

Heterogeneous oxidation of diclofenac in the presence of α -MnO₂ nanorods: influence of operating factors and mechanism

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ABSTRACT

Diclofenac (DCF), one of the pharmaceutical and personal care products that has been widely detected in water, was selected as a model pollutant to evaluate the oxidation activity of α -MnO₂ nanorods. The results showed that the heterogeneous oxidation process is highly pH dependent, with higher degradation efficiency at lower pH values. The complete removal of DCF was obtained within 80 min at the solution pH value of 2.5. The oxidation kinetics of DCF can be modeled by Langmuir–Hinshelwood equation ($R^2 > 0.999$). The effects of various operating parameters, including initial solution pH, α -MnO₂ dosage, anions, and cations, on the oxidation efficiency were investigated in detail. A possible reaction pathway for DCF was proposed. In addition, it was demonstrated that the α -MnO₂ nanorods can be recycled without decreasing their oxidation activity after 10 cycles.

Key words | diclofenac, heterogeneous oxidation, manganese dioxide, nanorods, pharmaceutical and personal care products

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INTRODUCTION

Diclofenac (DCF), commercially used as its sodium salt, DCF sodium, is one of the most important components of anti-inflammatory and antipyretic analgesic drugs. It is a typical example of non-steroidal anti-inflammatory drugs that have been widely used throughout the world to treat acute or chronic rheumatoid arthritis, osteoarthritis, trauma, and postoperative inflammatory pain. Recently, the presence of DCF has been reported in different aquatic systems in the range of ng/L to μ g/L due to its improper disposal or in industrial waste (Zhang *et al.* 2008). It is considered to be one of the most frequently detected pharmaceutical and personal care products (PPCPs) in water (Yu *et al.* 2013). Thus, it is of great importance to develop efficient technologies to remove or decompose DCF in water before it joins water distribution systems.

In the past decade, advanced oxidation processes such as photocatalysis, UV/H₂O₂, photo-Fenton, ozonation, and sonolysis (US) have been used for the removal of DCF. Pérez-Estrada *et al.* (2005) reported the photo-Fenton degradation of DCF, as well as the identified intermediates, and its tentative degradation pathway. Naddeo *et al.* (2009) investigated the efficiency of ozonation (O₃), US and their combined application (US + O₃) for the degradation and

potential mineralization of DCF in a water matrix. Madhavan *et al.* (2010) have investigated the sonolytic, photocatalytic, and sonophotocatalytic degradation of DCF using three photocatalysts (TiO₂, ZnO, and Fe-ZnO). Bagal and his co-workers (2013) used a novel combined approach of hydrodynamic cavitation and heterogeneous photocatalysis to investigate the degradation of DCF, and calculated the degradation efficiency by using a combined process of HC/UV/TiO₂/H₂O₂. Hu *et al.* (2011) synthesized the magnetic TiO₂/SiO₂/Fe₃O₄ (TSF) nanoparticles and used them in the photoelectrocatalytic degradation of DCF.

Manganese oxide used in oxidation has been proved to be an efficient chemical for the elimination of organic pollutants (Stone 1987; Bernard *et al.* 1997; Ge & Qu 2003; Dai *et al.* 2012). Manganese oxide is used mainly due to its abundance in nature, its relatively low cost in synthesis and environmental friendliness. Manganese oxide exists in many polymorphic forms (mainly as α -, β -, γ -, and δ -MnO₂) because of the different ways the basic unit [MnO₆] octahedral is linked together, thus exhibiting considerable activity in oxidation-reduction reactions. It has been reported that manganese oxides can oxidize a number of organic compounds. Stone *et al.* reported the oxidation of batches of

organic compounds such as hydroquinone (Stone & Morgan 1984), substituted phenols (Stone 1987), and chlorophenols (Ulrich & Stone 1989) by manganese (III/IV) oxides and proposed a possible oxidation mechanism early in the 1980s. Rudder *et al.* (2004) reported the removal of 17 α -ethynyles-tradiol (EE2) by manganese oxide. The results showed that 81.7% of EE2 can be removed by MnO₂, compared with 17.3% and 99.8% of removal by sand and granulated activated carbon, respectively. The MnO₂ removed significantly more EE2 than its adsorption capacity, which was mainly caused by its catalytic properties. However, little work has been carried out on the removal of PPCPs by oxidation processes using α -MnO₂ as the oxidant. Recently, our research group (Zhang *et al.* 2012) has used α -MnO₂ with different morphologies in the heterogeneous oxidation of naproxen in water. The experiment showed that MnO₂ could remove naproxen from water.

In this paper, α -MnO₂ nanorods were used for heterogeneous oxidation of DCF. The main purposes of this study are: (i) to obtain the reaction kinetics of the removal of DCF by α -MnO₂ nanorods; (ii) to optimize the oxidation parameters of the removal of DCF; and (iii) to check the mechanism of α -MnO₂-based heterogeneous oxidation.

EXPERIMENT AND ANALYSIS

Chemicals and reagents

All reagents were used without further purification. DCF sodium (C₁₄H₁₀Cl₂NNaO₂, >99.0%) was purchased from Sigma-Aldrich Corporation (St Louis, MO, USA). Potassium permanganate (KMnO₄, >99.5%) was purchased from Hangzhou Xiaoshan Chemical Reagent Factory (Hangzhou, China). Manganese sulfate monohydrate (MnSO₄·H₂O, >99.0%) was purchased from Shanghai Meixing Chemical Reagent Co. (Shanghai, China), Ltd. High-performance liquid chromatographic (HPLC) grade methanol (CH₃OH, >99.9%) and acetonitrile (CH₃CN, >99.9%) were purchased from Sigma-Aldrich Corporation (St Louis, MO, USA). Ultrapure water was obtained from Ultrapure Water System (arium 611VF, Sartorius Stedim Biotech GmbH, Göttingen, Germany).

Synthesis of α -MnO₂ nanostructures

The α -MnO₂ nanostructures were synthesized via a simple hydrothermal method (Wang & Li 2002). Briefly, aqueous solutions of 64.0 mL of MnSO₄ (0.125 mol/L) and 80.0 mL

of KMnO₄ (0.200 mol/L) were mixed together and stirred for 20 min at room temperature. Then, the mixed solution was transferred to Teflon-lined stainless steel autoclaves. The autoclaves were heated at 160 °C for 24 h and cooled to room temperature. The formed brown sediment was washed copiously with deionized water and ethanol several times. The sediment was then dried at 60 °C for 12 h.

Batch oxidation experiments

The oxidation of DCF was carried out in a thermostat-controlled room at 25 °C. All the experiments were conducted on 200 mL slurries in a conical flask with pH adjusted to 2.5. The concentration of DCF was 1.0×10^{-5} mol/L and the dosage of α -MnO₂ was 0.10 g/L. During the reaction, agitation was done with a magnetic stirrer. Experiments on the effects of pH were carried out with the pH of DCF aqueous solution adjusted to 2.5, 3.6, 5.1, 6.1, 7.7, and 10.2 by hydrochloric acid (HCl)/sodium hydroxide (NaOH). Experiments on the effects of α -MnO₂ concentration were carried out by varying the initial α -MnO₂ dosage of 0.05, 0.10, 0.20, 0.50, and 1.00 g/L. Additional inorganic ions (cation: Na⁺, Ca²⁺, Al³⁺, and Fe³⁺; anion: Cl⁻, NO₃⁻, CO₃²⁻, SO₄²⁻, and PO₄³⁻) with ion concentration kept at 1.0×10^{-5} mol/L were added to determine the effects of inorganic ions. The effects of DCF concentration on DCF removal were obtained by varying the initial concentrations of the DCF range from 1.0×10^{-6} to 2.0×10^{-5} mol/L with α -MnO₂ dosage of 0.10 g/L while keeping other reaction conditions unchanged. Approximately 10 mL suspensions were collected with a syringe each time and immediately filtrated through a 0.45 μ m filter membrane for the analysis of DCF concentration and dissolved manganese.

Analysis of DCF, TOC, Mn²⁺, and byproducts

The concentration of DCF was determined by high performance liquid chromatography (HPLC; Agilent 1200, Santa Clara, CA, USA) provided with a UV-visible light detector using a 4.6 \times 150 mm (5 μ m) XDB-C₁₈ column. The analysis was carried out with a 70/30 (v/v) acetonitrile/phosphoric acid solution (concentration of 0.50%) mobile phase and the flow rate was set at 1.0 mL/min. The injection volume was 20 μ L. The progress of the mineralization of DCF was monitored by measuring the total organic carbon (TOC) concentration via a TOC analyzer (TOC-V_{CPH}, Shimadzu, Kyoto, Japan). The concentration of the Mn²⁺ dissolved in the solution was determined by using a Thermo ICE3500 atomic absorption spectrometer (Thermo Electron Corp.,

Waltham, MA, USA). The reaction intermediate products were analyzed using an Agilent 6460 triple quad high performance liquid chromatography mass spectrometry (MS). The MS measurements were carried out in positive ion mode with MS source settings as follows: gas temperature at 325 °C, gas flow 5 L/min, nebulizer 45 psi, sheath gas temperature at 350 °C, sheath gas flow 11 L/min, capillary voltage at 3,500 V(-), nozzle voltage at 500 V(-), and fragmentor at 135 V. The analysis was carried out with a 55/45 (v/v) acetonitrile/water mobile phase in which the flow rate was set at 1.0 mL/min.

RESULTS AND DISCUSSION

The oxidation of DCF

Effects of the solution pH and inorganic ions

The oxidation of DCF in the presence of α -MnO₂ nanorods at different solution pH values is shown in Figure 1(a). As can be seen, the oxidation process of the DCF with α -MnO₂ nanorods is highly dependent on pH, with the oxidation efficiency decreasing considerably as the pH value increases. It takes under 2 h (in fact, 80 min) for the complete removal of

DCF at pH = 2.5, while it takes about 4 h when pH is adjusted to 3.6. The removal efficiency is slightly higher than that of the one reported, which indicates a maximum DCF degradation rate of 95% by UV/TiO₂/H₂O₂ process under optimized operating conditions at a reaction time of 2 h (Bagal & Gogate 2013). The oxidation efficiency decreases considerably when the solution is adjusted to pH \geq 5.1. A mechanism for the reaction of organic compounds with manganese (III/IV) oxide surfaces has been presented by Stone (Stone 1987; Ulrich & Stone 1989), which describes involving the specific adsorption of an organic compound onto the particle surface to first form a surface precursor complex, followed by electron transfer and byproduct release.

The α -MnO₂ nanorods have a zero potential point of pH 3.15, which was reported in our previous work (Zhang *et al.* 2012). The surface of α -MnO₂ nanorods is positively charged when the solution pH is adjusted to 2.5; the DCF can therefore be easily adsorbed onto the surface of α -MnO₂ nanorods. In addition, carboxylic acids are more easily adsorbed at low pH values, especially when the value is lower than the acid dissociation constant (pKa) of the corresponding acids, in which they are present in undissociated forms (Yang *et al.* 1991; Alkaya *et al.* 2009). As for the DCF (pKa = 4.0), the undissociated form can be adsorbed onto the surface of α -MnO₂ nanorods more easily when the pH value is below 4. At pH

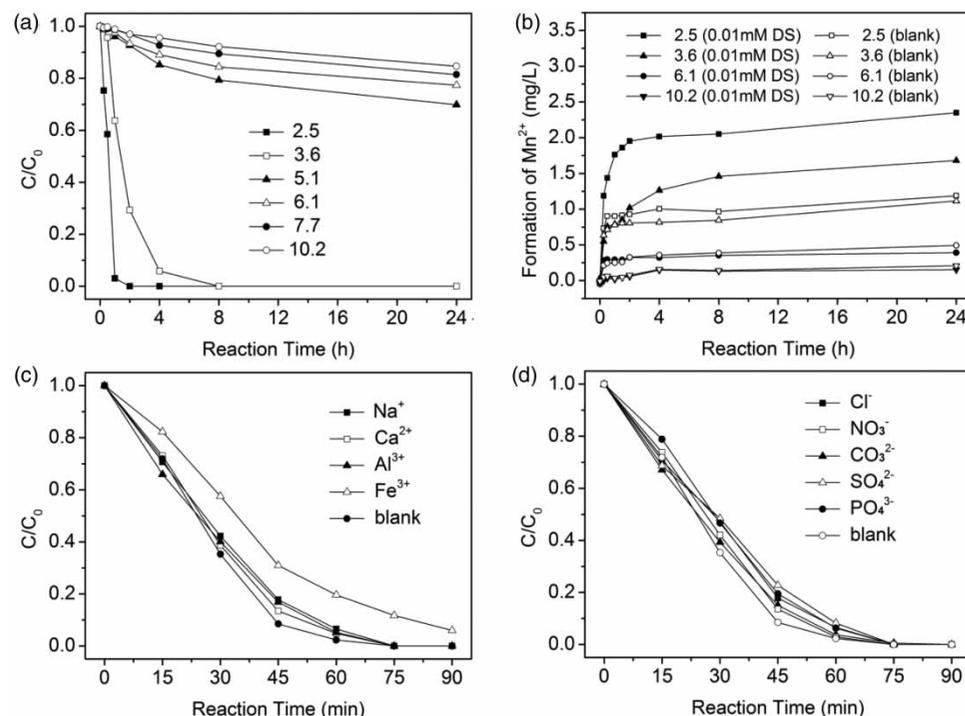


Figure 1 | (a) Effects of pH, (b) pH on the formation of Mn²⁺, (c) effect of cations, and (d) effect of anions on DCF removal in the presence of α -MnO₂ nanorods at [diclofenac]₀ = 1.0 × 10⁻⁵ mol/L, [α -MnO₂]₀ = 0.10 g/L and pH = 2.5.

≥ 6.1 , the removal efficiency of DCF is negligible due to the electrostatic repulsion between the dissociated form of DCF and the deprotonation of α -MnO₂.

Coupled with the oxidation of DCF, Mn²⁺ was generated by reduction of α -MnO₂ nanorods, and Mn²⁺ dissolved in the reaction solution was monitored, as shown in Figure 1(b). The appearance of Mn²⁺ can be observed from the early stage of the oxidation process in both solutions with or without DCF. The concentration of Mn²⁺ in the oxidation process with DCF is higher than that in the experiment without DCF. Moreover, the increased concentration of Mn²⁺ in the oxidation process increased as the solution pH decreased.

It has been reported that some of the anions and cations can be adsorbed onto the surface of the manganese oxides to occupy the active surface sites, thereby slowing reaction rates (Zhang & Huang 2005; Chen et al. 2011). A batch of experiments was carried out with different cations and anions in the aqueous solution in order to find out their effects on the DCF removal. The results are shown in Figure 1(c) and 1(d). It can be observed from Figure 1(c) and 1(d) that anions (SO₄²⁻ and PO₄³⁻) could decrease the reaction rate mainly due to their competition with DCF for the occupation of the active surface sites of α -MnO₂ nanorods. We found that the presence of Fe³⁺ cation could decrease the reaction efficiency, which was mainly caused by its formation of Fe-based metal complexes and, in turn, occupy the active surface sites of α -MnO₂ nanorods, thus leading to the decrease of reaction efficiency.

Oxidation kinetics

A series of experiments was carried out by varying the concentrations of α -MnO₂ and DCF in the reaction systems in order to find out their effects on the oxidation kinetics of DCF removal. The results are shown in Figure 2. We can see from Figure 2(a) that the oxidation efficiency increased with the increasing dose of α -MnO₂ nanorods; however, the oxidation efficiency decreased with the increasing initial concentration of DCF.

The oxidation kinetics for the removal of DCF by α -MnO₂ nanorods is modeled by Langmuir–Hinshelwood (L–H) models, as follows:

$$v_0 = \frac{kKC_0}{1 + KC_0}$$

where v_0 is the initial reaction rate (mmol/(L h)) and is calculated as $v_0 = (dC/dt)_{t=0}$, k is the reaction kinetic constant

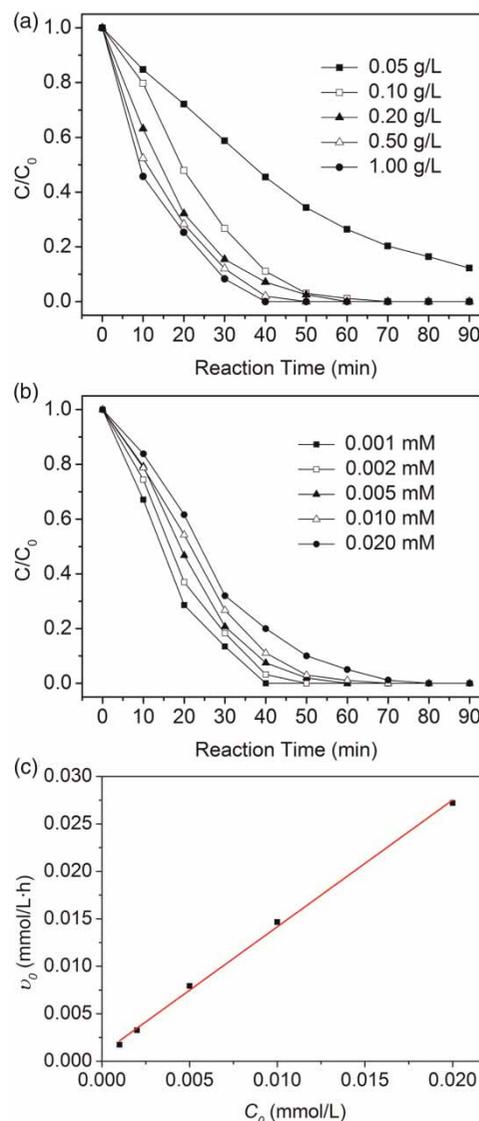


Figure 2 | Different concentrations of (a) α -MnO₂ and (b) DCF on DCF removal at pH = 2.5, and (c) oxidation kinetics of DCF modeled by L–H equation.

(mmol/(L h)), K is the Langmuir adsorption constant (L/mmol), and C_0 is the initial concentration of DCF (mmol/L). Figure 2(c) shows the experimental points obtained from the L–H equation for the α -MnO₂ nanorods. The reaction kinetic constants (k) and the Langmuir adsorption constant (K) for the α -MnO₂ nanorods are calculated as $k = 0.0823$ and $K = 21.318$ with a correlation coefficient (R^2) of 0.99924.

TOC removal and oxidation byproducts

The TOC of DCF at $[DCF]_0 = 2.0 \times 10^{-5}$ mol/L was monitored to obtain the mineralization of the DCF. The results

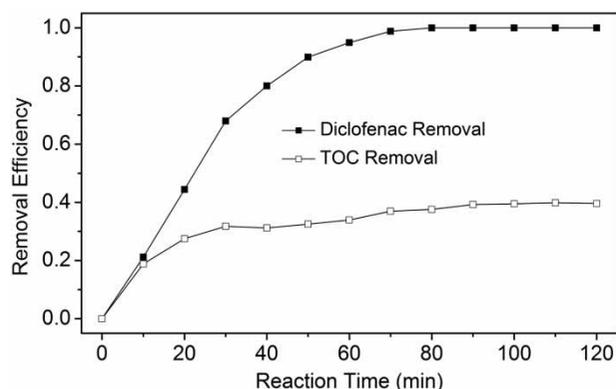


Figure 3 | TOC and DCF removal in the presence of α -MnO₂ nanorods at [DCF]₀ = 2.0 × 10⁻⁵ mol/L, [α -MnO₂]₀ = 0.10 g/L, and pH = 2.5.

are shown in Figure 3, from which it can be seen that after 80 min of α -MnO₂ treatment, DCF is completely removed while the TOC removal efficiency reached only about 40%. The difference between the degradation efficiency and TOC removal indicates the formation of intermediates during the oxidation process. To further identify these intermediates, the water samples collected at the reaction time of 30 and 60 min were separated and identified by liquid chromatography–mass spectrometry using an electrospray ionization source in positive ion mode.

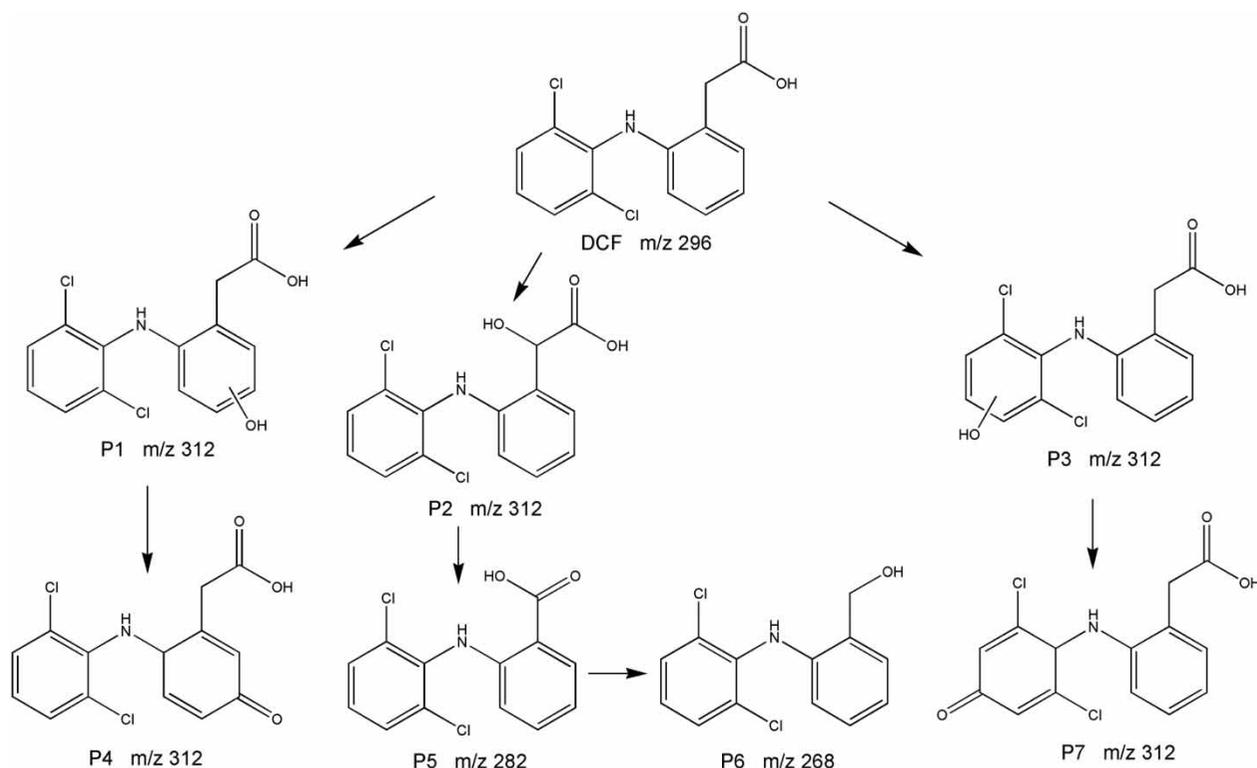


Figure 4 | Tentative degradation pathway of DCF.

The parent compound of DCF and seven by-products were tentatively identified by mass spectrometry in positive mode (as shown in Figure S1, Supplementary Material, available online at <http://www.iwaponline.com/wst/071/068.pdf>). A possible reaction pathway of intermediate products is proposed in Figure 4. In the proposed pathway, three compounds at m/z 312 were observed, corresponding to the addition of 16 mass units to the parent peak. This provided the possibility that hydroxylation may occur on both the benzene rings and the lateral chain, which leads to the formation of P1, P3, and P2, respectively. The further formation of P4 and P7 with m/z 312 was the result of the loss of water molecules from the by-products P1 and P3, respectively. The further oxidation of P2 could lead to the formation of P5. There is also a tentative way to form P6 as the carboxylic group transformed into a hydroxyl group from P5.

Recycling experiments

One-dimensional nanostructure has an advantage over powder catalysts for separating catalysts from solution by filtration or sedimentation (Yu *et al.* 2006). We recycled the α -MnO₂ nanorods from suspension by static sedimentation. The α -MnO₂ nanorods used in the

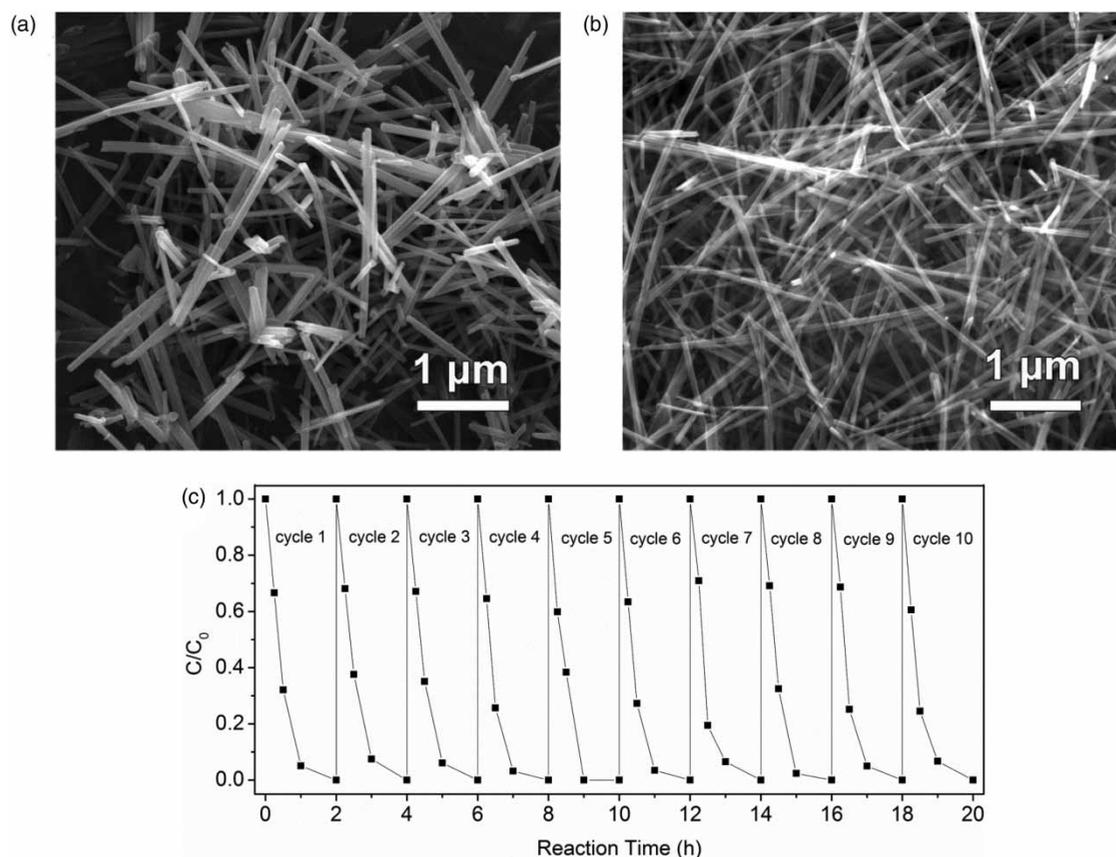


Figure 5 | SEM images of (a) as-prepared α -MnO₂ nanorods; (b) α -MnO₂ nanorods after 10 cycles of oxidation; and (c) 10 cycles of the oxidation of DCF in the presence of α -MnO₂ nanorods at [DCF]₀ = 1.0 × 10⁻⁵ mol/L, [α -MnO₂]₀ = 0.10 g/L and pH = 2.5.

experiment cycles can be easily separated from the aqueous suspension in less than 30 min by sedimentation. The stability of the as-prepared α -MnO₂ nanorods was tested by monitoring the oxidation activity during cycles of use. In our previous study, about 5.43%, 2.89%, and 0.92% of total MnO₂ dosage were dissolved in the blank experiments when using α -MnO₂ nanoparticles, flower-like nanostructures, and nanorods as the oxidants, respectively (Zhang *et al.* 2012). It means the nanorods' structure is relatively more stable than that of nanoparticles and flower-like structures. Moreover, the morphologies of the α -MnO₂ nanorods after 10 cycles had hardly changed, as can be seen in Figure 5(a) and 5(b), also indicating that the stability of the α -MnO₂ nanorods is good. This further proves that the oxidation reaction happened only on the surface of the α -MnO₂ nanorods, which keeps the morphologies of α -MnO₂ unchanged. Also shown in Figure 5(c), we find that the α -MnO₂ nanorods do not exhibit significant loss of oxidation activity even after 10 experiment cycles.

CONCLUSIONS

In summary, α -MnO₂ nanorods were employed to oxidize DCF in water. The oxidation kinetics of DCF by α -MnO₂ nanostructures can be fitted to the L-H model. The oxidation process is highly pH-dependent, with higher degradation efficiency at lower pH values. The addition of inorganic ions SO₄²⁻, PO₄³⁻, and Fe³⁺ could decrease the reaction efficiency. The incomplete mineralization of DCF indicated the formation of intermediates in the reaction system, and a possible reaction pathway of DCF was proposed. In addition, it has been demonstrated that the α -MnO₂ nanorods can be recycled without decreasing their oxidation activity after 10 cycles.

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