Iron encapsulated in boron and nitrogen codoped carbon nanotubes as synergistic catalysts for Fenton-like reaction

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Iron nanoparticles (NPs) encapsulated in B, N-codoped carbon nanotubes (Fe@C-BN) as heterogeneous Fenton-like catalysts were obtained by a simple and scalable pyrolysis method, and their performances were examined in the oxidative degradation of various organics in the presence of the different oxidants. The results showed that organic dyes can be effectively degraded by Fe@C-BN in the presence of peroxymonosulfate. Calcination temperature and mass of iron salt significantly affected the structures and performances of the catalysts. The effects of several reaction conditions, such as initial dye concentration, oxidant type (peroxymonosulfate, peroxodisulfate, and H2O2) and dosage, initial pH, inorganic anions, reaction temperature and dye types on oxidation as well as the stability of the composite were extensively evaluated in view of the practical applications. Through the investigation of reaction processes, HO· and SO4− radicals were identified using quenching experiments. Owing to the synergistic effects between the iron NPs and B, N-doped carbon, Fe@C-BN catalysts intrinsically display an excellent catalytic activity for Fenton-like reaction. This study gives new insights into the design and preparation of iron NPs encapsulated in B, N-codoped carbon nanotubes as an effective strategy to enhance the overall catalytic activity.

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1. Introduction

Advanced Oxidation Processes (AOPs) were regarded as an effective technology for the degradation of organic contaminants, owing to the creation of highly reactive radicals, such as hydroxyl radical (HO·), O2·-, OOH·, and sulfate radical (SO4−) (Wang et al., 2015a). Among them, SO4− based AOPs with the activation of peroxymonosulfate (PMS, 2KHSO5·K2SO4) have attracted increasing research interest as an alternative to conventional Fenton processes in recent years. Compared to HO· in Fenton reaction, SO4− demonstrates a comparable redox potential (2.5–3.1 V vs 1.9–2.7 V of HO·), and is more efficient to decompose some refractory organic contaminants for its selective oxidation ability (Duan et al., 2015a; Zeng et al., 2015). SO4− production can be performed via ultraviolet light, heat, and transition metal mediated activations. Among the activation mechanisms, a heterogeneous process involving metal cations (e.g., Fe2+, Mn2+, etc.) for the activation of PMS has received extensive attention as it can usually work in mild conditions and produce almost no byproduct sludge after reaction (Wei et al., 2015).

To date, iron-based nanoparticles (NPs) as heterogeneous catalysts are particularly studied due to the fact that they are highly accessible because iron is the second most abundant element in the earth’s crust (Jiang et al., 2015; Lei et al., 2015). In addition, it is easily separated from the reaction medium using an external magnetic field (Zhou et al., 2014). For example, our group previously fabricated iron-based hybrids (CuFe2O4/C3N4 (Yao et al., 2015b), ZnFe2O4/graphene (Yao et al., 2014), Fe3O4/graphene (Yao et al., 2012a), CoFe2O4/graphene (Yao et al., 2012b) and N-doped
TiO$_2$/ZnFe$_2$O$_4$ (Yao et al., 2015c)) as efficient catalysts for the mineralization of aqueous organic pollutants. However, many of those catalysts are often confronted with weak catalytic activity, which often needs the aid of electricity, ultrasonics, and UV or visible light irradiation. In addition, nano-iron catalysts are unstable and are easily deactivated because of aggregation or leaching of the active metal in the reaction mixture. The development of core–shell structured materials provides a possibility to solve these problems. In the case of iron NPs, the resulting materials are often protected by organic or inorganic shells, usually prepared at relatively harsh synthetic conditions, which limits the preparation and application of the potential catalysts (Cui et al., 2015). Thus, much effort has been devoted to developing low cost, non-precious-metal catalysts with the improved catalytic efficiency, durability, and anti-poisoning ability.

Recently, heteroatom doping of iron-based hybrids has been promoted as a promising route to improve the catalytic performances. N-doped carbon can efficiently facilitate electronic conductivity of the material since N atoms act as an electron donor and provide electron carriers and decrease the band gap energy. On the other hand, B-doping can also elevate the carbon conductivity by increasing the quantity of hole-type charge carriers and transforming the electronegativity of carbon materials (Zhang et al., 2015). Cui et al. (Cui et al., 2015) have shown that N-doped graphene can exhibit an increased activity in oxidative dehydrogenations of several N-heterocycles. Zhang et al. (Zhang et al., 2015) have successfully synthesized B, N codoped LiFePO$_4$/C materials which offer excellent high rates of electrochemical performance. It has been demonstrated that the difference in electronegativity between N/B and C in graphitic framework usually creates the charged sites to facilitate the oxygen reduction process (Zhang et al., 2014). Nowadays, B and N-doped carbon-based catalysts were applied in Fenton-like reaction (Duan et al., 2015b). However, it is still desirable but challenging to produce iron encapsulated in B, N codoped carbon catalysts with high amounts of active sites.

Inspired by the properties of B, N-doped carbon materials to activate PMS and encouraged by our recent investigations on the use of iron-based catalysts and B, N-doped heterogeneous materials, we started to explore the preparation of novel iron–carbon materials and their environmental application. Herein, we reported the preparation of novel iron NPs covered by B, N-doped carbon nanotube (Fe@C-BN), and described for the first time their activity in catalytic oxidations of organic pollutants. Various characterization techniques have been performed in order to understand the properties of the synthesized materials, and the performance was evaluated in terms of organic pollutant degradation in the presence of oxidants. Additionally, the influences of various experimental parameters, catalytic mechanisms, and active species were explored to understand the promotional effects of Fe@C-BN catalysts.

2. Materials and methods

2.1. Synthesis of Fe@C-BN catalysts

In a typical synthesis, H$_3$BO$_3$ (0.12 mol) and C$_3$N$_6$H$_6$ (0.06 mol) as B, N/C precursors were dissolved in 300 mL of distilled water at 85 °C. Then, Fe(NO$_3$)$_3$·9H$_2$O as an iron precursor with a designed loading (3, 4, 6 and 12 mmol) was introduced to achieve a homogeneous solution with continual stirring for 4 h. Subsequently, the reaction mixtures were heated and kept at 115 °C to completely evaporate the distilled water. After drying at 75 °C, the resulting precipitates were heated to different temperatures (700, 800, 900 and 1000 °C) with a heating rate of 2.5 °C/min and held for 3 h under flowing nitrogen. After that, the furnace was slowly cooled down to room temperature under nitrogen atmosphere. Finally, the resultant black product was dispersed in methanol and refluxed for 3 h at 75 °C. The obtained precipitates were washed with excessive ethanol, dried, and ground to powders for further use. The as-prepared catalysts were denoted as Fe@C – BN (where T represents the calcination temperature and X represents the initial mass of iron salts). The scheme for the synthesis of Fe@C-BN catalysts is illustrated in Fig. 1.

2.2. Catalyst characterization

The crystal phases of the as-prepared samples were evaluated by X-ray diffractometry (XRD, X’Pert PRO MPD) using Cu Kα radiations (λ = 1.5418 Å), and the data were acquired in the range of 10–80°. Thermogravimetric analysis (TGA) was performed using a Netzsch TG209 F3 system within a temperature range of 25–800 °C at a heating rate of 10 °C/min under static air atmosphere. The microstructures were characterized by field-emission scanning electron microscopy (FE-SEM, SU8020, Hitachi) and field-emission transmission electron microscopy (FE-TEM, JEM-2100F, JEOL). Energy dispersive X-ray (EDS) analyses were also performed during high-resolution transmission electron microscopy (HRTEM). X-ray photoelectron spectroscopy (XPS) using an ESCALAB250 spectrometer equipped with a focused monochromatic Al Kα at 12 kV and 20 mA was used to analyze the composition of the specimens.

2.3. Catalytic activity test

All the experiments were conducted in a 500 mL beaker with a water bath at desired temperature. Fe@C-BN catalyst was first dispersed into 500 mL organic dye solutions with desired initial concentrations under continuous stirring. Subsequently, the degradation reaction was initiated by adding a known concentration of PMS to the mixture. The samples were taken out at regular intervals, immediately quenched with the same amount of methanol, and then magnetized to remove essentially the catalyst solids for the following analysis. The concentrations of the residual organic dye were measured by monitoring the wavelength of maximum adsorption using a UV–vis spectrophotometer. A full spectrum scan was simultaneously obtained from 200 to 700 nm. The concentrations of leaching Fe ions in the solutions were also determined with atomic absorption spectroscopy (AAS, AA800, Perkin-Elmer). The initial solution pHs (pH$_i$) were adjusted with 0.1 M H$_2$SO$_4$ or NaOH solution, and the final solution pHs (pH$_f$) of the reaction were measured by a pH meter. The analysis of total organic carbon (TOC) was performed with a TOC analyzer (Vario TOC select, Elemental).

For a comparison, control experiments using an equivalent dosage of the different Fe@C-BN catalysts without PMS were carried out in the same steps as above. The effects of reaction parameters (including PMS dosages, reaction temperature, initial pH, and various inorganic anions) were also investigated. A few of tests were also carried out with other common oxidants, H$_2$O$_2$ and potassium peroxodisulphate (PDS). To determine the active species during batch experiments, tert-butyl alcohol (TBA), MeOH and benzoquinone (BQ) were employed to distinguish HO$^\cdot$ and SO$_4$$^\cdot$ radicals. Quenching experiments were performed by adding the quencher into the reaction solution before the addition of PMS. For the stability evaluation of catalysts, Fe@C-BN was magnetically separated after completion of the reaction, washed three times with the distilled water and dried at 85 °C, and used in the next run at the similar experimental conditions.
3. Results and discussion

3.1. Catalyst characterization

Fe@C-BN materials were prepared by simple thermal treatment of Fe(NO)\textsubscript{3}-9H\textsubscript{2}O, H\textsubscript{3}BO\textsubscript{3} and C\textsubscript{3}N\textsubscript{6}H\textsubscript{6} in nitrogen atmosphere. By adjusting the mass of Fe(NO)\textsubscript{3}-9H\textsubscript{2}O and calcination temperature, the porous structure of Fe@C-BN could be successfully controlled. Catalytic degradation of Orange II over different catalysts was carried out and Fe@C-BN\textsubscript{6800} was found to be the most efficient one. Hence, this catalyst was comprehensively characterized by XRD, TGA, FE-SEM, FE-TEM, EDS, and XPS techniques. Fig. 2 represents XRD patterns of various Fe@C-BN catalysts. The broad reflections at about 26.4° are from carbon nanotubes (CNTs). Weak peaks corresponding to maghemite \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3} are also observed, which is produced from the thermal decomposition of iron hydr(oxides) (Zhang et al., 2014). In contrast, strong and sharp diffraction peaks at 20 = 44.6° is assigned to (110) of \(\alpha\)-Fe (JCPDS 06-0696) (Chen et al., 2007; Huang et al., 2010). This suggests that Fe\textsuperscript{3+} was partially reduced to Fe\textsuperscript{0} by ammonia and as-formed carbon during heating process in N\textsubscript{2}. In addition, a sample pyrolyzed at higher temperature (1000 °C) showed sharper reflections caused by the crystalline phase Fe\textsubscript{3}C and a small amount of FeN.

The thermal stability of the Fe@C-BN nanocomposite was surveyed by TGA in an air flow (Fig. S1). It can be easily observed that two stages of weight loss occurred. Note that the major weight loss between 300 and 700 °C in the TGA curve corresponded to the degradation of amorphous carbon, while the slight weight increase above 800 °C was due to the oxidation of iron in the air (Shen et al., 2015). The content of Fe grew with increasing pyrolysis temperature, suggesting that the higher the pyrolysis temperature, the faster the reaction is. It can also be observed that the calcination temperature and feed ratio have a significant impact on morphology and graphitization of carbon as well as the composition and content of Fe species. Thus, calcination temperature and feed iron content affect the properties of iron compounds and the
nature of solid carbon.

The microstructure of Fe@C–BN\textsubscript{680} catalyst was further examined by FE-SEM and FE-TEM images. Fig. 3a indicates that the sample consists of randomly orientated and entangled CNTs. FE-TEM (Fig. 3b) reveals bubble-chain nanotubes encapsulated with iron particles (pointed by the white arrows). More specifically, the outer diameter of the nanotube is in a range of 20–150 nm with the wall-thickness of about 5–20 nm. EDS analysis (Fig. 3f) discloses the existence of C, B, N, Fe, and O elements in the composite. Elemental mapping further reveals that both nitrogen and boron species are homogeneously distributed throughout the whole mesoporous structure (Fig. S2). The typical HRTEM images show all iron-containing NPs are encapsulated into well-defined carbon shells and the size of the encapsulated particles varies from tens to hundreds of nanometers. The enlarged TEM image (Fig. 3d, e) of the region marked with a rectangle shows clear lattice fringes separated by 0.25 nm, which corresponds to the (3 1 1) lattice plane of Fe\textsubscript{2}O\textsubscript{3}. The region marked with a rectangle showing an interplanar distance of ca. 0.34 nm, corresponding to the d-spacing of the (0 0 2) basal planes in carbon layer. It is worth noting that the physical isolation of carbon wrapping not only suppresses the dissolution of core materials in acidic medium, but also enhances the chemical activity and stability of catalysts, which are plausibly attributed to the reduction of iron oxide surrounded by carbon layers (Wang et al., 2014).

3.2. Catalytic evaluation

To examine the activity of the catalysts for oxidative degradation of organic pollutants, we initially tested various Fe@C-BN materials prepared at different calcination temperatures and Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O dosages (Fig. 4a, b). The pseudo-first-order rate constants (\(k_{\text{obs}}\)) obtained by fitting the data in Fig. 4a, b are given in Fig. S3a, b. The values of \(k_{\text{obs}}\) were 0.020 min\textsuperscript{-1} for Fe@C–BN\textsubscript{700}, 0.058 min\textsuperscript{-1} for Fe@C–BN\textsubscript{800}, 0.011 min\textsuperscript{-1} for Fe@C–BN\textsubscript{900}, 0.004 min\textsuperscript{-1} for Fe@C–BN\textsubscript{1000}, 0.013 min\textsuperscript{-1} for Fe@C–BN\textsubscript{1200}, and 0.020 min\textsuperscript{-1} for Fe@C–BN\textsubscript{1800}. These results show that the change of the calcination temperature and Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O dosage remarkably influenced the ability of activating PMS, attributing to the different structures, which have been analyzed by XRD and TGA. This phenomenon demonstrates that calcination temperature and feed ratio of materials in synthesis are of great importance in Fenton-like system. The better catalytic performances of Fe@C–BN\textsubscript{800} catalyst is attributed to the specific structure of the material, in which all the catalytically active species are confirmed by the XPS analysis (Fig. 5). It was selected as a typical Fe@C-BN for the rest experiments.

It is difficult to compare the catalytic activity of various Fenton-like catalysts from literature due to the difference of experimental conditions. In the present study, different metal ions or oxides (Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, Fe\textsubscript{2}O\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}, and Co\textsubscript{3}O\textsubscript{4}) and h-BN mentioned frequently in references were employed to compare with the

Fig. 3. (a) FE-SEM, (b) FE-TEM, (c, d, e) HRTEM images, and (f) EDS pattern of Fe@C – BN\textsubscript{680} catalyst.
Fe@C – BN$_{800}$ catalysts (Fig. 4c). PMS alone was unreactive toward Orange II degradation. However, 94.5% of Orange II removal was achieved in 60 min with the Fe@C – BN$_{800}$/PMS coupled process. In contrast, Fe(NO)$_3$$\cdot$9H$_2$O (Fe$^{3+}$), Fe$_3$O$_4$, Fe$_2$O$_3$, and BN presented poor catalytic activities. FeSO$_4$$\cdot$7H$_2$O (Fe$^{2+}$) and Co$_3$O$_4$ were able to effectively activate PMS, leading to 27.4% and 14.8% Orange II oxidation after 120 min of reaction, respectively. No noticeable adsorption of Orange II on Fe@C-BN was observed (Fig. S4), indicating that Orange II was degraded in Fe@C – BN$_{800}$/PMS but not adsorbed on the particles. The results clearly show that Fe@C – BN$_{800}$ is the most active among the catalysts tested for PMS activation under our experimental conditions.

Figure S5 presents that initial pH can remarkably influence the degradation efficiency in the Fe@C – BN$_{800}$/PMS process. The very fast decomposition of Orange II over the pH$_r$ range of 2.97–9.45 in the Fe@C – BN$_{800}$/PMS process indicates that Fe@C – BN$_{800}$ may be effective for removing organic contaminants over a broad pH range, which is different with the traditional Fenton reaction with low pH$_r$ ~3. The variation in removal with pH$_r$ can be explained that pH changes the surface charge of the catalyst, the electrostatic interaction between the catalyst surface and organic dye molecule, and the number of charged radicals generated during the catalytic oxidation process (Guo et al., 2014a). It is noted that an obvious pH$_r$ decrease after reaction was observed, due to the formation of acid intermediates and the consumption/formation of H$^+$, which is consistent with the literature (Jiang et al., 2015).

Fig. 4d shows the temporal evolution of Orange II solution using Fe@C – BN$_{800}$/PMS system. The original absorption of Orange II mainly consists of three peaks at wavelengths of 228, 310 and 485 nm. The peak at 485 nm corresponds to the chromophore containing azo linkage. The absorption peaks at 228 nm and 310 nm are attributed to the benzene ring and naphthalene ring (Deng et al., 2008; Inchaurreondo et al., 2016). As the reaction proceeds, the characteristic absorption peaks in the visible region decreased dramatically and nearly disappeared after 120 min, suggesting that the two tautomeric forms react at the same time (Wang et al., 2015a). However, the spectrum in the UV region shows that the dye was not mineralized completely, though the absorption was reduced over the UV range. The increase of the absorbance at 250 nm during the reaction is due to the break-up of the azo bond and the formation of intermediate monoaromatic sub-products (Liang et al., 2016). This result is consistent with the gradual color change of the reaction solution from orange to almost colorless during the different reaction time (Fig. S6).

For a better insight of the chemical composition and electronic structure of the as-synthesized Fe@C-BN catalysts before and after the degradation experiments, XPS study was carried out. Fig. 5a presents XPS survey spectrum, which clearly shows five elements (Fe, O, B, N, and C) existing in both the samples. The high resolution curve-fitted elementary XPS peaks of Fe 2p, O 1s, B 1s, and N 1s are displayed in Fig. 5b–f. The analysis of B 1s level is displayed in Fig. 5b. Two components are identified in the spectra and assigned to h-BN (190.7 eV) and the C-NB group (192.2 eV) for BCN compound (Raziq et al., 2016; Yan et al., 2010). This indicates that some
of boron atoms are introduced into the carbon frame. The intensity of both components decreased after reaction. The XPS spectra of N 1s (Fig. 5c) are deconvoluted to two contributions at 398.3 and 400.2 eV, attributed to pyridinic N and graphitic N, respectively. The peak at a binding energy of 398.3 eV should also include a contribution from nitrogen bound to the metal (Fe–N), due to the small difference of their binding energies (Liang et al., 2013). Graphitic N and pyridinic N (probably including Fe–N) are generally believed to participate in the Fenton-like reaction (Peng et al., 2014; Raziq et al., 2016). The XPS spectra of C 1s (Fig. 5d) are fitted into three components, assigned to C–C at 284.8 eV, hydroxyl C–OH at 285.7 eV, and carbonyl C=O at 288.4 eV (Xu et al., 2015), respectively. For O 1s core level (Fig. 5e), the as-prepared NPs spectra displayed four contributions related to the presence of O–Fe bonds (530.3 eV), defective oxides and hydroxides (531.5 eV), O–B bonds (532.5 eV), and O–N bonds (533.7 eV). The Fe 2p core level (Fig. 5f) for the Fe-doped catalyst was deconvoluted to the existence of Fe0 (707.3 eV), Fe2+ (709.5 eV) and Fe3+ (711.5 and 713.2 eV). The relative proportion of these components is modified after the Fenton-like reaction, which might explain the high activity of the Fe@C-BN catalyst. A slightly positive shift of the Fe 2p, N 1s, B 1s, C 1s and O 1s binding energies was observed for Fe@C-BN catalysts after the catalytic degradation, which may be due to the redox reaction of electron transfer in the Fenton-like process and deposited intermediates from reactants.

The stability and reusability were further evaluated (Fig. 6a). It was found that about 62.8% of Orange II was degraded after five recycling runs, indicating adequate stability for organic pollutant elimination. It was observed that the reaction rate constant declined greatly from 0.058 min⁻¹ to 0.009 min⁻¹ over 5 runs (Fig. S7), due to intricate influences of surface chemistry and structural changes including the adsorption of intermediates, coverage of surface active sites, changes of pore structures, and dissolution of iron (Duan et al., 2015a). The concentration of the leached Fe was detected by AAS to be 0.54 mg L⁻¹. It should be noted that the leaching of Fe-ions remained below 1 mg L⁻¹, which is acceptable according to EU discharge standards (<2 ppm) (Deng et al., 2008). In addition, Fe@C-BN still remained in the spinel crystalline form in the cubic phase after reaction (Fig. S8), suggesting that this catalyst is relatively stable. Fig. 6b shows that the synthetic Fe@C-BN hybrids dispersed in a water solution can be magnetically separated from the suspension and re-dispersed for reuse after separation. These results show that Fe@C-BN can be manipulated by magnet attraction, thus providing a potential advantage for the separation, recovery, and reuse of the catalysts. Since Fe@C – BN 800 displayed the best activity, it was deployed in the scope study to optimize the parameters, different oxidizing agents, i.e., H₂O₂, PDS, and PMS were tested on the degradation of Orange II (Fig. 7a). It was found that the efficiency of oxidants followed an order: PMS > PDS > H₂O₂. It is likely that PMS has a higher oxidizing potential than PDS and H₂O₂, and that the PMS molecule is asymmetric and more readily activated than the other two
oxidants (Guan et al., 2013; Yao et al., 2013). In addition, the degradation rate increased by increasing the concentration of PMS up to 0.10 g/L, attributing to the formation of more amount of radicals during the reaction. However, beyond this concentration the rate decreased, which might be due to self-scavenging during the reaction (Sharma et al., 2015). Hence, optimized PMS concentration in the case of all the catalysts was taken at 0.10 g/L.

**Fig. 6.** (a) Recycle experiments for Orange II degradation using Fe@C – BN_6@6_800. (b) Photograph of the sample attracted by a magnet. Unless otherwise stated, the reaction conditions are: [Orange II] = 20 mg/L, [Fe@C – BN_6@6_800] = 20 mg/L, T = 25 °C, [PMS] = 0.10 g/L, without pH adjustment.

**Fig. 7.** Varying effects on the catalytic degradation of organic dyes: (a) different oxidizing agents and dosage, (b) Reaction temperature, (c) Different anions and (d) Different organics. Unless otherwise stated, the reaction conditions are: [Organics] = 20 mg/L, [Fe@C – BN_6@6_800] = 20 mg/L, T = 25 °C, [PMS] = 0.10 g/L, without pH adjustment.

Fig. 7b represents the effect of reaction temperature (10–55 °C) on Orange II degradation, which demonstrated that the increasing temperature was favorable to the enhancement of the catalytic activity. In general, the elevated temperature would promote more energy for the reactant molecules to overcome the activation energy barrier. In addition, an increase in temperature favors the thermal decomposition of PMS, thereby enhancing the radical’s generation (Yao et al., 2015b).

**Fig. 7c** shows the effects of naturally occurring anions on Orange II oxidation by PMS. We can observe that all of the added inorganic anions have a negative effect on the catalytic process and decrease the catalytic degradation rate of the dye. At the test concentrations, the negative effect of these inorganic anions was found to be in an
order of $S_2O_3^{2-}$ > $HCO_3^-$ > $CO_2^-$ > $NO_2^-$ > $HCOO^-$ > $Cl^-$ > $HPO_4^{2-}$ > $NO_2^-$ > $H_2PO_4^-$ > $SO_4^{2-}$ > $CH_3COO^-$. The main reason is attributed to the competitive adsorption of anions and the target organic substance onto the surface of the catalyst, resulting in blockage of the active sites on the catalyst surface (Eskandarloo et al., 2014).

Fig. 7d further demonstrates that Fe@C – BN$_{800}$ presented a great efficiency for catalytic oxidation of other organic pollutants. The use of Fe@C – BN$_{800}$ catalyst yielded a removal of 95% for Orange II, 92.1% for Methyl orange, 88.8% for Methyl violet, 57.7% for Methylene blue, 52.9% for Rhodamin B, and 20.3% for 4-chlorophenol under the similar operation conditions. The removal rates differed from each other, which may be attributed to the difference in molecular structures (Luo et al., 2015). These results clearly indicated that the Fe@C – BN$_{800}$/PMS is an efficient catalytic system for remediation of the organic matters present in industrial effluents.

The above results suggest that reactive oxidizing species is produced in the Fe@C-BN/PMS system, leading to the enhanced degradation of organic contaminants. Generally, $HO^-$ and $SO_4^{2-}$ are commonly considered to be the oxidizing species in the oxidation processes involving PMS (Zhou et al., 2015). MeOH is known as an effective quenching reagent for $HO^-$ ($k_{HO} = 1.2 \times 10^9$ M$^{-1}$s$^{-1}$) and $SO_4^{2-}$ ($k_{SO} = 1.6 \times 10^8$ M$^{-1}$s$^{-1}$) (Yao et al., 2015a). In addition, tert-butanol (TBA) is mainly used as a quenching agent for $HO^-$ ($k_{HO} = 3.8 \times 7.6 \times 10^8$ M$^{-1}$s$^{-1}$), but not for $SO_4^{2-}$ ($k_{SO} = 4 \times 9.1 \times 10^5$ M$^{-1}$s$^{-1}$) (Yao et al., 2015a). For the convenience, experiments to identify reactive oxidizing species were conducted at the same condition.

As shown in Fig. 8a, about 95% Orange II was degraded in 120 min when no quenching agent was added. However, the removal of Orange II was obviously decreased at the different concentrations of TBA, suggesting an amount of $HO^-$ should be generated in the catalytic oxidation. MeOH significantly inhibited Orange II degradation (Fig. 8b) at lower concentrations (1M). Meanwhile, the use of higher concentrations of MeOH did not induce a difference, indicating MeOH failed to capture surface-adsorbed radicals completely (Wang et al., 2015b). It was possible that the hydrophilic MeOH was difficult to be extensively adsorbed on the Fe@C-BN surface, but the generated $SO_4^{2-}$ was bounded on the Fe@C-BN surface. Therefore, BQ was used instead of MeOH, because BQ can react with surface-bound free radicals. Indeed, the addition of BQ suppressed the oxidation of Orange II (Fig. 8c). Therefore, the surface-bound $SO_4^{2-}$ played a dominant role and only a minimal amount of free $SO_4^{2-}$ was generated in the catalytic oxidation process. Based on the above observations, we conclude that $HO^-$ and $SO_4^{2-}$ are the dominant radical species responsible for Orange II degradation, which agrees with recent findings in the literature (Ding et al., 2013; Khan et al., 2013; Zhang et al., 2013). In addition, we selected fulvic acid (FA) as the model natural organic matter (NOM) to evaluate the effect of NOM on Orange II degradation efficiency because 70% of NOM is composed of FA (Fig. 8d). The degradation of Orange II in the presence of 10 mg FA was 50.5% as compared to 95% without FA. An increase of the FA concentration further increases the degree of inhibition. At high concentrations, FA may be in competition with Orange II for $HO^-$ or $SO_4^{2-}$ radicals, thereby reducing the availability of oxidizing radicals (Yao et al., 2015a).

![Fig. 8. Effects of (a–c) different scavengers and (d) FA concentration on the degradation of Orange II by the Fe@C – BN$_{800}$/PMS process. Unless otherwise stated, the reaction conditions are: [Orange II] = 20 mg/L, [Fe@C – BN$_{800}$] = 20 mg/L, T = 25 °C, [PMS] = 0.10 g/L, without pH adjustment.]
3.3. Reaction mechanism

From the observations above and the previous work, the possible mechanisms for Orange II degradation by the Fe@C-BN/PMS system were analyzed and illustrated in Fig. 9. As previously reported, Fe⁰ was able to activate PMS to generate large amounts of SO₄²⁻ (Eq. (1)). The concentration of SO₄²⁻ produced by Fe⁰ is higher than that of Fe²⁺ per mole, thus Fe⁰ shows a higher activity than Fe ions and oxides (Sun et al., 2012). Fe²⁺ could also catalyze PMS decomposition to generate SO₄²⁻ and Fe³⁺ may react with PMS to produce SO₅⁰⁻ and Fe⁴⁺ (Eqs. (2) and (3)). It is known that, under all pH values, HO⁻ radical can be produced in the presence of SO₄²⁻ (Avetta et al., 2015). Additionally, CNTs have been proved to be excellent electron transfer supports in recent catalytic degradation studies, and can also activate PMS via non-radical mechanisms to produce reactive species (Duan et al., 2014). Previous studies also pointed out that SO₄²⁻ generally participates in electron transfer reaction during the degradation of environmental pollutants by AOPs (Feng et al., 2015; Sun et al., 2014). Previous studies also pointed out that SO₄²⁻ generally participates in electron transfer reaction during the degradation of environmental pollutants by AOPs (Feng et al., 2015; Sun et al., 2014). In this sense, the activation of PMS was markedly accomplished by Fe@C-BN catalysts, and therefore the degradation of Orange II was significantly accelerated.

It was interesting that Fe@C-BN with a unique structure can enhance the number of active sites. It was suggested that sp² carbon, zigzag edges, and electron rich containing oxides of carbon materials might work as the real active sites to activate PMS (Duan et al., 2015a, 2015b). The highly covalent π electrons could activate the O–O bond in PMS, and B, N dopants would further activate the adjacent carbons and dramatically enhance the catalytic performance (Duan et al., 2015c). Furthermore, some reports have stated that the difference in electronegativity between N/B and C in graphitic framework usually creates the charged sites on adjacent carbon framework to facilitate the oxygen reduction process (Guo et al., 2014b). On the other hand, Fe NPs interact with nitrogen, boron and oxygen to form intimate bonds (Fe–Nₓ, Fe–Bₓ, Fe–Oₓ), also contributing to the improvement of the catalytic performance by generating more efficient catalytic active sites. In fact, it was previously shown that Fe NPs embedded in CNTs could lower the local work function of the carbon surface due to the facile electron transfer from the iron to the carbon (Wang et al., 2015d). The donor–acceptor properties promoted by the B, N dopants and the embedded Fe NPs would improve the interfacial electron transfer. In addition, the carbon shell would also prevent the fast corrosion of iron as bare nano Fe⁰ did. Therefore, owing to the synergistic effects between iron NPs and B, N-doped carbon, Fe@C-BN catalyst intrinsically displays an excellent catalytic activity for Fenton-like reaction. These results are conformed with the recent studies on Fe NPs encapsulated inside B, N co-doped carbon toward Fenton-like oxygen reduction/hydrogen evolution reactions (Wang et al., 2015c; Zou et al., 2014).

\[
2\text{HSO}_5^- + \text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{OH}^- \\
\text{HSO}_5^- + \text{Fe}^{2+} \rightarrow \text{SO}_4^{2-} + \text{Fe}^{3+} + \text{OH}^- \\
\text{HSO}_5^- + \text{Fe}^{3+} \rightarrow \text{SO}_5^{2-} + \text{Fe}^{2+} + \text{H}^+ 
\]

Fig. 9. Possible reaction mechanism for organic dyes degradation by the Fe@C-BN/PMS system.

4. Conclusions

In summary, we demonstrated for the first time that magnetic iron cores encapsulated in B, N-co-doped carbon nanotubes hybrids constitute an active Fenton-like catalyst for oxidative degradation of organic pollutant. The catalytic material is easily obtained in a practical and scalable one-step method via pyrolysis of Fe(NO₃)₃·9H₂O, H₃BO₃ and C₆N₆H₁₂. The optimized materials were confirmed by XRD, TGA, FE-SEM, FE-TEM, HRTEM, EDS, and XPS techniques. Fe@C-BN catalyst was found to be efficient and environmentally benign for the heterogeneous activation of PMS. XPS analysis has demonstrated the B, N and Fe codoping in carbon framework in Fe@C-BN, which serve as main active catalytic sites for the effective oxygen reduction in the Fenton-like process. The study presented here not only shows a low-cost and promising Fenton-like catalyst for pollution control, but also might be extended to the preparation of other porous carbon materials for wide applications.
efficient oxygen reduction electrocatalysts derived from carbon dioxide. Chem. Commun. 50 (48), 6349–6352.