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TOC removal from laundry wastewater by photoelectrochemical process on Fe_2O_3 nanostructure

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ABSTRACT

Organic compounds in laundry wastewater were degraded by photoelectrochemical (PEC) and electrochemical (EC) processes on a mesoporous α-Fe_2O_3 nanostructured film. The applied voltage was between 1 and 3 V. The PEC process exhibited higher TOC removal rate than EC process for all testing conditions. The synthesized α-Fe_2O_3 electrodes remained stable over 3 h of operating time. Moreover, lumped kinetics was applied to model the TOC removal. The experimental data were successfully described by a binary model, which consists of both complete and partial oxidation. It was found that the applied voltage influenced the kinetics constants. The results can be applied to improve the current application of laundry water recycling at domestic level.

Keywords: Laundry wastewater; α-Fe_2O_3; Photoelectrochemical process; TOC removal

1. Introduction

The demand for water has significantly increased due to population growth and economic development. Since the freshwater resource is limited, reusing and recycling wastewater have been considered to be an effective and sustainable solution. In addition, to centralized wastewater plants, treatment at household level has also been promoted. Such treatment will reduce the required capacity of the centralized wastewater plants and also reduce well the overall water usage [1]. A simple recycling process, in which the recycled water is used for household application such as toilet flushing and garden irrigation [2], significantly reduces municipal water demand [3]. The domestic treatment has fundamentally different requirement from the wastewater treatment plants: (i) it does not need to be run continuously (ii) it only needs a simple maintenance, and (iii) it requires automatic and routine operation. Laundry wastewater, in particular, can be readily recycled at households to water lawns and ornamental gardens [4], which accounts as much as 30% of household potable water consumption in the developed world.

At the moment, few domestic laundry wastewater treatment units are running in Australia. Most of these units rely on physical filtration and removal of suspended particles only. As a result, the discharge effluent contains large quantities of dissolved organics which has to be removed. This wastewater contains soluble surfactant, such as linear alkyl benzene sulfonates, alkyl sulfate, alkyl ether sulfate, and alkyl ethoxylates [5]. Most of these can be classified as anionic or nonionic surfactants [6], which cannot be removed by

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physical filtration. Due to their strong surface activities, these compounds can be harmful to soil ecology. Furthermore, they are not easy to be digestible and can be accumulated in the environment [7]. Consequently, developing a complementary method for removing dissolved TOC will significantly improve the feasibility of laundry water treatment plant at household level.

The conventional techniques for TOC removal from wastewater include filtration, adsorption, chemical, electrochemical (EC) oxidation, and various biological methods. Among these, filtration and adsorption [8] are simple to operate, which can be used with renewable materials [9]. However, these physical processes cannot remove dissolved contaminants or small particles [10]. While biological digestions are well developed for wastewater plants, the method is not practical at domestic level. Chemical oxidation tends to be expensive and requires complicated operation/maintenance [11,12]. Hence, we focus on EC techniques. In particular, this study also focuses on developing the application of the photoelectrochemical (PEC) processes. Here, organics are degraded by hydroxyl free radicals generated from the electron–hole pairs of photocatalyst [13]. Among the photocatalysts, iron oxides are the most affordable and has been investigated intensively [14]. The electrical current for a typical PEC process is very low and can be easily obtained by commercially available solar panels.

This study reported the potential of the PEC process, which is based on highly porous α-Fe_2O_3 nanostructured films for laundry wastewater treatment. The method is combined with the filtration process, which removes larger particles. Moreover, the kinetics model was also applied to describe the characteristics of degradation process. Ultimately, we aim to develop a simple and an effective method for the removal of dissolved TOC from laundry wastewater.

2. Mechanism of TOC removal by PEC

The decomposition of organic compounds on the metal oxide anode via EC process can be illustrated by the formation of adsorbed hydroxyl radicals (Eq. (1)) or adsorbed oxygen (Eq. (2)) or both [15]:

$$MO_x + H_2O \xrightarrow{\text{bias}} MO_x(^{\bullet}OH) + H^+ + e^- \tag{1}$$

$$MO_x(^{\bullet}OH) \rightarrow MO_{x+1} + H^+ + e^- \tag{2}$$

At the cathode, the counter reaction is:

$$2H_2O \xrightarrow{\text{bias}} H_2 \uparrow + 2OH^- \tag{3}$$

By applying a potential to photoanode, both anode reactions occur in the PEC process. Under illumination, photoenergy further generates holes and electrons on the photoanode as the following equations:

$$MO_x \xrightarrow{hv} \left(MO_x e^-_{cb}\right)_{anode} + \left(MO_x h^+_{cb}\right)_{anode} \tag{4}$$

$$\left(MO_x h^+_{cb}\right)_{anode} + H_2O \rightarrow MO_x(^{\bullet}OH) + H^+ \tag{5}$$

The electrons on photoanode are withdrawn by the applying bias potential and transfer through external circuit to the cathode. It should be also noted that electron and holes can be recombined within photoanode:

$$\left(MO_x e^-_{cb}\right)_{anode} + \left(MO_x h^+_{cb}\right)_{anode} \rightarrow MO_x + \text{heat} \tag{6}$$

At high applied bias, the movement of electrons to cathode is very fast and thus the electron–hole recombination is hindered. Overall, with the presence of photoenergy, the PEC will generate more MO_{x+1} and MO_x ($^{\bullet}OH$) than the EC process.

The produced hydroxyl radicals can oxidize the organic compounds adsorbed on anode. The laundry wastewater contains a wide range of dissolved organics, with complex oxidation steps. Consequently, lumped kinetics is required [16]. Generally, the organics can be oxidized completely or partially as the following:

$$MO_x(^{\bullet}OH) + P \xrightarrow{k_1} CO_2 + H_2O + MO_x \tag{7}$$

$$MO_x(^{\bullet}OH) + P \xrightarrow{k_2} Q + MO_x + CO_2 + H_2O \tag{8}$$

where P is the original organics, Q is product of the partial oxidation.

It can be assumed that Q comprises the organic compounds that are not adsorbed into the anode and, hence, cannot be oxidized by PEC process. The TOC of solution equals to the sum of P and Q. Hence, the initial and the dynamic TOC concentration (mg/l) at time (t) are given as $C_{TOC}(0) = C_P(0)$ and $C_{TOC}(t) = C_P(t) + C_Q(t)$.

During the PEC and EC processes, the produced rate of free radicals is assumed to be constant. Assuming both oxidizing reactions are first-order kinetic, the rate of equations of lumped kinetics can be written as [17]:

$$\frac{dC_P}{dt} = -(k_1 C_P + k_2 C_P) \tag{9}$$

$$\frac{dC_Q}{dt} = k_2 C_P \tag{10}$$

Integrating the above system yields:

$$\frac{C_{\mathrm{TOC}}(t)}{C_{\mathrm{TOC}}(0)} = \left\{\frac{k_2}{k_1+k_2} + \frac{k_1}{k_1+k_2}\exp[-(k_1+k_2)t]\right\} \tag{11}$$

It should be noted that the above differentiate equation is the simplest form of the lumped kinetics. More complicated forms, involving three or more different steps, have also been developed in the literature [16]. Nevertheless, the binary system has been successfully verified for the TOC degradation of an industrial bleaching effluent [17]. The above equation, Eq. (11), will be used to model the TOC removal in this study.

3. Experiment

3.1 Materials

All chemicals used for this study were obtained from Sigma Aldrich (Table 1). Stainless steel (SS) substrates were purchased from Haynes Educational (Australia).

3.2. Synthesis of α-Fe_2O_3 electrode

Sol-gel spin coating method was used to deposit α-Fe_2O_3 thin films onto stainless steel substrates [18]. The SS substrates with dimension of 25 mm × 75 mm × 2 mm (width/length/thickness) have been subsequently rinsed in ultrasonic bath with deionized water, ethanol before being dried by nitrogen for 10 min. TMAB (0.5 g) was mixed with 5 ml deionized water. The solution was stirred for 30 min, before adding 4 g Iron (III) nitrate, and then stirring for 2 h. The sample deposition was as the following steps: (i) drop prepared solution onto SS substrate that tightly held on the chuck of spin coater, (ii) two fixed speeds (200 rpm, 300 rpm) used to spin the substrate for 1 min in total, and (iii) the samples were heated on a ceramic plate at 80℃ for 15 min before placing into the furnace at 450 ± 1℃, for 2 h, in air, with fixed heating and cooling rate of ~4℃/min.

Table 1
List of the chemicals used in the study

Name	Formula	Grade (%)
Iron (III) nitrate	$Fe(NO_3)_3{\cdot}9H_2O$	99.9
Tetramethylammonium bromide (TMAB)	$C_4H_{12}BrN$	99
Ethanol	C_2H_5OH	99.9

3.3. Anode characterization

The morphology of electrodes before and after treating was obtained using Field emission scanning electron microscopy (FESEM, Tescan Mira3). Additionally, the α-Fe_2O_3 were also characterized by X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα radiation ($\lambda = 0.15418$ nm) and for qualitative analysis, XRD diagrams were recorded in the interval $20^\circ \le 2\theta \le 60^\circ$ at scan rate of $0.01^\circ\,s^{-1}$. The characterization results provided insights into the structures of the samples and verified the oxidation process on anode.

3.4. TOC removal

The synthetic laundry was prepared by dissolving 5 g of detergent powder in 500 ml water. This study used a commercial detergent FAB™ (Unilever, Australia). The solution was magnetically stirred for 2 h before leaving for two more hours in room temperature. It was then transferred to a vacuum membrane filtration system with polycarbonate membrane filter with pore size of 0.1 μm (SterliTech Corporation, USA). This filtration step represents the physical removal, which is often applied in the commercially available units. Subsequently, the solution was used in the PEC glass reactor (114 ml in volume). The reactor was covered by quartz and placed under a solar simulator. The α-Fe_2O_3 anodes had apparent surface area of 18.75 cm^2. The reference electrode was Ag/AgCl immersed in KCl 3 M, while Pt rod was also used as the cathode. The electrical circuit was completed using Cu-wire connected to the DC power supply (Fig. 1).

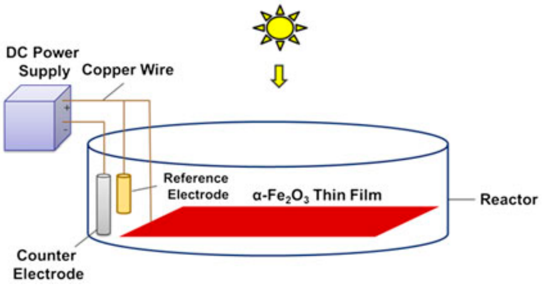

Fig. 1. PEC setup.

For PEC processes, all nonsemiconductor parts, i.e. the substrate, wire were covered by nonconductive plastic film to prevent exposure of the solution to these components. The system was illuminated under 500 W Xenon lamp (100 $mWcm^{-2}$, 25°C) solar simulator (Abet Technologies, Model 11016A Sun 3000).

To evaluate TOC removal efficiency as a result of an applied electric field, this study applied different combinations: (i) EC and (ii) PEC process. The reference electrode was used to maintain a constant voltage, and thus ensure all experiments were consistent. Three different combinations of power were employed: 1; 2; and 3 V. The forward bias values to the working electrode were generated by a DC power supply (QJ3003XC DC Regulated Power Supply 30 V-3A LCD, Australia). Treated solution samples (1 ml) were periodically transferred from this reactor to test tubes after every 15 min. Afterward, the samples were analyzed by the TOC analyzer (TOC-VWS/TOC-VWP, Shimadzu, Japan) using wet oxidation method [19].

4. Results and discussion

4.1. Anode characterization

The morphology of α-Fe_2O_3 anode was examined. As shown in Fig. 2, the deposited film consists of α-Fe_2O_3 nano-tuft structure. This film presented a highly porous structure illustrated to have the larger absorption capacity than that of particle films [20].

Crystalline properties and the phase formation of α-Fe_2O_3 film were verified by X-ray diffraction analysis (Fig. 2). The α-Fe_2O_3 peaks were observed at 28.09°, 38.65°, 42.44°, 47.86°, 58.08°, 64.72°, 67.65°, 74.84°, and 76.85°. Thus, it can be concluded that a complete of hematite phase was formed by annealing process. A similar prevalence of the peaks has also been observed for α-Fe_2O_3 film previously [18].

4.2. Overall TOC removal

TOC removal analysis was performed by analyzer wet oxidation method. The TOC removal efficiency was defined as the following equation:

$$\mathrm{TOC}(\%) = \frac{C_{\mathrm{TOC}}(0) - C_{\mathrm{TOC}}(t)}{C_{\mathrm{TOC}}(0)} \times 100 \tag{12}$$

where $C_{\mathrm{TOC}}(0)$ and $C_{\mathrm{TOC}}(t)$ are the initial and transient TOC concentration (mg/l) respectively.

Besides, the comparative oxidation power of PEC system can also be explained from its mineralization current efficiency (MCE) [21]:

$$\mathrm{MCE} = \frac{C_{\mathrm{TOC}}(0) - C_{\mathrm{TOC}}(t)}{8I\,\Delta t} \times FV \tag{13}$$

where F is the Faraday constant (96.487 Ceq^{-1}), I is the current applied (A), and V is the volume of solution (L).

For the EC system, increasing the applied bias increased the TOC removal (Table 2). At 1 V the total degradation rate was 68% at 180 min, and MCE was 4.98. By comparing to higher power (2 V), a much considerable improvement in the degradation of organics was observed (73.1% at 180 min, MCE = 5.36). Likewise, when a further higher current (3 V) was applied, a larger TOC removal efficiency via α-Fe_2O_3 was

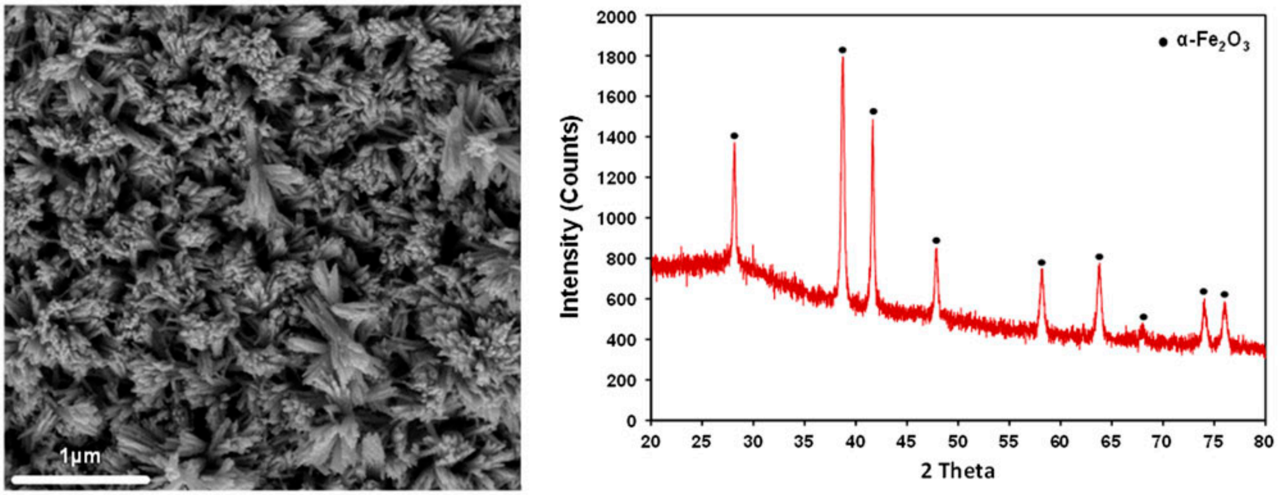

Fig. 2. SEM image and X-ray diffraction of nano-structured α-Fe_2O_3.

Table 2
TOC removal by α-Fe_2O_3 under various conditions

DC bias (V)	Solar Simulator	Total degradation rate, %	MCE at 180 min
1	On	68.78	5.05
1	Off	68	4.98
2	On	74.68	5.48
2	Off	73.1	5.36
3	On	77.47	5.68
3	Off	74.7	5.48

obtained via the PEC reaction (74.7% at 180 min, MCE = 5.48). This gradually increasing trend was repeated in EC processes under the same bias values used. A good agreement between these results and reported values in the literature for pentachlorophenol [22]. Overall, the PEC process had higher removal efficiency than the EC method.

4.3. Kinetics

The modeling, Eq. (11), was fitted against experimental data (Fig. 3) to obtain kinetics constants. It can be seen that the binary model fitted well in all experimental data. The obtained kinetics coefficients, k_1 and k_2, reflected the efficiencies of different treating processes. Generally, when a higher bias applied crossing electrodes, the rate constants of completed oxidizing reactions were higher for both EC and PEC processes. For PEC treatment, the rate constants of the completed oxidation, k_1, was almost proportional to the applied voltage.

As anodic bias increases, a large amount of current carrier (photoelectrons) passes through the anode and photocurrent excited holes and electrons used to oxidize organics. Consequently, the higher the bias the larger TOC is removed.

In Table 3, it can be seen that at the low bias value (1 V), the partial oxidization (k_2) were higher than those of complete oxidation (k_1). This phenomenon can be explained via the role of electric power applied. It is well known that laundry wastewater includes a wide range of organic compounds, mainly including polar (anionic, cationic) and nonpolar (nonionic) surfactants [2]. When these surfactants are brought into contact, polar surfactants form aggregates at α-Fe_2O_3 surface on account of electrostatic interactions between separately charged species and the oppositely charged α-Fe_2O_3 surface [23].

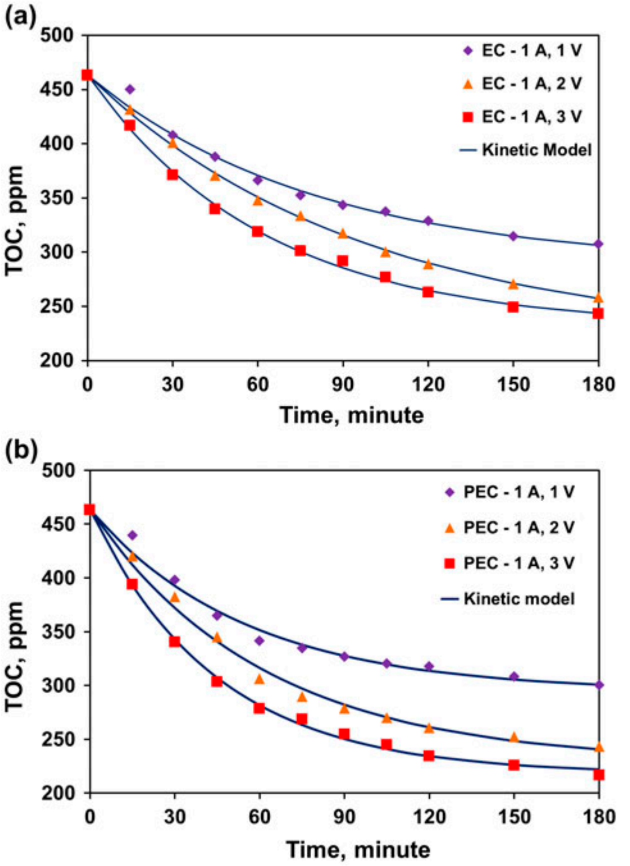

Fig. 3. TOC removal under different processes: (a) EC and (b) PEC.

Table 3
Kinetic parameters of TOC removal

DC bias (V)	Solar simulator	k_1, min^{-1}	k_2, min^{-1}
1	On	6.5×10^{-3}	1.1×10^{-2}
1	Off	4.7×10^{-3}	7.7×10^{-3}
2	On	8.1×10^{-3}	7.8×10^{-3}
2	Off	5.2×10^{-2}	4.4×10^{-3}
3	On	1.2×10^{-2}	1.1×10^{-2}
3	Off	8.0×10^{-3}	7.9×10^{-3}

The degradation kinetics of organics occurred via two mechanisms: (1) complete oxidation to form CO_2 and water and (2) break down to shorter chains [24]. These intermediates were less oxidized by generated holes, but often by electrons running from anode to cathode [25,26]. Therefore, when a relatively low bias was applied, the produced electrons were not enough to keep the organics close to the surface. Consequently, partial oxidizing is the dominant ($k_2 > k_1$), and the remaining organic compounds were suspended within the solution. With the increasing voltage (e.g. 3 V); however, the rate coefficients of the completely oxidizing reactions, k_1, was higher than that of the partial ones. In this instance, organics were

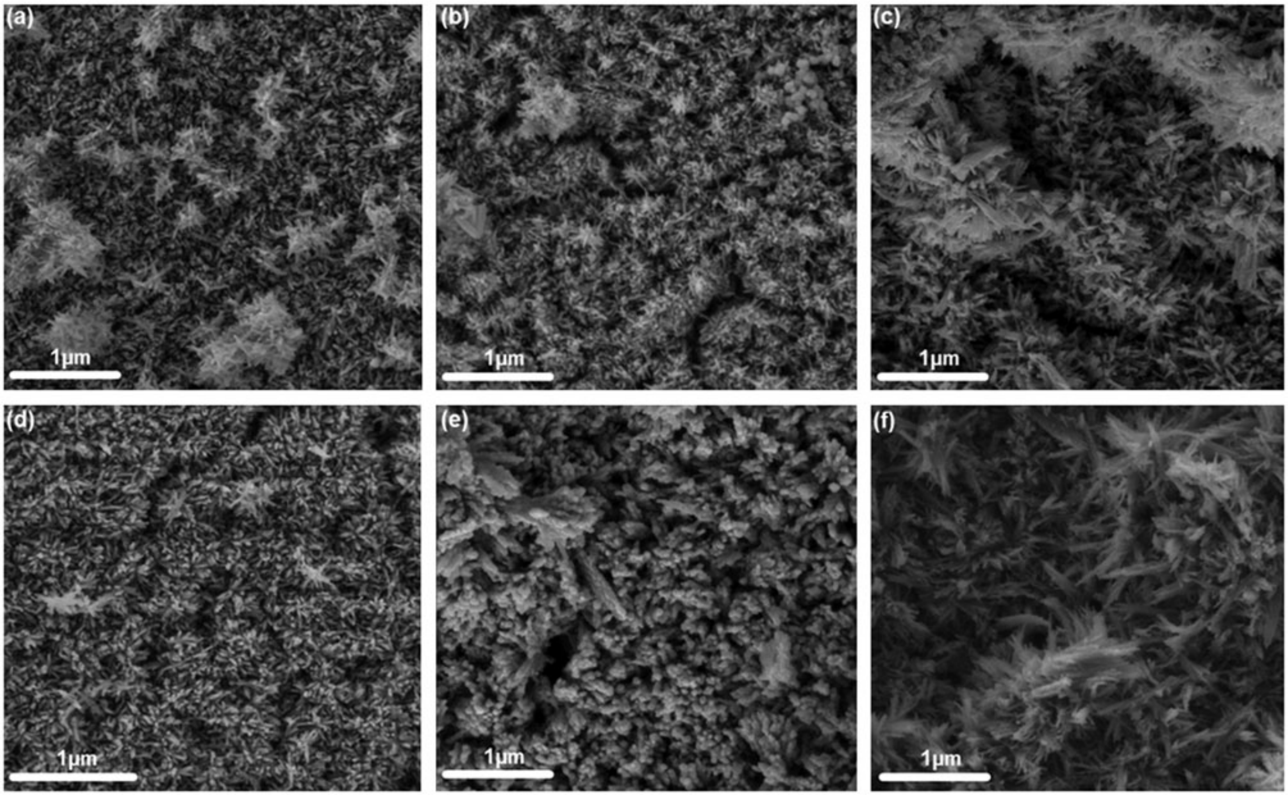

Fig. 4. SEM images of α-Fe_2O_3 surface after EC treatment at: (a) 1 A, 1 V; (b) 1 A, 2 V; (c) 1 A, 3 V; and PEC treatment at: (d) 1 A, 1 V; (e) 1 A, 2 V; (f) 1 A, 3 V.

much more prone to complete oxidation. While the molecular nature of the original and remaining organics is not known, it is expected that most of the surfactant "heads" were oxidized (since they have strong surface adsorption). Hence, the remaining TOC should contain mostly nonionic compounds, such as alcohols, which are less harmful than the original compounds.

4.4. Stability of the electrodes

The stability of the α-Fe_2O_3 electrodes was clarified via FESEM. Generally, the α-Fe_2O_3 electrodes showed a good stability over three hours of reactions in both EC and PEC processes (Fig. 4). Furthermore, in comparison with untreated anodes (Fig. 2), treated α-Fe_2O_3 surfaces were changed by EC reactions. Accordingly, the corrosion of α-Fe_2O_3 surface resulted in formation of smaller nano-tufts in EC (Fig. 4(a–c)), and vigorous deformation by PEC process (Fig. 4(d–f)). The deformation is expectedly increased with increasing voltage.

The PEC process had more noticeable impact on α-Fe_2O_3 films more than EC process. This is due to the larger adsorption capacity, and higher catalysis activity under solar illumination. These were consistent with the higher TOC removal, i.e. the oxidation of organics on the α-Fe_2O_3 surface. Nevertheless, α-Fe_2O_3 thin films used in this study generally exhibits a good stable under bias applied over treating time. The results provide important foundation for further scaling up for practical applications.

5. Conclusion

In this study, the TOC of synthetic laundry wastewater was removed by EC and PEC processes. The process was applied with a focus on the domestic application: (i) it is a batch process running for few hours per day, (ii) the energy can be supplied by solar panels, and (iii) the effluent is used for low-quality applications such as watering lawn. It was found that the PEC can reduce TOC to nearly 200 ppm after 180 min. The stability of the α-Fe_2O_3 anodes, which can be inexpensively produced, is feasible for this application. The remaining organics are expectedly less surface active and consequently less harmful than the original compounds. In addition to domestic application in Australia, the method can be used for rural areas in developing countries, where centralized wastewater treatment and electricity are not available.

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