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Significant enhancement of micropollutant photocatalytic degradation using a TiO₂ nanotube array photoanode based photocatalytic fuel cell



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- TNA-Cu PFC can significantly enhance MCPA removal from aqueous streams.
- Acidic pH further promotes the enhancement of MCPA removal.
- MCPA degradation mechanisms in the TNA-Cu PFC system was elucidated.
- Efficient MCPA removal was obtained in real wastewater effluent.

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ABSTRACT

This study evaluated the application of a membrane-free photocatalytic fuel cell composed of a TiO₂ nanotube array photoanode and a Cu cathode, i.e. TNA-Cu PFC system, for micropollutant removal from water. Significantly enhanced removal of a commonly present aqueous micropollutant 4-chloro-2-methylphenoxyacetic acid (MCPA) was obtained in this TNA-Cu PFC system: the TNA-Cu PFC system achieved better MCPA degradation compared to the conventional photocatalytic method using the same catalyst. In the TNA-Cu PFC system, the MCPA degradation was largely promoted under acidic conditions, indicating this as an important operational condition. The enhancement of MCPA degradation in the TNA-Cu PFC system involved better e^{-/h+} separation and generation of other oxidants: in conventional photocatalytic process, hydroxyl radicals in liquid phase contributed to 93.7% MCPA degradation while only 2.4% MCPA degradation was mediated by other oxidants like O₂⁻, H₂O₂, HO₂; for MCPA degradation in the TNA-Cu PFC system, the contribution of hydroxyl radicals in the liquid phase decreased to 83.6%, while contribution of other oxidants like 'O2-, H2O2, 'HO2 increased to 15.3%. This change in MCPA degradation mechanisms was confirmed via degradation intermediates analysis by LC-MS/MS. The study on the effect of electrolyte concentration suggests that when operated under acidic conditions, addition of electrolyte is not required. The TNA-Cu PFC system was shown to work well in the presence of up to 15 mg/L natural organic matter (originating from two large rivers), high amounts of common inorganic ions, and even in WWTP effluent. The TNA-Cu PFC system also exhibited relatively good stability after several cycles of repeated use. The obtained results demonstrated that this is an adequate system for micropollutant removal from water at various places in the water cycle, i.e. as polisher of WWTP effluents before discharge or for cleaning intake water before producing drinking water.

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1. Introduction

In recent decades, emerging organic pollutants, including pharmaceutical compounds, herbicides, pesticides, and personal care products, are gaining increasing concerns because they are potentially hazardous to aquatic life and human health [1]. Among them, the synthetic carboxylic acid herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA) has been detected in different water bodies [2,3]. Toxicity and endocrine disrupting effects of MCPA on living species have been well studied, and abundantly evidenced in the literature [4,5]. However, owing to its poor biodegradability, conventional water treatment processes are usually insufficient for MCPA removal [6]. In addition, once the compound enters natural water bodies and becomes exposed to solar irradiation, more toxic compounds are generated from direct photolysis of MCPA [3].

Given this context, many water treatment techniques have been tested for cleaning MCPA contaminated water, and among them photocatalysis has received increasing research interests [7,8], with a focus on TiO₂. TiO₂ is commonly used because it has relatively high quantum efficiency, easy accessibility, low toxicity, and high chemical/physical stability. TiO₂ photocatalytic pollutants degradation processes involve production of electron/hole pairs (e^{-}/h^{+}) upon illumination of TiO₂ by radiant energy higher than its band gap energy (3.2 eV and 3.0 eV for anatase and rutile respectively [9]), followed by formation of reactive oxidative species (ROS), e.g. hydroxyl radicals ('OH), superoxide radical anions (O_2^-) , which has been extensively described in the literature [10-15]. A few attempts have been made to apply TiO₂ for MCPA removal from water [8,16–19]. Most of the previous studies have been done in slurry systems with TiO₂ nanoparticles suspensions. Although the large surface area of TiO2 nanoparticles is beneficial for mass transfer, some major drawbacks are preventing the scale-up of such slurry systems: (1) costly liquid/solid separation process is required for retention and reuse of the catalyst particles: (2) light scattering by the catalyst particles; (3) the suspension of catalyst particles are unstable and easy to form aggregates in complex water matrices [20]. Therefore, immobilization of TiO₂ should be considered. The electrochemical anodic produced TiO₂ nanotube arrays (TNAs) is a promising alternative to conventional TiO₂ suspensions. The TNAs exhibit multiple merits: (1) relatively large surface area; (2) high chemical/mechanical stability; (3) oriented direction of electron transport which can reduce e^{-}/h^{+} pairs recombination; (4) relatively easy to make; (5) tunable morphologies. Examples of using TNAs for organic pollutants elimination and renewable energy production are available in literature [21-29]. Up to now, very limited studies have been conducted to use TNAs for MCPA degradation [6].

Another major drawback of TiO₂ photocatalytic (PC) processes is the fast recombination of e^{-}/h^{+} pairs, where a large amount of energy from absorbed photons is lost as heat, resulting in seriously reduced treatment efficiency [30]. Therefore, reducing the recombination of e^{-}/h^{+} pairs is a key, and efforts have been made on this aspect, e.g. integrating TiO₂ with other active materials to form in-situ heterojunction for better e^{-}/h^{+} separation [31–33], applying voltage bias – Generally known as photoelectrocatalysis (PEC) - To separate e⁻/h⁺ from the catalyst [30,34]. Recently a novel concept of PEC, known as photocatalytic fuel cell (PFC) has been introduced into the field of water treatment [35-41]. In PFC systems, the photo-induced electrons are able to migrate from TiO₂ to the counter electrode through an external circuit driven by the photon-induced voltage between the two electrodes spontaneously. Hereby the photo-induced holes are left at the TiO_2 surface triggering degradation of the target pollutants [35,42]. In this way, the recombination of e^{-}/h^{+} pairs is reduced, and consequently enhanced target contaminants removal and simultaneous electricity production can be expected. The PFC concept is gaining increasing attention in the field of water treatment in recent years. Examples are available in literature reporting the use of PFC systems with various photoanodes and cathodes for treatment of different target

pollutants, and enhanced degradation of organic pollutants compared with conventional photocatalysis [35,42,43]. However, very limited attempts have been made to apply PFC for micropollutant removal from water. In addition, little is known on micropollutants degradation mechanisms in PFC systems, effects of commonly present background water constituents, and applicability of PFC systems for micropollutants removal in real wastewater matrices.

In the present study, we demonstrate enhanced MCPA degradation in a membrane-free PFC system consisting of a TNA photoanode and a Cu foil acting as the cathode (TNA-Cu PFC). Key influencing factors, *i.e.* initial pH and electrolyte concentration were investigated. In addition, to elucidate the mechanism of enhanced MCPA degradation in the TNA-Cu PFC system, the contribution of different reactive oxidizing species (ROS) were evaluated by adding specific scavengers and via analysis of degradation intermediates by LC-MS/MS. To test its applicability in a more complex water matrix, effects of natural organic matters (NOMs), commonly present inorganic ions, and real wastewater treatment plant (WWTP) effluent were studied. Furthermore, the stability of the system was evaluated over several reuse cycles.

2. Materials and methods

2.1. Chemicals

Ammonium sulphate (\geq 99.0%), ammonium fluoride (\geq 98.0%), formic acid (\geq 96%), and *tert*-Butanol (\geq 99.0%) were purchased from Sigma-Aldrich (Germany). Sulfuric acid (95%), sodium hydroxide (1 mol/L aqueous solution), acetone (\geq 99.7%), sodium sulphate (\geq 99.0%), and 2-propanol (\geq 99.9%) were purchased from VWR (Belgium). MCPA (\geq 98.0%) was purchased from Dr Ehrenstorfer GmbH (Germany). A stock solution of MCPA was prepared at a concentration of 200 mg/L. Dry solid extracts of two aquatic NOM Suwannee River NOM (2R101N) and Upper Mississippi River NOM (1R110N) were purchased from International Humic Substances Society (IHSS). 100 mg/L stock solutions of the two NOMs were prepared. Unless otherwise mentioned, all reaction solutions and stock solutions in this study were prepared with ultrapure water from a Milli-Q Advantage A10 system (Merck Millipore, Darmstadt, Germany).

2.2. Synthesis and characterization methods of the TNA

A two-electrode electrochemical anodization cell was used to prepare the TiO₂ nanotube array photoanode, as reported earlier by our group [25] (shown in Scheme S1 in the Supplementary materials). The anode was a 3 cm \times 4.5 cm Titanium foil (\geq 99.5%, 0.3 mm thick), and the cathode was a $4.5 \text{ cm} \times 5 \text{ cm}$ Titanium plate (1 mm thick). As pretreatment, the Ti foils were first degreased by successively ultrasonication for 15 min in 2-propranol, acetone and Milli-Q water, and were then dried in N2 atmosphere. The electrochemical anodization was performed in 100 mL aqueous electrolyte containing 0.15 M NH₄F and 1 M (NH₄)₂SO₄ at 20 V for 2 h, followed by a thorough wash of the obtained TNAs and annealing at 600 °C for 0.5 h. The surface morphology of the TNA photoanode was characterized using a JEOL JSM 6480 scanning electron microscope (JEOL Europe B.V., Nieuw-Vennep, The Netherlands). The crystallographic phase of the TNA photoanode was analyzed by a Horiba LabRAM spectrometer. The surface area of the TNA photoanode was measured by using a Tristar 3000 Surface area and Porosity Analyzer (Micromeritics, USA), where nitrogen adsorption isotherms were collected at 77 K (-196 °C) and the Brunauer-Emmertt-Teller model was used to determine the specific surface area.

2.3. MCPA degradation experiments

Fig. 1 shows the schematic representation of the TNA-Cu PFC system used for MCPA degradation experiments. The experimental setup was a two-electrode system, where the TNA electrode ($3 \text{ cm} \times 3 \text{ cm}$)



Fig. 1. Schematic representation of the TNA-Cu PFC system.

and a copper foil (Grade M2, 3 cm × 4.5 cm) were used as photoactive anode and counter electrode, respectively. A rectangular quartz cube was used as the reaction cell (6 cm × 6 cm × 6 cm). The interval between the two electrodes was 2 cm. A 450 mW UV-LED emitting UV light with peak intensity at 365 nm (NCSU033B, NICHIA, Japan) was placed outside the reaction cell (on the side of TNA photoanode), enabling 11.6 mW/cm² radiant power at the TNA surface. The reaction solutions contained 1.0 mg/L MCPA (with a total volume of 140 mL). Unless otherwise stated, 0.1 M Na₂SO₄ was added into the reaction solutions as supporting electrolyte. The experiments were conducted with unadjusted natural pH (~6), unless specifically noted. For experiments using conventional photocatalysis method (PC method), only the copper foil cathode was removed from the system, while all other components of the set-up were kept unchanged. Duplicate experiments were performed in parallel.

2.4. Analytical procedures

The open circuit voltage and the short circuit current of the TNA-Cu PFC system were measured by Vertex potentiostat (Vertex One, Ivium Technologies B.V, The Netherlands) according to a method introduced in literature [43]. MCPA concentrations and degradation intermediates were measured by an Agilent LC-MS/MS system. More details on the MCPA concentrations and degradation intermediates measurement methods can be found in our previous work [44].

3. Results and discussion

3.1. The TiO_2 nanotube array photoanode

Surface morphology of the TNA photoanode is shown in Fig. 2a. It

can be seen that the TNA anode is covered by a self-organised tubular structure layer, which has an average pore size of around 80 nm. It has been reported that such a nanotubular structure results in oriented electron transport from TiO₂ surface to Ti which can facilitate e^-/h^+ pairs' separation in photoelectrocatalytic processes [45]. The specific surface area of the TNA photoanode is around 0.39 m²/g. The Raman spectrum of the TNA anode surface shown in Fig. 2b demonstrates that the TNA layer has a crystallographic phase containing both anatase and a small amount of rutile. Good photocatalytic performance of TiO₂ contains both anatase and rutile has been documented in literature [25,46].

3.2. MCPA removal in the TNA-Cu PFC system

3.2.1. Enhanced MCPA removal in the TNA-Cu PFC system

The efficacy of different methods, *i.e.* photocatalysis (PC), photocatalytic fuel cell (PFC), on MCPA removal was evaluated. Both the kinetics and the total removal efficiency of MCPA degradation were studied. The results show that MCPA degradation followed the pseudofirst-order kinetic model:

$$\ln\left(\frac{C}{C_0}\right) = -k_{app} \times t \tag{1}$$

where C and C_0 stand for the MCPA concentration at time t and 0, respectively; kapp stands for the pseudo-first-order rate constant (also known as apparent rate constant) for MCPA degradation. In order to avoid confounding effects of degradation products, only initial degradation data (0-60 min) was used to calculate initial apparent rate constant k_{app} [47]. The results are shown in Fig. 3. Compared with TNA based photocatalysis, the MCPA removal by the PFC method was successfully enhanced: after 120 min of treatment, the PC method resulted in 52.2% MCPA removal and the PFC method resulted in 62.0% MCPA removal. The initial apparent rate constant (kapp) for MCPA degradation was found 0.0058 min^{-1} for the PC system, and 0.0072 min^{-1} for the TNA-Cu PFC system. The obtained results suggest that MCPA degradation can be effectively enhanced by using the TNA-Cu PFC system. Successful enhancement of various organic pollutants degradation over photocatalysts by adding a cathode material has been reported in recent years. Li et al. (2014) [42] applied TiO₂ (coated on Ti substrate) as photocatalyst and a platinized Ti as the cathode to degrade Reactive Brilliant Red X-3B, a dye, from wastewater. They found that the colour removal after 80 min of treatment could reach 85% by the PFC method, while the conventional PC method without cathode connection could achieve only 55% colour removal under the same conditions. Such enhancement was due to better e^{-}/h^{+} separation achieved by electron transfer from catalyst to cathode assisted by the self-bias between the two electrodes [42]. The same phenomenon was reported by Du et al. (2014) [48]: enhanced photocatalytic methyl orange degradation was obtained when a Pt/C coated bio-cathode was applied, because better



Fig. 2. SEM top view image (a) and Raman spectrum (b) of the TNA photoanode surface.



Fig. 3. Initial apparent degradation rate constant and total removal of MCPA by PC method and TNA-Cu PFC method. Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}$, natural pH (~6), 0.1 M Na₂SO₄ as electrolyte, 120 min treatment.

 e^-/h^+ separation was achieved by the bias between the $\rm TiO_2$ catalyst electrode and the bio-cathode.

Fig. 4a shows that a V_{oc} value of 0.24 V was generated in the TNA-Cu PFC system upon UV illumination. The V_{oc} is a measure of accumulation of photo-generated electrons in the TNA anode upon illumination, as previously explained by Chen et al. [49]. As shown in Fig. 4b, upon UV irradiation, the TNA-Cu PFC system generated rapid photocurrent response, with a steady state value of about 0.37 mA, which represent the photo-generated electrons migration from the TNA anode to the Cu cathode.

Experiments in tap water samples were conducted to evaluate the effect of natural water constituents (Table SI 1 shows the characteristics of the tap water samples). In tap water samples, although MCPA degradation performances of both the conventional PC system and the



Fig. 4. Open circuit voltage (a) and short circuit current (b) of the TNA-Cu PFC system. Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}$, natural pH (~6), 0.1 M Na₂SO₄ as electrolyte.



Fig. 5. Initial apparent degradation rate constant and total removal of MCPA in tap water samples by PC method and PFC method. Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}$, natural pH (~6), no electrolyte addition, 120 min treatment.

TNA-Cu PFC system were reduced, the TNA-Cu PFC system still resulted in much more rapid MCPA degradation compared with that in the conventional PC system, as shown in Fig. 5. The output voltage of the TNA-Cu PFC system operated in tap water was measured to be nearly 0.35 V, and the circuit current was nearly 0.3 mA (Fig. SI 1).

The results presented herein demonstrate that, compared with the PC system, applying the TNA-Cu PFC system is a facile and effective way to enhance the removal of MCPA (and potentially also other micropollutants), and can simultaneously produce electricity for other low-power requiring applications.

3.2.2. Crucial role of acidic pH to promote MCPA degradation efficiency

It has been documented that the pH can affect various photochemical systems on the degradation of organic pollutants [50,51]. Therefore, MCPA degradation experiments were performed at varied initial pH (pH₀), from 3 to 11, to examine the effect of pH on the TNA-Cu PFC system. Experiments with varied pH₀ were also performed in the TNA PC system. The solution pH was nearly constant during treatment, so the effect of pH fluctuation can be neglected.

As shown in Fig. 6, better performance was achieved with a lower pH level in both the PC system and the TNA-Cu PFC system. The obtained results (Fig. 6) show that acidic pH (pH₀ = 3) plays a significant role in enabling effective degradation: (1) the fastest MCPA degradation in the PC system and the TNA-Cu PFC system were both achieved at acidic pH (pH₀ = 3); (2) under same conditions at acidic pH, MCPA degradation in the TNA-Cu PFC system (with initial k_{app} of



Fig. 6. Effect of pH on the MCPA initial degradation rate constant (k_{app}) by PC method and PFC method. Conditions: [MCPA]₀ = 1.0 mg/L, H₂SO₄ or NaOH solutions were added to obtain designated pH₀, 0.1 M Na₂SO₄ as electrolyte.

 0.0351 min^{-1}) was almost three times faster than that in the PC system (with initial k_{app} of 0.0123 min⁻¹). This demonstrates that acidic conditions can significantly promote the micropollutants removal performance of the TNA-Cu PFC system. In a study on a dual photo-electrodes ferrous ions PFC system conducted by Zhao et al. [52], lower pH was found to be beneficial for the PFC (Fe^{2+}) system pollutant degradation performance, the same effect of low pH on a conventional PFC system was also reported. In another study conducted by the same authors Zhao et al. [43] on a Fenton-PFC system, the same findings were presented, and this phenomenon was attributed to two facts: (1) other oxidants, e.g. 'O2-, H2O2, 'HO2, are more easily produced at the cathode under acidic conditions; (2) a positively charged TNA anode surface would be beneficial to organic pollutants degradation taking place on the anode surface. Liu et al. [53] studied diclofenac photoelectrocatalytic degradation in a persulfate assisted PEC (external voltage was supplied to drive electron transmission) system, and reported that diclofenac degradation decreased with an increase of pH₀. This finding was explained by higher redox potential SO₄⁻ (derived from the Na₂SO₄ electrolyte) at acidic pH in their studied system. These explanations are also reasonable for our findings that acidic pH is favourable to MCPA degradation in both the PC system and the TNA-Cu PFC system. Moreover, in the present study, the beneficial effect of acidic pH was even more profound in the TNA-Cu PFC system. Considering that the same Na₂SO₄ concentration and the same TNA was applied as the photocatalyst in the PC system and the PFC system, the promotion of pollutant degradation on the TNA surface, and redox potential of ·SO₄⁻ at same acidic conditions should be the same for both systems. Therefore, in the TNA-Cu PFC system, the increased generation of other oxidants is likely the crucial factor that contributes to the enhanced MCPA degradation performance under acidic conditions. Since the best MCPA degradation performance was achieved under acidic condition, the remaining experiments were performed with a pH₀ value of 3.

3.3. Degradation mechanisms

The working principle of PFC systems has been introduced in literature [42,43]. Fig. 7 is a schematic illustration of the TNA-Cu PFC working principle. Initially, electrons (e⁻) from the TiO₂ valence band will migrate to its conduction band upon UV illumination, and subsequently holes (h⁺) are left in the TiO₂ valence band. The h⁺ is a strong oxidant that can oxidize organics readily adsorbed on the TiO₂ surface. Moreover, h⁺ can convert surrounding water molecules or OH⁻ to hydroxyl radicals ([•]OH), a well-known oxidant that rapidly degrades broad range of organics in various advanced oxidation processes. Part of the [•]OH is adsorbed on the TNA surface ([•]OH surface) and can readily degrade organic pollutants that diffused towards and adsorbed onto the TNA surface. The rest of the [•]OH radicals can diffuse into the liquid phase ([•]OH _{free}) and react with organic pollutants there. Usually organic pollutants are degraded predominantly by h⁺ and [•]OH in



Fig. 7. Schematic of the proposed degradation mechanism of MCPA in the PFC system.

photocatalytic processes [25,54]. The conduction band electrons can be quenched rigorously by various electron acceptors in the reaction solution to generate water and/or other oxidants like 'O2-, H2O2, 'HO2. In conventional photocatalytic systems, the conduction electrons can easily migrate back to valence band and recombine with the holes. This recombination of h^+/e^- pairs is a limiting factor of photocatalytic processes, because such recombination leads to energy loses as heat and less availability of h⁺ for subsequent 'OH production and organic pollutant degradation. In a PFC system, by applying an external circuit and a cathode, the electrons can transfer to the cathode driven by the potential difference between the two electrodes via the external circuit. resulting in better separation of h^+/e^- pairs. In this way, recombination of h^+/e^- pairs can be largely suppressed and more valence band holes are available for 'OH production and organic pollutant degradation, and more electrons are available for generation of other oxidant like 'O₂⁻, H₂O₂, 'HO₂. Thus, enhanced organic pollutant degradation is achieved in the PFC system, and electricity is obtained simultaneously as a side benefit.

To elucidate the mechanism of enhanced MCPA removal in the TNA-Cu PFC system, specific oxidant scavengers were added to study the role of different ROS in TNA-Cu system and the conventional TNA PC system. The addition of formic acid can hinder MCPA degradation triggered by both h^+ and 'OH [9]; while the addition of *tert*-butanol only hinders MCPA degradation triggered by free 'OH in the liquid phase [9]. Fig. 8 shows that the MCPA degradation in the PC system was decreased from 81.5% to 5.1% and 1.9% by adding *tert*-butanol and formic acid, respectively; while the MCPA degradation in the TNA-Cu system was decreased from 99.4% to 16.3% and 15.2% by adding *tert*-butanol and formic acid, respectively.

Therefore, the contribution of different ROS was elucidated (detailed calculation procedures can be found in the Supplementary materials). Fig. 9 illustrates the contribution of different oxidants to MCPA degradation in the PC system and the TNA-Cu PFC system. In the



Fig. 8. Effect of different ROS scavengers on the MCPA total removal after 120 min treatment by PFC method (a) and PC method (b). Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}, pH_0 = 3, [Na_2SO_4] = 0.1 \text{ M}.$



conventional PC system, reactions with $\, \dot{} \text{OH} \,_{\text{free}}$ was the predominant MCPA degradation route (accounts for 93.7% MCPA degradation), while a very small portion of MCPA was degraded by h⁺ and 'OH surface (accounts for 3.9% MCPA degradation), and other oxidant species, e.g. 'O₂⁻, H₂O₂, 'HO₂ (accounts for 2.4% MCPA degradation). However, in the TNA-Cu PFC system, although primary MCPA degradation oxidant was still $^{\circ}\text{OH}$ _{free} (accounts for 83.6% MCPA degradation), the contribution of other oxidants (e.g. O_2^- , H_2O_2 , HO_2) became a significant part (accounts for 15.3% MCPA degradation). The same findings were also found under neutral pH (shown in Fig. SI 3). The increased contribution of other oxidants, e.g. O_2^- , H_2O_2 , HO_2 , in the TNA-Cu PFC system can be ascribed to reduced e^{-}/h^{+} recombination. In the TNA-Cu system, better separation of h^+/e^- pairs were achieved. Consequently, on the one hand more h⁺ were available to trigger h⁺ and 'OH mediated MCPA degradation, on the other hand, more e^- were available to produce other oxidants like O_2^- , H_2O_2 , 'HO₂ (shown in equations below) and subsequent MCPA degradation. Such enhancement of micropollutants removal by better h^+/e^- separation and generation of oxidants like 'O2-, H2O2, 'HO2 is in line with previous studies: in a study performed by Zhao et al. (2017) [43] on enhanced organic pollutant removal in a Fenton-PFC system, the involvement of 'O2⁻, H2O2, 'HO2 was also proposed.

$$O_2 + e^- \to O_2^- \tag{2}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 (3)

The difference in MCPA degradation pathways in PC and PFC systems was confirmed via intermediates analysis. Two main transformation products (TP) were identified: one with a molecular weight of 214 and retention time of 2.4 min (TP1) which is likely to be resulted from addition of hydroxyl group to the MCPA molecule by hydroxyl radical attack [19], and the other with a molecular weight of 144 and retention time of 0.84 min (TP2) which is likely to be 2-methyl-4-chlorophenol [19]. Tentative structures of these two transformation products are shown in Fig. 10, which have been previously reported by Djebbar et al. [19]. The results show that evolution of two main transformation products during different treatment varied (Fig. 10): TP1 formation and degradation in the PFC system were much more rapid than that in the PC system.

3.4. Effect of water constituents and operational parameters

3.4.1. Effect of electrolyte concentration

Electrolyte concentration is known as an important operational parameter in photocatalytic systems and photoelectrocatalytic systems (including photocatalytic fuel cell systems) [43,55]. MCPA experiments



Fig. 10. MCPA degradation transformation products formation during PC treatment and PFC treatment. Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}, \text{ pH}_0 = 3, [Na_2SO_4] = 0.1 \text{ M}.$



Fig. 11. Effect of electrolyte concentration on the MCPA removal by PC method (dashed line) and PFC method (solid line). Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}$, $pH_0 = 3$.

were conducted in both conventional PC system and the TNA-Cu system with varied Na_2SO_4 concentrations from 0 M to 0.5 M (conductivity ranging from 0.48 to 59.48 mS/cm), at acidic conditions (pH₀ = 3).

The results (Fig. 11) show that varied electrolyte concentration in the tested range has no effect on the MCPA removal in the TNA-Cu PFC system. Even without the addition of Na₂SO₄, MCPA degradation in the TNA-Cu PFC system was still greatly enhanced compared with that in the PC system: degradation of MCPA in the TNA-Cu PFC system ($k_{app} = 0.0389 \text{ min}^{-1}$) was about 3.6 times faster than that in the PC system ($k_{app} = 0.0109 \text{ min}^{-1}$). This reveals that, under acidic



Fig. 12. Effect of different natural organic matters on the MCPA removal in the TNA-Cu PFC system: (a) Suwannee River NOM; (b) Upper Mississippi River NOM. Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}, \text{ pH}_0 = 3$, no electrolyte addition.

conditions, the reaction solution conductivity is not a limiting factor on the separation of h^+/e^- pairs, and consequently oxidants production and MCPA degradation were not affected by varied electrolyte concentration. Therefore, unless otherwise stated, remaining experiments were conducted without Na₂SO₄ addition.

3.4.2. Effect of background organic matters

Dissolved natural organic matter (NOMs) is a very common background water constituents in various water bodies. It is well known that those NOMs can interfere with many AOPs [47]. Therefore, experiments were carried out to study the effect of NOMs on the MCPA removal performance of the TNA-Cu PFC system, to evaluate its potential in complex water matrices.

The results (Fig. 12) demonstrate that the presence of NOMs has no significant detrimental effect on MCPA degradation performance of the TNA-Cu PFC system: even 15 mg/L Suwannee River NOM (SR-NOM) had no noteworthy effect on MCPA degradation (Fig. 12a); while the presence of 15 mg/L Upper Mississippi River NOM (UMR-NOM) only caused a slight decrease in the MCPA degradation rate (Fig. 12b). NOMs usually interfere with photocatalytic system by blocking the active site of the catalyst surface, and competing for reactive oxidant species against target pollutants [56,57]. Therefore, the null effect of NOMs on the TNA-Cu system could be attributed to two facts: (1) under acidic condition, adsorption of NOMs onto the TNA surface and the subsequent blocking of the active site is greatly suppressed; (2) in the TNA-Cu system, contribution of more selective oxidants like ' O_2^- can compensate the 'OH scavenging effect of NOMs.

3.4.3. Effect of inorganic ions

Besides organic matter, many commonly present inorganic species, e.g. nitrate ions, chloride ions, calcium ions, are also known to be able to interfere with TiO_2 based photocatalytic processes [51,58,59]. Therefore, experiments were conducted in presence of various



Fig. 13. Effect of common inorganic ions on the MCPA removal in the TNA-Cu PFC system: (a) Chloride ions; (b) Nitrate ions; (c) Calcium ions. Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}, \text{ }pH_0 = 3.$

concentration levels of these inorganic ions to evaluate their impact on MCPA degradation performance of the TNA-Cu PFC system.

The results (Fig. 13) suggest that both nitrate and calcium had no detrimental effect on the MCPA removal performance of the TNA-Cu PFC system. As reported in previous studies, chloride ions can strongly adsorb onto TiO2 surface and block the active site under acidic conditions [59]. Interestingly, in contrast to conventional photocatalytic systems (Fig. SI 4) chloride ions could even significantly promote MCPA degradation in the TNA-Cu PFC system. This finding could be attributed to the fact that chlorine based strong oxidants (e.g. ClO⁻) could be produced in the TNA-Cu PFC system, and stimulates MCPA degradation. In a study conducted by Lee, et al. employing a ZnO/Zn based PFC system for removal of an azo dye Reactive Green 19 (RG 19), it was found that chloride ions could promote the oxidation of RG 19 by production of hypocrite from chloride in the system [60]. The same finding was very recently reported by another research group employing graphite-PVC composite based electrochemical oxidation system for diclofenac degradation [61].

The results presented indicate that the TNA-Cu PFC system has the

Table 1Characteristics of the WWTPE sample.

Parameters	Concentration (mg/L)
PO4 ³⁻ -P	0.68
COD	39.1
SO_4^{2-}	> 40
TC	75
TOC	20
IC	55
Ca ²⁺	> 20
K ⁺	13.4
Mg ²⁺	13.82
NH4 ⁺	0.36

potential to overcome interference of common inorganic ions in complex water matrices.

3.5. MCPA removal and simultaneous electricity generation in real wastewater treatment plant effluent

In order to better evaluate the applicability of TNA-Cu PFC system in real wastewater treatment implications, MCPA removal experiments were also done in wastewater treatment plant effluent (WWTPE) sample. The WWTPE was from the activated sludge system of the Sneek municipal wastewater treatment plant (Sneek, Friesland, The Netherlands). Table 1 lists characteristics of the WWTPE sample. MCPA was spiked into the WWTPE sample to a concentration of 1.0 mg/L, and H_2SO_4 was added to obtain an initial pH of 3.

As demonstrated in Fig. 14, MCPA degradation in WWTPE by conventional PC method resulted in an initial k_{app} value of 0.0108 min⁻¹ and a total removal of 75.2% after 120 min treatment. When the TNA-Cu PFC system was applied, MCPA underwent more rapid degradation (1.5 times faster) with an increased initial k_{app} value of 0.0157 min⁻¹ and a total removal of 87.6% after 120 min treatment. Meanwhile, an open cell voltage of around 0.12 V and a photocurrent of around 0.25 mA were obtained in the TNA-Cu PFC system when operated in WWTPE (Fig. 15). The obtained results suggest that applying the TNA-Cu PFC system is a facile and effective way to enhance MCPA removal from complex water matrix, and it is possible to produce electricity which can be used for other processes.

3.6. Stability of the TNA-Cu PFC system on MCPA removal

The stability of the TNA-Cu system was examined, in terms of its MCPA removal performance over six operation cycles. The operational conditions of each cycle were kept identical: with initial MCPA concentration of around 1 mg/L, with an initial pH of 3, without the



Fig. 14. Initial apparent degradation rate constant and total removal of MCPA in WWTP effluent treated by PC method and PFC method. Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}$, pH₀ adjusted to 3 by H₂SO₄, 120 min treatment.



Fig. 15. Open circuit voltage (a) and short circuit current (b) of the TNA-Cu PFC system. Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}$, in WWTP effluent, pH₀ adjusted to 3 by H₂SO₄.



Fig. 16. MCPA degradation in the TNA-Cu PFC system during repeated runs. Conditions: $[MCPA]_0 = 1.0 \text{ mg/L}$, $pH_0 = 3$, no addition of electrolyte.

addition of electrolyte. Before each subsequent run, the system was firstly washed thoroughly by pure water, followed by drying in nitrogen gas flow. The results (Fig. 16) indicate that MCPA degradation in the TNA-Cu PFC system did not change significantly after repeated treatment cycles. The initial apparent rate constant for MCPA degradation was 0.0556 min⁻¹ for the first run, after 6 cycles, the initial apparent rate constant for MCPA degradation was 0.0556 min⁻¹. The total removal of MCPA for each run was nearly constant (\geq 99%). The stability of the TNA-Cu PFC system is comparable to other PFCs previously reported [52,62]. The obtained results reveal relatively good stability and reusability of the TNA-Cu PFC system.

4. Conclusions

In this study, we demonstrate that TNA-Cu PFC system is a simple and effective method to enhance MCPA photocatalytic degradation from aqueous streams compared to TNA based photocatalysis system under the same operation conditions. The main outcomes of the present work are summarized as below:

- Under the same operation conditions, enhanced MCPA removal can be obtained by simply connecting the TNA to a Cu cathode to form a PFC system, even in tap water samples and wastewater treatment plant effluent.
- Acidic pH is a crucial operational parameter of the TNA-Cu PFC system: the enhancement of MCPA degradation in the TNA-Cu PFC system was largely promoted under acidic conditions.
- The enhancement of MCPA degradation in the TNA-Cu PFC system involved better e⁻/h⁺ separation and generation of other oxidants: in the TNA-Cu PFC system, contribution of other oxidants like 'O₂⁻, H₂O₂, 'HO₂ increased.
- For the acidic TNA-Cu PFC system studied in the present work, conductivity of the reaction solution was not a limiting factor. Even without addition of extra supporting electrolyte, enhanced MCPA removal can be obtained in the acidic TNA-Cu PFC system.
- Commonly present water constituents like NOMs, nitrate anions, chloride anions, and calcium cations impose no noteworthy detrimental impact on the MCPA removal in the acidic TNA-Cu PFC system.
- The acidic TNA-Cu PFC system shows good stability over repeated treatment cycles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cej.2018.08.064.

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