond with Fe₃O₄ nanoparticles leading to a stacking structure. The peaks at around 3100 cm⁻¹ for C-H stretching vibration of aromatic ring, 800 cm⁻¹ for C-H bending vibration of aromatic ring and 750 cm⁻¹ for C-H bending vibration of aromatic ring

were observed (Fig. 4). These peaks indicated the distance of two grapheme oxide nanosheets was close enough to form a strong interaction among the aromatic rings of two grapheme oxide nanosheets in GO-Fe₃O₄ composites. This is the main reason to form two substantially different microstructures of GO-Fe₃O₄ composites. The overall results from TEM, XRD and FT-IR evidently demonstrated that GO-Fe₃O₄ composites were successfully synthesized in this study. With the overall available results, a route for the synthesis of GO-Fe₃O₄ nanocomposites was given in Scheme 1.

232

233 **3.2. Effect of GO Loading on Catalytic Activities**

234 The catalytic performance of as-synthesized GO-Fe₃O₄ composites was examined by 235 removing isatin in the presence of H₂O₂. Different loadings of GO formed various 236 $GO-Fe_3O_4$ composites, and their catalytic activities may be different. In the isatin removal system only added H_2O_2 or as-prepared GO-Fe₃O₄ composite, the 237 238 concentration of isatin was still very high, indicating isatin cannot be effective removed within 3-h reaction (Fig. S4). In contrast, in the presence of both $GO-Fe_3O_4$ 239 composite and H₂O₂, over 80 % of isatin could be removed (Fig. 5). Generally, with 240 241 greater loading of GO in the catalyst, its catalytic activities should be higher. For 242 instance, near 95 % of isatin was removed by GO-Fe₃O₄ (3/20) composite. With the 243 combination of GO and Fe₃O₄, the catalytic activities of GO-Fe₃O₄ composites were significantly enhanced, as less than 40% of isatin was removed in Fe₃O₄-H₂O₂ system 244 245 after 180 min. In order to further assess the mineralization efficiency of isatin by GO-Fe₃O₄ composites, total organic carbon (TOC) analysis was performed and the 246 247 results were shown in Fig. 6. As can be seen, all GO-Fe₃O₄ composites exhibited higher TOC removal efficiency of isatin rather than that of only using Fe₃O₄ 248 nanoparticles. Within all the catalysts, Catalyst 4 showed the highest TOC removal 249 250 efficiency (i.e., 60%). The removal efficiency of isatin by different catalysts was 251 concluded as follows: Catalyst 4 > Catalyst 3 and 5 > Catalyst 2 > Catalyst 1. Since 252 the weight of Fe₃O₄ was identical in all the GO-Fe₃O₄ composites, the varied GO

253 loading is the key factor for the removal of isatin. By increasing GO/Fe₃O₄ weight 254 ratios, the catalytic activities correspondingly increased from Catalyst 1 to Catalyst 4. 255 The reasons could be attributed as follows: (i) Fe₃O₄ nanoparticles were well 256 dispersed on GO surface via coordination bonds thus markedly reducing aggregation 257 effect and enhancing effective surface area [52]. It has been demonstrated that the 258 enhancement of mass transfer of reactants toward the active sites could stimulate the 259 degradation of organics in the Fenton-like process [53,54]. (ii) Strong interactions 260 between GO and Fe₃O₄ via C-O-Fe bonds could facilitate the migration of electron among Fe₃O₄ nanoparticles and GO nano-sheets. GO has been well recognized as a 261 262 π -conjugated system, electrons generated from Fenton reaction could be effectively 263 transferred to GO surface [55,56], which would significantly enhance the catalytic 264 activities of GO-Fe₃O₄ composites. The reductive GO could also facilitate the electron transports thus accelerate the redox cycle among the active sites [36,57]. Ferrous ions 265 could be regenerated during the reaction, mostly due to the reducibility of GO. Notice 266 267 that Catalyst 5 is in highest concentration of GO but did not show the highest catalytic 268 efficiency on isatin degradation. It is most likely attributed to the particular GO-Fe₃O₄ 269 bedded structure (Fig. 2a and Fig. 2b), which could reduce the effective surface of 270 product thus hinder hydroxyl radical generation. Among the as-obtained catalysts, 271 $GO-Fe_3O_4$ composite with weight ratio of 3/20 (Catalyst 4) showed the highest catalytic activity for isatin degradation in this study. As indicated previously, Catalyst 272 273 4 had a single GO-Fe₃O₄ layer structure and with less Fe₃O₄ aggregation. Catalyst 4 is therefore used for further catalytic study. 274

275

It was reported that the intermediate products may be absorbed or bound with the catalyst via GO-coupling or ionic interactions during the degradation reaction [52].
Fig. S5 showed the FT-IR spectra of Catalyst 4 collected at 120 min and 180 min in the Fenton process. The FT-IR spectrum of the used Catalyst 4 was nearly identical with that of fresh Catalyst 4, indicating that the potential intermediate products from

isatin degradation were not bound or absorbed by the catalyst. The intermediate products remained in the solution. Therefore, the degradation of isatin was mainly due to the Fenton oxidation with $GO-Fe_3O_4$ composite as catalyst.

284

285 **3.3. Effect of pH on Isatin Degradation**

286 As to Fenton-like reaction, pH is well known to be one of the most critical parameters. The effect of pH on the catalytic activities of Catalyst 4 was thoroughly investigated. 287 Fig. 7 showed the results from the degradation of isatin by Catalyst 4 at pH 2.5, 3.5, 288 289 5.0 and 8.0, respectively. At pH 2.5 and 3.5, over 90% of isatin was removed within a 290 short reaction time (i.e., 30 min). At pH 5.0, the removal efficiency was relatively 291 high at the initial stage (first 15 min) and degradation rate tended to be much slower 292 in the rest. In the case of pH 8.0 (without adding sulfuric acid), only 15% of isatin was degraded over a period of 180 min. The experimental results demonstrated that the 293 294 highest removal efficiency of isatin by Catalyst 4 via heterogeneous Fenton-like process could be achieved at pH 3.5. In Fenton process, interactions among H_2O_2 and 295 296 Fe-based materials will generate hydroxyl radical which could attack and completely 297 destroy the pollutant due to its high oxidation potential (2.8 eV). Tert-butanol is a kind 298 of hydroxyl radical scavenger, which could rapidly scavenge the hydroxyl radicals 299 during the degradation reaction. With the addition of *tert*-butanol, the degradation of 300 isatin was significantly impeded, further implied the generation of hydroxyl radical 301 was the major process for isatin degradation.

302

303 3.4. Effect of Temperature and Ionic Strength on Isatin Degradation

Since dyeing water is usually with high salinity, and its temperature may vary significantly, the effect of ionic strength and temperature was explored to assess the application of GO-Fe₃O₄ composites in the industrial dyeing wastewater treatment (Fig. 8 and Fig. 9). As to the influence of temperature, the degradation of isatin was undertaken at 25 °C, 35 °C, 45 °C, and 55 °C. Fig. 8 showed the results as a function

309 of temperatures. By increasing the temperatures from 25 °C to 55 °C, the degradation 310 rate of isatin was accelerated remarkably, which is consistent with previous studies 311 [58,59]. For the ionic strength effect, it can be seen from Fig. 9 that the degradation 312 efficiency of isatin gradually decreased when NaCl concentration was increased from 313 0 mg/L to 3000 mg /L, indicating high concentrations of NaCl tend to hinder the 314 catalytic activity of GO-Fe₃O₄ composites.

315

316 **3.5.** Durability and Reusability of GO-Fe₃O₄ Composites

317 The durability and reusability of $GO-Fe_3O_4$ composites were examined by conducting 318 the degradation of isatin with the same catalyst recycled from various reaction cycles. 319 Fig. S6 showed the results from 5 successive reactions. After the reaction, Catalyst 4 was magnetically collected from the aqueous solution and washed with deionized 320 water for several times. In next Fenton process, the recycled Catalyst 4 was used. 321 322 Nearly all isatin could be removed by either fresh or recycled Catalyst 4 (Fig. S6), suggesting the recycled Catalyst 4 could maintain a highly efficient removal of isatin. 323 XRD, TEM and FT-IR were employed to characterize the recycled Catalyst 4 to 324 325 further investigate its stability. The phase structure and morphology of the recycled Catalyst 4 are almost identical (Fig. S7 and Fig. S8). Though some new peaks 326 appeared at 1648, 1279, 1070 and 841 cm⁻¹ in FT-IR spectrum of these recycled 327 sample (Fig. S9), these peaks belonged to C=O stretching of carbonyl group (1648 328 cm⁻¹) and C-O stretching (1279 cm⁻¹), C-O-C asymmetric stretching (1070 cm⁻¹) and 329 ring vibration (841 cm⁻¹) of epoxides. It suggested that some hydroxyl radicals were 330 absorbed by GO sheets. In addition, the TOC of the mixed solution increased with ca. 331 0.3 mg/L after Catalyst 4 was mixed with H₂O₂ (without isatin) at pH 3.0 for 15 h. 332 333 Comparing with GO loading of 45 mg/L for Catalyst 4, less than 1% of GO was oxidized after 5 cycles Fenton reaction, demonstrating the excellent reusability and 334 335 durability of GO-Fe₃O₄ nanocomposites in Fenton-like process.

337 4. Conclusions

338 Graphene oxide-magnetite (GO-Fe₃ O_4) composites were successfully synthesized by 339 chemical precipitation of iron salts onto GO surface in the presence of ammonia. 340 FT-IR spectrum indicated that Fe₃O₄ particles integrated with GO via C-O-Fe coordination bond. The loading of GO has a great impact on the morphology, 341 342 appearance and catalytic activities of as-synthesized GO-Fe₃O₄ composites. With GO loading increased, less Fe₃O₄ particles were aggregated and smaller particle sizes of 343 Fe₃O₄ were observed in GO-Fe₃O₄ composites. Two GO-Fe₃O₄ structures could be 344 constructed at different GO loading. Single layer structure of GO-Fe₃O₄ composites 345 346 was obtained at low GO loading (i.e., 1/20, 2/20 and 3/20 for GO/Fe₃O₄), and 347 stacking structure was formed at high GO loading (i.e., 4/20 for GO/Fe₃O₄). 348 $GO-Fe_3O_4$ composites could stimulate the formation of hydroxyl radicals in the presence of H_2O_2 . Isatin was able to be degraded by these highly active GO-Fe₃O₄ 349 350 composites, and 3/20 is the optimum ratio of GO-Fe₃O₄ composites for the 351 degradation of isatin, as the highest catalytic activity achieved. The suitable pH for 352 the isatin degradation by GO-Fe₃O₄ composites is 3.5. Evaluating temperature did not 353 show significant impacts on the removal efficiency when the reaction temperature is 354 long enough. The removal efficiency was hindered when the ionic strength is increased. The high catalytic activity of the catalyst was mainly attributed to the 355 effective functional combination of GO and Fe₃O₄ nanoparticles. GO-Fe₃O₄ 356 357 composites have great potential to be the high-performance catalysts for practical applications. 358

359

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554	Figure Captions				
555					
556	Scheme 1. Synthesis of GO-Fe ₃ O ₄ composites and the degradation of isatin by				
557	GO-Fe ₃ O ₄ composites.				
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559	Fig. 1. TEM images of Fe_3O_4 and $GO-Fe_3O_4$ composites as catalyst for isatin				
560	degradation. (a) Catalyst 1 (Fe ₃ O ₄), (b) Catalyst 2 (GO-Fe ₃ O ₄ , 1/20), (c) Catalyst 3				
561	(GO-Fe ₃ O ₄ , 2/20), (d) Catalyst 4 (GO-Fe ₃ O ₄ , 3/20) and (e) Catalyst 5 (GO-Fe ₃ O ₄ ,				
562	4/20).				
563					
564	Fig. 2. TEM images of Catalyst 5 (GO-Fe ₃ O ₄ , $4/20$). The arrows indicate the edge of				
565	graphene oxide.				
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567	Fig. 3. XRD patterns of GO, Fe ₃ O ₄ and GO-Fe ₃ O ₄ composites.				
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569	Fig. 4. FT-IR spectra of GO, Fe ₃ O ₄ , and GO-Fe ₃ O ₄ composites.				
570					
571	Fig. 5. Efficiency of isatin removal (Isatin concentration = 20 mg/L, initial H_2O_2				
572	concentration = 25 mmol/L, Fe_3O_4 suspension = 0.3 g/L, $GO-Fe_3O_4$ composites				
573	suspension = 0.3 g/L in concentration of Fe_3O_4 and initial solution pH = 3.5).				
574					
575	Fig. 6. Efficiency of TOC removal (Isatin concentration = 20 mg/L, initial H_2O_2				
576	concentration = 25 mmol/L, Fe_3O_4 suspension = 0.3 g/L, $GO-Fe_3O_4$ composites				
577	suspension = 0.3 g/L in concentration of Fe ₃ O ₄ , initial solution pH = 3.5 and T =				
578	25 °C).				
579	Fig. 7. The pH effect on isatin removal (Isatin concentration = 20 mg/L , initial H_2O_2				
580	concentration = 25 mmol/L, Fe_3O_4 suspension = 0.3 g/L, $GO-Fe_3O_4$ composites				
581	suspension = 0.3 g/L in concentration of Fe ₃ O ₄ and T = 25 °C).				

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583	Fig. 8. The temperature effect on isatin removal (Isatin concentration = 20 mg/L ,				
584	initial H_2O_2 concentration = 25 mmol/L, Fe_3O_4 suspension = 0.3 g/L, $GO-Fe_3O_4$				
585	composites suspension = 0.3 g/L in concentration of Fe_3O_4 and initial solution pH =				
586	3.5).				
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588	Fig. 9. The NaCl concentration effect on isatin removal (Isatin concentration $= 20$				
589	mg/L, initial H_2O_2 concentration = 25 mmol/L, Fe_3O_4 suspension = 0.3 g/L,				
590	GO-Fe ₃ O ₄ composites suspension = 0.3 g/L in concentration of Fe ₃ O ₄ and initial				
591	solution $pH = 3.5$).				
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Fig. 1. TEM images of Fe_3O_4 and $GO-Fe_3O_4$ composites as catalyst for isatin degradation. (a) Catalyst 1 (Fe_3O_4), (b) Catalyst 2 ($GO-Fe_3O_4$, 1/20), (c) Catalyst 3 ($GO-Fe_3O_4$, 2/20), (d) Catalyst 4 ($GO-Fe_3O_4$, 3/20) and (e) Catalyst 5 ($GO-Fe_3O_4$, 4/20).

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Fig. 2. TEM images of Catalyst 5 (GO-Fe₃O₄, 4/20). The arrows indicate the edge of

645	graphene oxide.
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Fig. 5. Efficiency of isatin removal (Isatin concentration = 20 mg/L, initial H_2O_2 concentration = 25 mmol/L, Fe₃O₄ suspension = 0.3 g/L, GO-Fe₃O₄ composites suspension = 0.3 g/L in concentration of Fe₃O₄ and initial solution pH = 3.5).





Fig. 6. Efficiency of TOC removal (Isatin concentration = 20 mg/L, initial H_2O_2 concentration = 25 mmol/L, Fe₃O₄ suspension = 0.3 g/L, GO-Fe₃O₄ composites suspension = 0.3 g/L in concentration of Fe₃O₄, initial solution pH = 3.5 and T = 25 °C).





Fig. 7. The pH effect on isatin removal (Isatin concentration = 20 mg/L, initial H₂O₂ concentration = 25 mmol/L, Fe₃O₄ suspension = 0.3 g/L, GO-Fe₃O₄ composites suspension = 0.3 g/L in concentration of Fe₃O₄ and T = 25 °C).



Fig. 8. The temperature effect on isatin removal (Isatin concentration = 20 mg/L, initial H_2O_2 concentration = 25 mmol/L, Fe₃O₄ suspension = 0.3 g/L, GO-Fe₃O₄ composites suspension = 0.3 g/L in concentration of Fe₃O₄ and initial solution pH =

3.5).



Fig. 9. The NaCl concentration effect on isatin removal (Isatin concentration = 20 mg/L, initial H_2O_2 concentration = 25 mmol/L, Fe₃O₄ suspension = 0.3 g/L, GO-Fe₃O₄ composites suspension = 0.3 g/L in concentration of Fe₃O₄ and initial solution pH = 3.5).

771 Supplementary Material

- Inclusive of one table and nine figures over ten pages

Table 1. Synthesis of Fe_3O_4 and $GO-Fe_3O_4$ composites.

	GO	FeCl ₂ ·6H ₂ O	FeCl ₃ ·6H ₂ O	Weight Ratios of GO-Fe ₃ O ₄
Catalyst 1	0.000 g	0.405 g	0.932 g	0:20
Catalyst 2	0.020 g	0.405 g	0.932 g	1:20
Catalyst 3	0.040 g	0.405 g	0.932 g	2:20
Catalyst 4	0.060 g	0.405 g	0.932 g	3:20
Catalyst 5	0.080 g	0.405 g	0.932 g	4:20

*The pH is 11.0, adjusted by $NH_3 \cdot H_2O$.



Fig. S1. TEM images of GO (a and b), Fe_3O_4 (c and d, Catalyst 1), GO-Fe₃O₄ (f and g,

- Catalyst 2) with GO/Fe₃O₄=1/20, GO-Fe₃O₄ (i and j, Catalyst 3) with GO/Fe₃O₄=2/20,
- GO-Fe₃O₄ (l and m, Catalyst 4) with GO/Fe₃O₄=3/20, GO-Fe₃O₄ (o and p, Catalyst 5)
- with GO/Fe₃O₄=4/20, and SAED pattern of Catalyst 1 (e), Catalyst 2 (h), Catalyst 3
- 797 (k), Catalyst 4 (n) and Catalyst 5 (q).



Fig. S2. Images of Fe_3O_4 and $GO-Fe_3O_4$ composites, (a) Catalyst 1 (Fe_3O_4), (b) Catalyst 2 ($GO-Fe_3O_4$, 1/20), (c) Catalyst 3 ($GO-Fe_3O_4$, 2/20), (d) Catalyst 4 ($GO-Fe_3O_4$, 3/20) and (e) Catalyst 5 ($GO-Fe_3O_4$, 4/20).



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Fig. S4. Efficiency of isatin removal (Isatin concentration = 20 mg/L, initial H_2O_2 concentration = 25 mmol/L, Fe₃O₄ suspension = 0.3 g/L, GO-Fe₃O₄ composites suspension = 0.3 g/L in concentration of Fe₃O₄ and initial solution pH = 3.5).







Fig. S6. Catalytic stability of Catalyst 4 for isatin removal with 5 successive cycles of the same reaction condition. (Isatin concentration = 20 mg/L, initial H_2O_2 concentration = 25 mmol/L, Fe_3O_4 suspension = 0.3 g/L, GO-Fe₃O₄ composites suspension = 0.3 g/L in concentration of Fe₃O₄ and initial solution pH = 3.0).



Fig. S7. XRD patterns of Catalyst 4 (GO-Fe₃O₄, 3/20) after several successive cycles

under the same reaction condition.





Fig. S8. TEM images of Catalyst 4 after (a) 0 cycle, (b) 3 cycles and (c) 5 cycles.

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Fig. S9. FT-IR spectra of Catalyst 4 (GO-Fe₃O₄, 3/20) after several successive cycles

- under the same reaction condition.

HIGHLIGHTS

1. Recyclable graphene oxide (GO) - magnetite (Fe₃O₄) composites were successfully synthesized.

2. Highly efficient removal of isatin by GO-Fe₃O₄ composites was achieved.

3. The effective functional combination between GO and Fe_3O_4 played a crucial role on isatin mineralization.

4. The technology's advantages are a facile and cost-effectiveness.