Collagen fiber immobilized Fe(III): a novel catalyst for photo-assisted degradation of dyes

Rui Tang, Xue-Pin Liao, Xin Liu and Bi Shi*

Received (in Cambridge, UK) 30th August 2005, Accepted 26th September 2005
First published as an Advance Article on the web 20th October 2005
DOI: 10.1039/b512184a

A novel catalyst for the Fenton reaction was prepared by immobilizing Fe(III) onto collagen fiber and its high activity as a catalyst for degradation of dyes under irradiation of UVC was proved.

Wastewater containing organic pollutants, such as dyes, may bring about serious environmental problems if directly discharged into waters. Fenton reaction degradation is highly efficient and of low cost[1] for treatment of the wastewater. But the homogeneous catalysts employed are hard to recover and may lead to discharge of metal ions into the water which would cause other environmental problems.[1] To overcome these disadvantages, heterogeneous catalysts have been developed by immobilizing Fe(III) or other metal ions onto zeolite, laponite RD, resin, Nafion membrane, *etc*[1]. But, in general, the immobilization stability of the metal ions should be further improved by enhancing the association of metal ions with supporting matrices.

In this paper, a novel heterogeneous catalyst for the Fenton reaction, collagen fiber immobilized Fe(III)(CFIF), was prepared and its catalytic activity for degradation of organic pollutants was investigated. Collagen fiber, an abundant natural biomass, comes from the skins of domestic animals which are traditionally used as a raw material in leather making. On the basis of the principles of leather processing, collagen fiber which contains abundant functional groups, like -OH, -COOH and -NH_2, is capable of chemically reacting with many kinds of metal ions, such as Cr(III), Al(III), Zr(IV), Fe(III), *etc*., and it is confirmed that Fe(III) primarily reacts with -COOH in the formation of hydroxyl complexes.[2]

CFIF was prepared according to the reference method.[3] It was indicated by SEM that there was no precipitation on CFIF surface, implying that Fe(III) was chemically bonded with collagen fiber. The denaturing temperature of CFIF was increased to 84–86 °C compared with 60–65 °C for raw collagen fiber, determined by DSC (Netzsch 200PC). Thus, the particular advantage of this method is that the chemical and physical stability of the supporting matrices is remarkably improved whilst Fe(III) is immobilized. Orange II, a typical acidic dye, was used as the model pollutant for the catalytic degradation investigation. Our primary experiments indicated that the natural pH of Orange II solution was 6.2, and it decreased to 3.7 after the degradation reaction. Considering the fact that the complex of Fe(III) and -COOH of collagen is stable in the pH range of 3.2–7.0, all the degradation processes were undertaken at the natural pH value of Orange II solutions (pH = 6.2) to prevent leakage of Fe(III) during the whole degradation process. The tube reactor with air stirring was irradiated by an 8 W or 4 W low-pressure mercury vapor lamp with wavelength 254 nm (UVC) at room temperature. A UV–vis spectrophotometer (Shimadzu UV-2501PC) was used to monitor the concentration of Orange II during the degradation processes and ICP-AES (Perkin Elmer Optima 2100DV) was used to detect the leakage of Fe ions in solution. The total organic carbon (TOC) was measured by a TOC analyzer (Tekmar Dohrmann Apollo 9000).

Fig. 1 shows that no considerable degradation of Orange II took place when only irradiated by UVC (process 6). However, a fast degradation rate was observed in the presence of both H_2O_2 and UVC (processes 1 and 2), attributing to the generation of high activity oxidant ·OH from H_2O_2 induced by UVC.[4] In comparison with the situations above, the fastest degradation rate was achieved in the presence of H_2O_2, UVC and catalyst (processes 3 and 4). With the help of the catalyst, the degradation equilibria of Orange II were approached in only 20 min, as illustrated by processes 3, 4 and 5. Comparing processes 3, 4 and 5, it can be found that the catalyst has high catalytic activity whether or not the UVC is employed, but the extent of degradation is higher with the help of

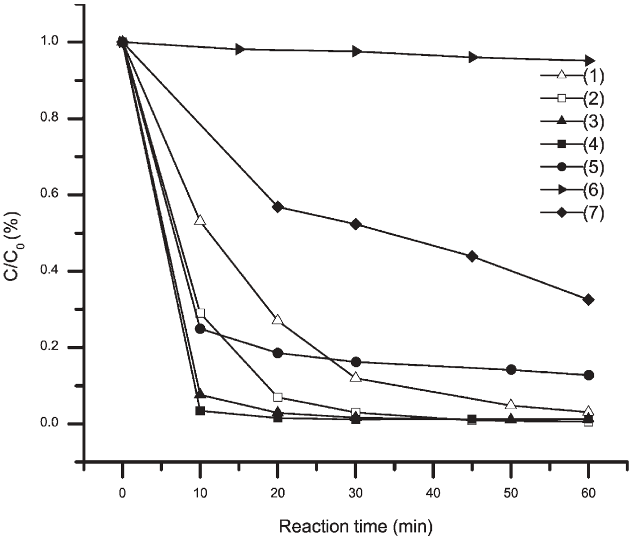

Fig. 1 Degradation of Orange II (initial conc. 0.2 mM, 400 mL, pH = 6.2) under different conditions: (1) H_2O_2 (5 mM) + UV (4 W); (2) H_2O_2 (5 mM) + UV (8 W); (3) H_2O_2 (5 mM) + UV (4 W) + catalyst (2 g); (4) H_2O_2 (5 mM) + UV (8 W) + catalyst (2 g); (5) H_2O_2 (5 mM) + catalyst (2 g); (6) UV (8 W) only; (7) reduce of dye due to adsorption on catalyst (2 g).

The Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu, P. R. China 610065.
E-mail: sibitannin@vip.163.com; Fax: +86 (0)28 8540 5237;
Tel: +86 (0)28 8540 5508

UVC. The decrease of irradiation intensity leads to a decrease of degradation rate when no catalyst is used (processes 1 and 2). However, the effect of irradiation intensity on the degradation rate is not significant in the presence of the catalyst (processes 3 and 4).

Process 7 in Fig. 1 shows that the catalyst itself has a high adsorption capacity for the dye. In fact, it could be observed in experiments that the catalyst was fully colored by Orange II when it was soaked in the dye solution. But it was decolorized on the degradation of Orange II under irradiation, indicating the recovery of the catalyst surface. Therefore, it is suggested that the catalytic degradation mechanism of Orange II could be that the dye molecules are first adsorbed by CFIF and then oxidized by ·OH radicals generated *in situ*. These deductions are consistent with the results in Fig. 1.

It seems that there is no obvious difference in the extent of degradation with or without catalyst, as presented by processes 2 and 4 in Fig. 1. However, the TOC residues of the two processes are around 93% and 50%, respectively, as shown in Fig. 2. This fact indicates that higher mineralization of Orange II can be attained by catalytic degradation.

Fig. 3a shows that the first degradation cycle removes 60% TOC, and the TOC removal ability of CFIF was a little reduced after recycling. Our experiments indicated that the TOC loss amounts to 45% after recycling ten times. This could be due to the fact that Fe ions leaked slightly during the degradation process, as shown in Fig. 3b. But the TOC loss can be returned to 60% by re-loading Fe(III) using 1–2% $Fe_2(SO_4)_3$ based on the weight of CFIF. Meanwhile, it was found that the leakage of Fe ion first increased and then decreased during catalytic degradation process, as shown in Fig. 3b. This phenomenon has been reported for other Fe(III) immobilized catalysts.[5] It has been proved that the conversion of Fe(III) and Fe(II) is involved in the reaction mechanism of Fe(III) and H_2O_2 under UVC,[4] that is, Fe(III) is first reduced to Fe(II) due to the electron transformation of coordination groups, such as OH^-, under irradiation, and then Fe(II) reacts with H_2O_2 to produce ·OH and Fe(III).[5] Therefore, it could be inferred that the conversion of Fe(III) and Fe(II) should exist in the process of catalytic degradation of Orange II in the presence of CFIF, and this may lead to some extent of leakage of Fe ion from CFIF. However, Fe ions in solution can be re-bonded by collagen fiber due to the conversion of Fe(II) into Fe(III) in the presence of H_2O_2. This deduction is based on the well-known conclusion that Fe(III) but not Fe(II) can easily combine with collagen fiber.[6] The conversion between Fe(II) and Fe(III) occurs very quickly, and most of the Fe(II) was changed into Fe(III) immediately before it could leak out. Therefore, the amount of Fe ion leaked out in total is very small and decreases at the end of the degradation process, as shown in Fig. 3b.

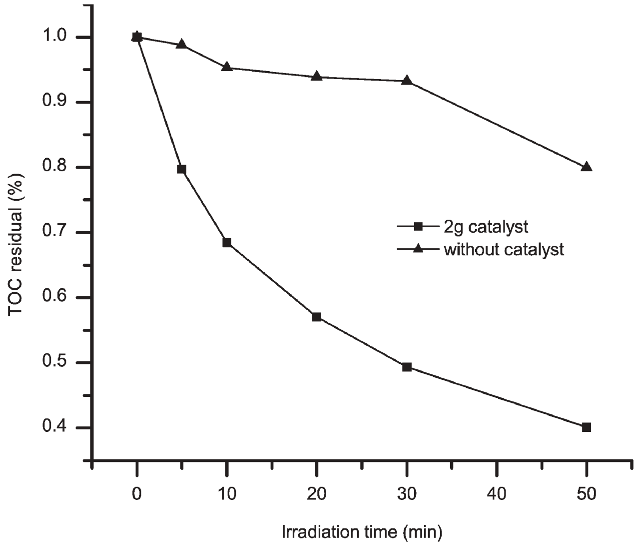

Fig. 2 TOC residue of Orange II in solutions (initial conc. 0.2 mM, 400 mL; H_2O_2 5 mM; UV 8 W, pH = 6.2).

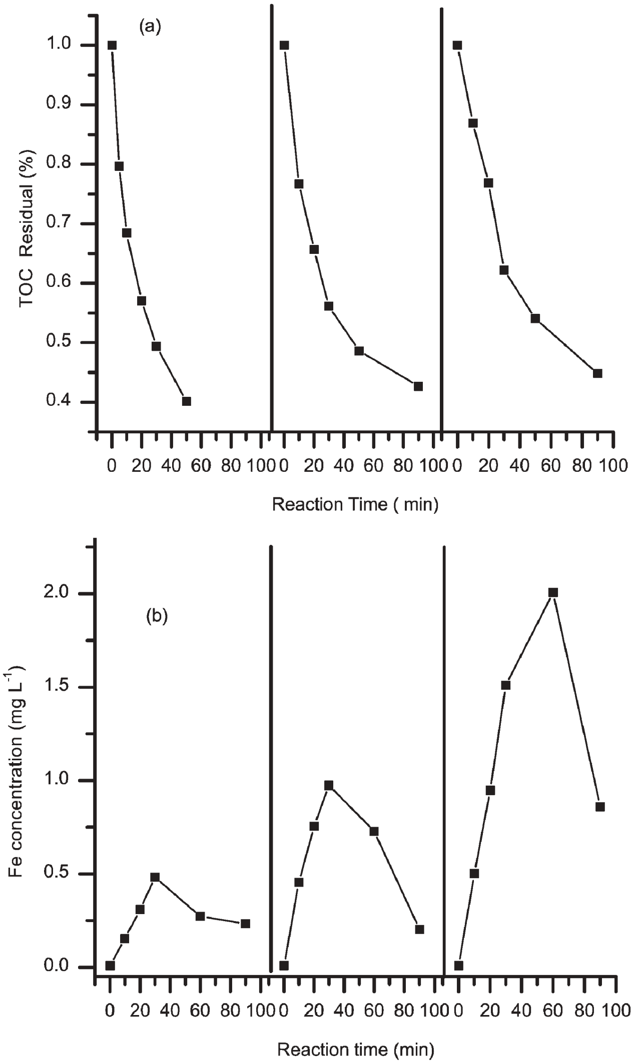

Fig. 3 Reuse of CFIF (0.2 mM Orange II solution, 400 mL; H_2O_2 5 mM; UV 8 W; catalyst 2 g; pH = 6.2): (a) TOC residue in three degradation processes; (b) Fe ion concentration in the solution in three degradation processes.

In conclusion, this novel catalyst belongs to the adsorption–degradation type so that both the degradation and TOC removal are fast. The catalyst has satisfactory chemical and physical stability, and the results of reuse experiments show the potential value of this heterogeneous catalyst in application. In addition, the catalytic ability of CFIF might be controlled by adjusting the amount of Fe(III) immobilized, and the catalytic activity can be fully recovered by reloading the Fe(III). Therefore, collagen fiber immobilized Fe(III) is an efficient and cost-effective heterogeneous catalyst for the photo-assisted Fenton reaction.

Furthermore, photo-assisted degradation of *p*-nitrophenol by CFIF was also investigated. Compared with Orange II, *p*-nitrophenol was little adsorbed by CFIF, but its degradation rate was only a little slower than that of Orange II. Thus, the degradation of *p*-nitrophenol in the presence of CFIF does not occur by the adsorption–degradation mechanism, and therefore, the multiple mechanisms presented by the catalyst should be further investigated.

This work was supported by the National Major Research Plan (pilot) of China (2004CCA06100), the National Natural Science Foundation of China (20476062) and the National Science Fund for Distinguished Young Scholars (20325619).

Notes and references

1 K. Fajerwerg and H. Debellefontaine, *Appl. Catal., B*, 1996, **10**, L229–L235; X. Tao, W. H. Ma, J. Li, Y. P. Huang, J. C. Zhao and J. C. Yu, *Chem. Commun.*, 2003, **1**, 80–81; J. Fernandez, J. Bandara, A. Lopez, P. Buffat and J. Kiwi, *Langmuir*, 1999, **15**, 185–192; C. Pulgarin, P. Peringer, P. Albers and J. Kiwi, *J. Mol. Catal. A: Chem.*, 1995, **95**, 61–74; A. C. Yip, F. L. Lam and X. J. Hu, *Chem. Commun.*, 2005, **25**, 3218–3220.

2 N. A. Evans, B. Milligan and K. C. Montgomery, *J. Am. Leather Chem. Assoc.*, 1987, **82**, 86–95; E. Heidemann, in *Fundamenals of Leather Manufacturing*, Eduard Roether KG, Darmstadt, 1993, ch. 13, pp. 301–302.

3 Collagen fiber (15.0 g) was soaked in 400 mL of distilled water at room temperature for 24 h. The pH of the distilled water was preadjusted to 1.7–2.0 by H_2SO_4. Then, 20.0 g of $Fe_2(SO_4)_3$ was added and the reaction proceeded at 30 °C with constant stirring for 4 h. The appropriate amount of $NaHCO_3$ solution (15% w/w) was gradually added within 2 h in order to increase the pH of the solution to 4.0–4.5 and then the reaction proceeded continuously at 40 °C for another 4 h. When the reaction was completed, the product was collected by filtering, washed with distilled water, and dried at 50 °C for 12 h, and then the catalyst of Fe(III) immobilized collagen fiber was obtained.

4 J. J. Plgnatello, D. Liu and P. Huston, *Environ. Sci. Technol.*, 1999, **33**, 1832–1839.

5 J. Y. Feng, X. J. Hu, P. L. Yue, H. Y. Zhu and G. Q. Lu, *Ind. Eng. Chem. Res.*, 2003, **42**, 2058–2066.

6 D. D. Jackson and T. P. Hou, *J. Am. Leather Chem. Assoc.*, 1921, **16**, 63; D. D. Jackson and T. P. Hou, *J. Am. Leather Chem. Assoc.*, 1921, **16**, 139; D. D. Jackson and T. P. Hou, *J. Am. Leather Chem. Assoc.*, 1921, **16**, 202; D. D. Jackson and T. P. Hou, *J. Am. Leather Chem. Assoc.*, 1921, **16**, 229.