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An efficient approach for the photodegradation of organic pollutants by immobilized iron ions at neutral pHs†

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Supported Fe ions on ion-exchange resin can be used to efficiently photodegrade organic pollutants in water with H_2O_2 at neutral pHs; this catalyst also significantly depresses the side-reaction of H_2O_2 conversion to O_2.

The homogeneous (photo-)Fenton reaction has been used as an alternative method for the degradation of organic pollutants in water.[1] One crucial limitation in such an application is the necessity for acidic conditions ($pH < 3$) so as to avoid Fe ion precipitation.[2] Some covalent iron–organic compounds such as tetrasulfophthalocyanine (FePcS),[3] show high activity for oxidation of organic compounds by H_2O_2 or other oxidants at neutral pHs. These iron-complexes could be supported on the resin to obtain an immobilized catalyst.[4,5] However, these catalysts need the presence of co-solvent, such as acetonitrile in water, to sustain catalytic cycles but an organic solvent-containing system is not practicable for water treatment and when water is used as the sole solvent, the reaction rate becomes quite slow. Recently, we have found that in aqueous solutions of H_2O_2/FePcS the degradation of organic pollutants can be significantly accelerated by visible light irradiation regardless of the presence of acetonitrile.[6] Collins *et al*. reported an efficient catalyst, tetraamidomacrocylic iron (Fe-TAML),[7] which can degrade effectively 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) in aqueous H_2O_2. However, the organic ligand moiety of the iron-complex was found to decompose during the reaction, probably causing secondary contamination.[6,7]

Here we report a novel Fe-loaded heterogeneous catalyst prepared by direct exchange of Fe^{III} ions onto a strong acidic ion-exchange resin. This simple organic ligand-free catalyst can efficiently trigger the photooxidation reaction of organic pollutants in water by H_2O_2 at neutral pHs. We used a macroreticular poly vinylbenzene sulfonate resin (Amberlite IRA 200), a cheap and commercial ion-exchange resin. The sulfonate groups in the resin interacted strongly with Fe ions *via* electrostatic interaction.[8] X-Ray photoelectron spectroscopy (XPS) revealed that the loaded iron on the resin was present in mixed Fe^{II} and Fe^{III} ionic states before and after reactions (see ESI).† The surface atomic concentration of Fe was about 0.7%. No discernible Fe hydroxide clusters and/or Fe oxides were seen by scanning electron microscopy (SEM).

Several model pollutants, nonbiodegradable Malachite green (MG), benzyltrimethylammonium chloride (BTAC), and 2,4-dichlorophenol (DCP) were used to examine their degradation and mineralization in such a system at neutral pHs.† The Fe-loaded resin exhibited dramatic photocatalytic activity for oxidation of these nonbiodegradable organics by H_2O_2 at neutral pHs (Fig. 1A). Under similar conditions, however, the general (photo-)Fenton reaction (H_2O_2/Fe^{II} or Fe^{III}) gave only little activity for substrate degradation at $pH > 4$ due to precipitation of the Fe ions. It was noted that the resin itself had no obvious catalytic activity except for a little adsorption of the substrates. The degradation of substrates in the dark was negligible in the presence of H_2O_2 and catalyst. Clearly, UV irradiation accelerated significantly the degradation of organic substrates in this system.

More interesting was the behavior of H_2O_2 decomposition during the photoreaction (Fig. 1B). The decomposition of H_2O_2 was almost controlled by the degradation of substrates. The faster the substrate degradation, the faster the decay of H_2O_2. No H_2O_2 decomposition was observed either when the organic substrates were absent under UV irradiation in the presence of catalyst, or when the reaction was performed in the dark in the presence of both substrates and catalyst. This is significantly different from the general homogeneous (photo-)Fenton reaction, in which H_2O_2 suffers rapid decomposition regardless of the presence/absence of organic substrates.[1,2] This rigorous correlation suggests that the present system provides more economical H_2O_2 usage for the oxidation of organic pollutants at neutral pHs.

Furthermore, high TOC (total organic carbon) removal was obtained for these substrates (Table 1) and the catalyst could be recycled by simple filtration. After three recycles, almost the same conversion rate was obtained for MG degradation (0.2 mM MG per cycle, 2.5 mg catalyst per 50 ml), while less than 0.1% of the total anchored Fe ions was found dissolved in the

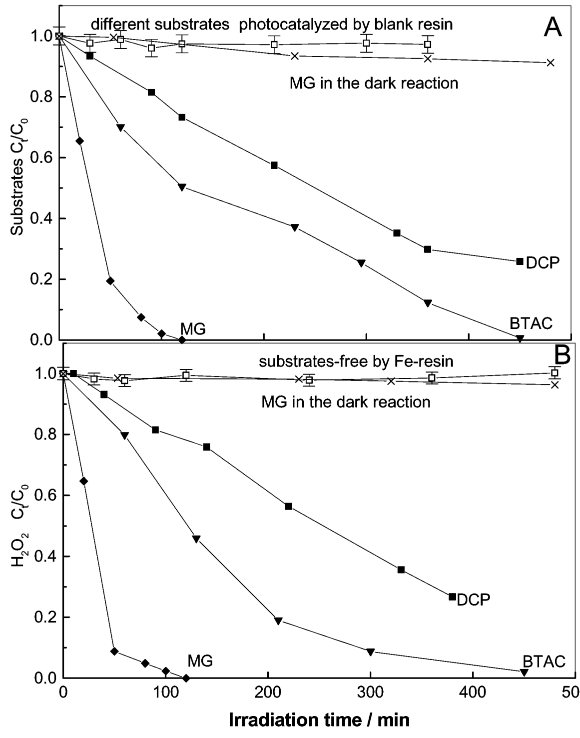

Fig. 1 Concentration changes of substrates (**A**) and H_2O_2 (**B**) as a function of irradiation time during the degradation. A typical sample consisted of 2.5 mg catalyst, 0.2 mM substrate and 1 mM H_2O_2 (total volume 50 ml), initial pH 6.0 ~ 7.0.

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† Electronic supplementary information (ESI) available: experimental details and XPS spectra of the Fe $2p_{3/2}$ region for the Fe^{III}-resin catalyst before and after degradation of MG. See http://www.rsc.org/suppdata/cc/b3/b304309f/

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solution, indicating that the catalyst was very stable during the photocatalytic processes.

To reveal the reaction mechanism, we used spin-trapping ESR to obtain information on the active radicals involved (Fig. 2). When Fe-free resin was employed as the catalyst, no ESR signals were observed, regardless of the organic substrates. For the loaded Fe catalyst, the characteristic quartet peaks of DMPO–$^{\cdot}$OH adducts appeared gradually upon UV light irradiation of the aqueous solution, while such signals were not observed in the dark (Fig. 2A). In homogeneous Fenton and/or photo-Fenton reactions, $^{\cdot}$OH and $^{\cdot}$OOH/$O_2^{\cdot -}$ radicals are both included (eqns. 1–4).[1,8]

$$Fe^{II} + H_2O_2 \rightarrow Fe^{III} + {}^{\cdot}OH + OH^{-} \quad k_1 = 58\ M^{-1}\ s^{-1} \tag{1}$$

$$Fe^{III} + H_2O_2 \rightarrow Fe^{II} + {}^{\cdot}OOH + H^{+} \quad k_2 = 0.02\ M^{-1}\ s^{-1} \tag{2}$$

$$Fe^{III} + {}^{\cdot}OOH \rightarrow Fe^{II} + O_2 + H^{+} \tag{3}$$

$$[Fe^{III}OH]^{2+} \xrightarrow{h\nu} Fe^{II} + {}^{\cdot}OH \tag{4}$$

The possible involvement of $^{\cdot}$OOH/$O_2^{\cdot -}$ radicals in the present system was then examined in methanol (Fig. 2B), since the $^{\cdot}$OOH/$O_2^{\cdot -}$ radicals in water are very unstable and undergo facile disproportionation rather than slow reaction with DMPO.[9] Unlike the case for general dark-Fenton and photo-Fenton reactions,[9d] however, the ESR signals of DMPO–$^{\cdot}$OOH/$O_2^{\cdot -}$ adducts were very weak in the present system. Because $^{\cdot}$OOH/$O_2^{\cdot -}$ radicals can undergo further conversion into O_2 (eqn. 3) that is useless to organic degradation,[1,8] little detection of superoxide radicals suggests that the present Fe-resin catalyst utilizes H_2O_2 more economically than the general homogeneous (photo-)Fenton system.

Based on the information above, we propose the following pathway for Fe cycling on the loaded states (eqns. 5–9), that is significantly different from that in the homogeneous Fenton reaction.

$$\text{loaded } Fe^{II} + H_2O_2 \xrightleftharpoons{h\nu \text{ or dark}} \text{loaded } Fe^{III}\text{ -OOH} + H^{+} \tag{5}$$

$$\text{loaded } Fe^{III}\text{-OOH} + \text{substrates} \xrightarrow{h\nu} \text{loaded } Fe^{III}OH + \text{degraded products} \tag{6}$$

$$\text{loaded } Fe^{III}OH \xrightarrow{h\nu} \text{loaded } Fe^{II} + {}^{\cdot}OH \tag{7}$$

Table 1 TOC changes in the photodegradation of several substrates (0.2 mM, 50 ml) in the presence of H_2O_2 (10 mM) and catalyst (2.5 mg)

Substrates	Initial pH	Irradiation time/h	TOC removal (%)
MG	6.2	4.0	50.6
		7.5	97.2
BTAC	6.8	2.0	59.8
		12.0	73.1
DCP	5.8	2.4	31.5
		9.0	47.0

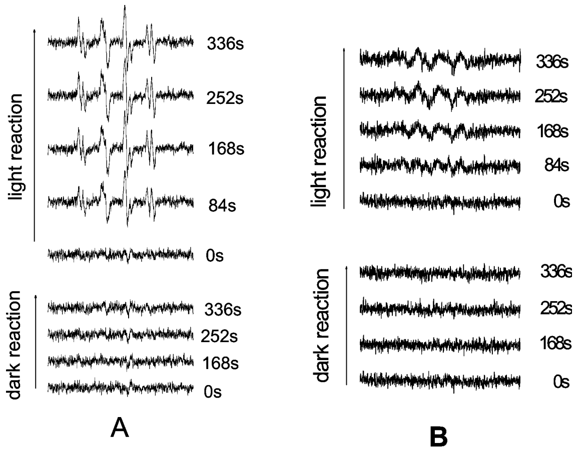

Fig. 2 DMPO spin-trapping ESR spectra recorded at ambient temperature in aqueous (for DMPO–$^{\cdot}$OH, **A**) and methanol solutions (for DMPO–$^{\cdot}$OOH/$O_2^{\cdot -}$) when the MG/H_2O_2/catalyst system was irradiated at 355 nm. *Conditions*: 2.5 mg catalyst, 0.4 mM MG, 1 mM H_2O_2, 1.6 mM DMPO, initial pH = 6.5.

First of all, the reduction of Fe^{III} species to Fe^{II} on the loaded state is mainly driven by UV light irradiation (eqn. 7), other than by H_2O_2 (eqn. 2) and/or by $^{\cdot}$OOH (eqn. 3). The formed Fe^{II} on the resin then reacts with H_2O_2 (eqn. 5), but this heterogeneous reaction will be not as fast as in a homogeneous solution (eqn. 1). It was noted that after the catalyst was treated with H_2O_2 at neutral pHs (ESI),† both Fe(II) and Fe(III) states were still present on the resin, while no Fe^{II} was detectable in homogeneous Fenton or photo-Fenton reactions with excess H_2O_2. There may be an equilibrium between Fe^{II} and Fe^{III}–OOH species on the catalyst surface. The formed Fe^{III}–OOH on the resin is then decomposed into loaded Fe^{III} species with the aid of both the organic substrate and UV light irradiation (eqn. 6). The mechanism involving similar Fe^{III}–OOH intermediate species has been well evidenced in the $Fe^{II}(TPA)(CH_3CN)_2$ [TPA = tris(2-pyridylmethyl)amine]/H_2O_2/substrate system.[10] On the other hand, the tendency for substrate degradation reflects different interactions with the catalyst. In fact, different adsorption capacities on the Fe-resin catalyst have been observed among three organic substrates studied, following the order MG $\gg$ BTAC > DCP. Detailed investigation into the adsorption effect and mechanism is in progress.

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Notes and references

1 (*a*) C. Walling, *Acc. Chem. Res.*, 1975, **8**, 125–131; (*b*) F. Chen, W. Ma, J. He and J. Zhao, *J. Phys. Chem. A*, 2002, **106**, 9485–9490; (*c*) F. Chen, J. He, J. Zhao and J. C. Yu, *New J. Chem.*, 2002, **26**, 336–341; (*d*) W. R. Haag and C. D. Yao, *Environ. Sci. Technol.*, 1992, **26**, 1005; (*e*) J. J. Pignatello, *Environ. Sci. Technol.*, 1992, **26**, 944.

2 (*a*) J. De Laat and H. Gallard, *Environ. Sci. Technol.*, 1999, **33**, 2726–2732; (*b*) Y. Sun and J. J. Pignatello, *Environ. Sci. Technol.*, 1993, **27**, 304–310; (*c*) K. Wu, Y. Xie, J. Zhao and H. Hidaka, *J. Mol. Catal. A: Chem.*, 1999, **144**, 77–84; (*d*) J. Ferrandez, J. Bandara, A. Lopez, Ph. Buffat and J. Kiwi, *Langmuir*, 1999, **15**, 185–192.

3 A. Sorokin, J.-L. Séris and B. Meunier, *Science*, 1995, **268**, 1163–1166.

4 A. Sorokin and B. Meunier, *J. Chem. Soc., Chem. Commun.*, 1994, 1799–1780.

5 R. F. Parton, I. F. J. Vankelecom, M. J. A. Casselman, C. P. Bezoukhanova and J. B. Uytterhoever, *Nature*, 1994, **370**, 541–544.

6 (*a*) X. Tao, W. Ma, T. Zhang and J. Zhao, *Angew. Chem.*, 2001, **113**, 3103–3105 (*Angew. Chem., Int. Ed.*, 2001, **40**, 3014–3016); (*b*) X. Tao, W. Ma, T. Zhang and J. Zhao, *Chem. Eur. J.*, 2002, **8**, 1321–1326; (*c*) X. Tao, W. Ma, J. Li, Y. Huang and J. Zhao, *Chem. Commun.*, 2003, 80–81.

7 (*a*) S. S. Gupta, M. Stadler, C. A. Noser, A. Ghosh, B. Steinhoff, D. Lenoir, C. P. Horwitz, K.-W. Schramm and T. J. Collins, *Science*, 2002, **296**, 326–328; (*b*) T. J. Collins, *Acc. Chem. Res.*, 2002, **35**, 782–790.

8 R. G. Zepp, B. C. Faust and J. Hoigne, *Environ. Sci. Technol.*, 1992, **26**, 313.

9 (*a*) D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.*, 1981, **14**, 393–400; (*b*) E. Finkelstein, G. M. Rosen and E. J. Rauckman, *J. Am. Chem. Soc.*, 1980, **102**, 4994–4999; (*c*) T. Wu, G. Liu, J. Zhao, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, 1999, **33**, 1379–1387; (*d*) F. Chen, Y. Xie, J. He and J. Zhao, *J. Photochem. Photobiol. A: Chem.*, 2001, **138**, 139–146.

10 (*a*) M. Costas, A. K. Tipton, K. Chen, D.-H. Jo and L. Que Jr., *J. Am. Chem. Soc.*, 2001, **123**, 6722–6723; (*b*) K. Chen and L. Que Jr., *Chem. Commun.*, 1999, 1375–1376; (*c*) C. Kim, K. Chen, J. Kim and L. Que Jr., *J. Am. Chem. Soc.*, 1997, **119**, 5964–5965.