Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22799

126 (2018) 208–215
September

Electrochemical reductive degradation of diclofenac using a palladium-modified multi-walled carbon-nanotubes electrode

Pingzhou Duan[a], Zhao Cheng[b], Xiang Hu[a,]*, Zhirong Sun[c]

[a]*College of Chemical Engineering, Beijing University of Chemical Technology, No. 15, Beisanhuan East Road, Chaoyang District, Beijing, 100029, P.R. China, Tel. +86 10 64427356; Fax: +86 10 64436781; email: huxiang@mail.buct.edu.cn (X. Hu)*
[b]*School of Environment, Tsinghua University, Beijing, P.R. China, 100084*
[c]*College of Environmental & Energy Engineering, Beijing University of Technology, Beijing, P.R. China, 100124*

Received 18 November 2017; Accepted 1 July 2018

ABSTRACT

Electrochemical reductive degradation of diclofenac in aqueous solution was studied using a palladium-loaded multi-walled carbon nanotubes (Pd/MWCNTs) electrode. The Pd/MWCNTs electrode was characterized using scanning electronic microscopy, X-ray diffraction, and cyclic voltammetry (CV). The Pd/MWCNTs electrode was used as the cathode and a platinum wire was used as the anode for the CV experiment. The various electrolysis parameters that affect the degradation of diclofenac, including feed concentration, applied voltage, pH, supporting electrolyte concentration, and electrolysis time were investigated. The Pd/MWCNTs electrode demonstrated the best performance compared with that of the graphite and MWCNTs electrodes and achieved a removal efficiency of 90.6% after 2 h. The electrochemical reduction degradation followed pseudo-first-order kinetics. Finally, two possible degradation pathways were proposed based on the degradation products identified using high performance liquid chromatography-mass spectrometry (HPLC-MS).

Keywords: Multi-walled carbon nanotubes; Palladium; Electrochemical reduction; Diclofenac; Degradation

---

1. Introduction

Pharmaceuticals and personal care products (PPCPs) have attracted considerable attention in recent years because they are broadly used to improve the quality of daily life and may have an ecological impact. PPCPs are consisted of a large class of compounds, including drugs (such as antibiotics, steroids, analgesics, antihypertensive drugs, contraceptives, sleeping pills, and diet pills), cosmetic ingredients, food supplements, and other personal care products, as well as their respective metabolites and transformation products [1]. Although some PPCPs are degraded by water self-purification process, low levels of PPCPs accumulated over time [2] can affect water quality and may adversely impact drinking water supplies, ecosystem, and human health [3–5].

The main discharge source of PPCPs into water environment is raw wastewater or insufficiently treated effluents [6]. Effluents from urban sewage treatment plants still contain small amounts of various PPCPs [7–9]. Some PPCPs (e.g., antibiotics antiepileptic drugs, blood lipid regulators, and antiseptics) have been detected in the aquatic environment [10,11]. It has been reported that PPCPs can produce a long-term threat to the ecosystem [12–14]. Although the toxicity of PPCPs is unknown at trace levels, chronic exposure to these compounds may pose a risk to human health [15–17]. Diclofenac, a non-steroidal anti-inflammatory drug, is broadly used to reduce pain and headache attacks, and eventually excreted through urine and feces. As high as 4.7 and 1.2 μg/L of diclofenac were detected in municipal WWTPs effluent and aqueous environment, due to its persistence to biological metabolism process. These levels of diclofenac

---

* Corresponding author.

1944-3994/1944-3986

concentration can be a threat to aquatic living life such as rainbow trout, salmon, etc., and enriched in human bodies through the food chain [18].

The most widely used method in conventional wastewater treatment is coagulation and filtration [19,20]. However, physical methods cannot thoroughly degrade PPCPs and some are recalcitrant and toxic to the microorganisms; as a result, conventional processes fail to effectively treat these compounds [21–23]. Thus, new alternative methods for the effective removal of PPCPs have been developed. The electrochemical processes are versatile, cost-effective (energy efficiency, possibility of automation, small in construction area), and clean methods to remove toxic organic compounds [24,25]. In an electrochemical process, the pollutants can be destroyed by direct anodic oxidation, in which pollutants are first adsorbed on the electrode surface and then destroyed by an anodic electron transfer reaction or by cathodic deposition [26,27]. However, the majority of practical cathodes are still in plane structure with low electro-reduction and energy efficiencies. Therefore, the electrode surface morphology is very important, and its control can be used to improve the pollutant removal efficiency.

Multi-walled carbon nanotubes (MWCNTs) have been extensively studied because of their outstanding thermal and chemical stability [28]. Moreover, MWCNTs exhibit superior physical and chemical properties, including excellent electrical conductivity, extremely high mechanical strength and toughness, and large specific surface area, which make it excellent candidates for electrode material, and also modified MWCNT electrodes have been prepared to oxidize ceftazidime [29], bisphenol A [30] and electrocatalytically reduce thiamphenicol and florfenicol [31].

Some reports have shown that noble metals such as ruthenium (Ru), platinum (Pt) and palladium (Pd) can promote catalytic dechlorination [32]. Thus, we prepared the Pd/MWCNTs electrode for the removal of diclofenac by establishing optimal reaction conditions. The possible degradation mechanism for diclofenac was also analyzed.

2. Materials and methods

2.1. Chemicals and instruments

Experimental chemicals include diclofenac (purity > 99%, National Institutes for Food and Drug Control, Shanghai, China), NaOH, Na_2SO_4, H_2SO_4, Ag_2SO_4, HNO_3, $PdCl_2$, polytetrafluoroethylene (PTFE) (w/w = 70%), NH_4Cl, aqueous ammonia (v/v = 28%), and NaH_2PO_3. Except for diclofenac, all others used in this study were of analytical grade, and purchased from Beijing Chemical Works (Beijing, China).

Instruments used for electrode preparation include AR2140-type electronic analytical balance, DHG-9041A electrothermal constant-temperature oven, DS-5510DTH-type ultrasonic cleaner, DZTW-type heating jacket, HH-501-type super thermostatic water-circulator bath, 769 YP-15A-type manual powder tablet machine, and DZF-6020-type vacuum dry box.

The detection and analytic equipment include high performance liquid chromatography (HPLC, Shimadzu, Japan), Thermo 3-star table model pH meter, and RST electrochemical workstation (Zhengzhou Shiruisi Technology Co., Ltd., China).

2.2. Preparation of electrodes

1. Pristine MWCNTs were refluxed in the HNO_3 solution for 12 h followed by filtering and washing with deionized water until the solution reaches pH 7. The purified MWCNTs were dried in an oven at 100°C for 24 h.
2. The purified MWCNTs and PTFE were added into a 100 mL beaker containing 60 mL of ethanol and then dispersed uniformly by ultrasonication to form a homogeneous black suspension. After oven drying, the mixture was crushed into powder and pressed by tablet press machine at room temperature to prepare the MWCNTs reference electrode.
3. To make the Pd/MWCNTs-modified electrode, the purified MWCNTs were added to the palladium electrolyte in a water bath for 1 h followed by filtering and washing with de-ionized water. The modified MWCNTs were dried in a vacuum dry box at 100°C for 24 h. Then, the Pd/MWCNTs electrode was prepared using the above-mentioned procedure in step 2, except for the use of modified MWCNTs.

The composition of the palladium electrolyte used for the modified electrode was 4 $g{\cdot}L^{-1}$ $PdCl_2$, 54 $g{\cdot}L^{-1}$ NH_4Cl, 320 $mL{\cdot}L^{-1}$ aqueous ammonia (v/v = 28%), and 20 $g{\cdot}L^{-1}$ NaH_2PO_3.

2.3. Experimental procedure and analysis

Electrolysis experiments were carried out in an electrochemical cell using the Pd/MWCNTs cathode and Pt anode. The pH was adjusted to a target value using NaOH and H_2SO_4. The reaction mixture was magnetically stirred under a given applied voltage at room temperature for a given time. After completion of the electrochemical reaction, the concentration of diclofenac was determined using HPLC-MS.

The removal efficiency of diclofenac was calculated using Eq. (1), where η is the removal efficiency, C_0 is the initial diclofenac concentration, and C is the residual diclofenac concentration:

$$\eta = \left(C_0 - C\right) / C_0 \tag{1}$$

3. Results and discussion

3.1. Characterization of Pd/MWCNTs electrode

3.1.1. SEM analysis

To be useful in electro-reduction applications, it is necessary to overcome CNT's extreme hydrophobicity which could result in serious aggregations in polar solutions. HNO_3 is frequently used to tailor their surfaces without affecting the intrinsic structures. As high as 9.5% of oxidation level (measured by X-ray photoelectron spectroscopy) can be achieved with 70% HNO_3 and modified by hydroxyl, carboxyl, and carbonyl functional groups [33]. Fig. 1 shows scanning electronic microscopy (SEM) images of pristine (a) and purified (b) MWCNTs. It was found that MWCNTs were trimmed much shorter after the acid treatment, which improved their specific surface area, number of active sites, dispersity, and hydrophilicity. The surface functional groups played a key role as active centers in the deposition of Pd on the surface of MWCNTs, which promoted the uniform deposition of Pd [34].

Fig. 1(c) shows that well-dispersed Pd nanoparticles were homogeneously attached to the functional groups on the external walls of MWCNTs and the deposition of Pd on MWCNTs was similar to that on metals [35]. Although it is revealed the well distribution of Pd on MWCNT and a relatively large degree of agglomeration is observed which is in accordance with previous study [36], the particle sizes observed were distributed in a very narrow range (2–5 nm). These results accord with the general opinion that the activated MWCNTs surface is suitable for anchoring metal particles [37]. On the other hand, the very small sizes of Pd particles could provide substantial amount of catalytic sites combining with the X-ray diffraction (XRD) analysis. It can also be seen from Fig. 1(c) that there are carbon nanotubes that bridge the palladium agglomerations, which can serve to enhance the electrochemical connection between palladium catalyst particles [38].

3.1.2. XRD analysis

The XRD spectra of the Pd standard, MWCNTs and the modified electrode are presented in Fig. 2. In comparison with pure MWCNTs, the XRD spectrum of the Pd/MWCNTs electrode showed three additional diffraction peaks at 40.1°, 68.1°, and 82.1° corresponding to the respective (1 1 1), (2 2 0), and (3 1 1) planes of Pd standard. These peak positions are consistent with a face-centered cubic arrangement [39]. A peak at 26.5° was noticed, which is indicative of the excess carbon nanotubes present. Another carbon (004) peak is also observed at 54.6°. The XRD results illustrate that the active phases of catalysts are in the form of metallic Pd [40], and the intensity of Pd with and without PTFE is identical which means no aggregation or other change occurred. The (220) peak can be used to calculate the crystallite sizes of the Pd nanoparticles because the isolation from graphite diffraction peaks, according to Scherrer's equation:

$$d = \frac{0.9\lambda}{B\cos\theta} \qquad (2)$$

where d is the crystallite size, B is the width of the diffraction peak (in radians), θ is the angle at the position of the peak, and λ is the X-ray wavelength (CuKα = 1.54056 Å). Thus, the mean particle size of these Pd-MWCNT catalysts is 3.2 nm. The MWCNTs-supported Pd catalyst had much smaller crystallite size than AC (6.6 nm) and graphite (10.6 nm). The calculated Pd size is quite approximated to the size observed in SEM which proved the uniform and homogeneous deposition of Pd particles [41].

3.1.3. Cyclic voltammetry analysis

The Pd/MWCNTs working electrode was tested using an Hg/$HgCl_2$-saturated KCl as the reference electrode and a platinum wire as the auxiliary electrode. The cyclic voltammetry (CV) curve of the Pd/MWCNTs-modified electrode was recorded in 0.1 mol·L^{-1} Na_2SO_4 solution at 50 mV·s^{-1} scan rate with 5 s residence time. The reference CV curves were recorded separately in 0.1 mol·L^{-1} Na_2SO_4 solution (blank solution) and the diclofenac solution.

No redox peaks were detected for the blank solution as seen in Fig. 3. For the two CV cycles in diclofenac solution, the peak oxidation (anodic) current was –4.59 mA for potentials between 0.4 and 0.6 V, and the peak reduction (cathodic) current was 3.94 mA for potentials between 0.1 and 0.3 V at the Pd/MWCNTs electrode. The higher redox peak intensities indicate enhanced electrochemical reactivity [42]. Moreover, the peak potential for diclofenac reduction is more positive than the evolution potential of hydrogen (approximately –1.0 V vs. an Ag/AgCl electrode), which illustrate a higher

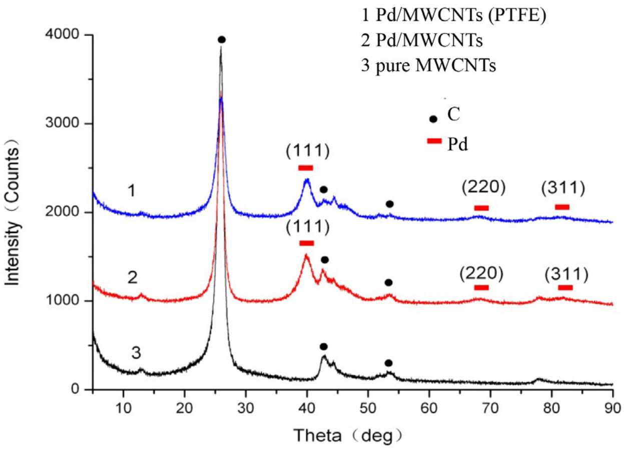
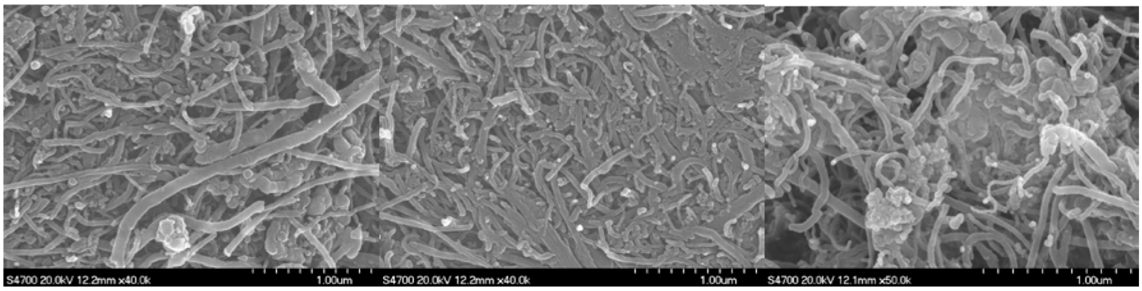


Fig. 2. XRD patterns of Pd/MWCNTs (PTFE), Pd/MWCNTs and pure MWCNTs.



(a) (b) (c)

Fig. 1. SEM analysis of pristine MWCNTs (a), purified MWCNTs (b), and Pd/MWCNTs (c).

energy efficiency at a proper potential. These results confirmed the reductive degradation of diclofenac, and a good dechlorination performance on Pd/MWCNTs electrode. Moreover, the CV analysis is a useful method for pharmaceutical drug detection [31].

3.2. Effect of feed concentration

The influence of the feed concentration of diclofenac was investigated under the following electrolysis conditions: 1,000 mg·L^{-1} Na_2SO_4, pH 10, and 30 V for 2 h. Fig. 4 shows the removal efficiency of diclofenac as a function of the initial diclofenac concentration.

It is found that the removal efficiency of diclofenac increased continuously with feed concentration of diclofenac. This result can be explained by electrocatalytic dechlorination mechanism put forward by Quintus Fernando and Korte [43] and Tsyganok [44]. The electro-catalytic reduction of diclofenac is initiated by the reduction of hydrogen ions, rather than the direct reduction of chlorinated organic compounds. Instead, dechlorination is completed with active hydrogens on the surface of the electrode which is an indirect reduction reaction limited by mass transfer. Therefore, relative high mass transfer coefficients tend to be achieved in higher density of diclofenac, resulting in enhanced dechlorination efficiencies, which is in accordance with previous study [45].

The MWCNTs electrode demonstrated higher removal efficiency compared with that of the graphite electrode due to its larger surface area and excellent hydrogen storage capacity. The main active catalysts for the diclofenac degradation were H· and hydrogen from the dechlorination process. The formation of a large number of bubbles on the graphite electrode during the electrolysis process was observed, whereas almost no bubbles were generated on the MWCNTs electrode. This further confirmed that the MWCNTs electrode has excellent hydrogen storage capacity. In addition, the bubbles formed on the graphite electrode may prevent the direct contact between the intermediates of diclofenac and the electrode, affecting the electrolysis process.

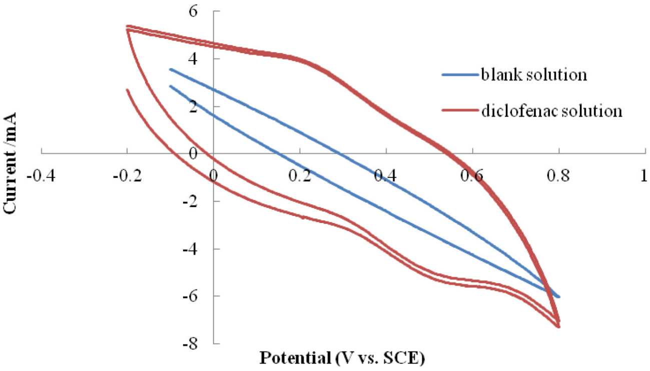


Fig. 3. CV of Pd/MWCNTs in the blank solution and diclofenac solution.

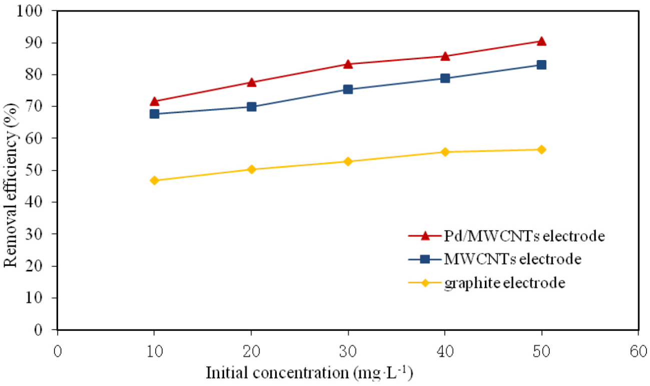


Fig. 4. Effect of feed concentration on diclofenac removal efficiency.

The Pd/MWCNTs electrode exhibited higher diclofenac removal efficiency indicating the dechlorinating ability of Pd [32]. Diclofenac formed different chlorinated and non-chlorinated compounds as the degradation intermediates; hence, the dechlorination efficiency greatly increased with increase in the initial diclofenac concentration. The reduction reaction at the cathode was: $H^+ + e \rightarrow H\cdot$, $H\cdot + RCl \rightarrow R + H^+ + Cl^-$, and the Cl^- ions oxidized into Cl_2 at the anode. Moreover, Cl_2 is a strong oxidant, which could promote the electrolysis.

Diclofenac degradation is preferred over the dechlorination because it is easy to break at the –NH– bond connecting the aromatic rings in diclofenac. However, the presence of palladium could effectively improve the dechlorination efficiency.

3.3. Effect of applied voltage

Electrolysis process was carried out under different constant voltages to study the effect of applied voltage on the degradation process of diclofenac. The electrolysis conditions used for this study were as follows: 50 mg·L^{-1} diclofenac, 1,000 mg·L^{-1} Na_2SO_4, and pH 10 for 2 h. The applied voltage varied from 5 to 35 V, ensuring the value was below 36 V, which meant the safety voltage for human body.

The removal efficiency of diclofenac was found to be higher at a higher applied voltage. Fig. 5 shows that the removal efficiency of diclofenac significantly increased from 52.7% to 90.6% with increase in the applied voltage from 10 to 30 V using the Pd/MWCNTs electrode, and finally increased to 92% at 35 V. A rapid increase in the diclofenac removal efficiency was observed below 30 V, whereas the removal rate slowed down and increased more gradually above 30 V. The graphite and MWCNTs electrodes exhibited similar trend to

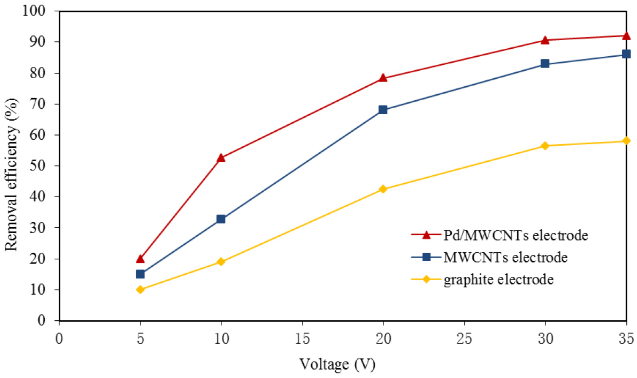


Fig. 5. Effect of applied voltage on diclofenac removal efficiency.

that of the modified MWCNTs electrode. The observed trend is because of the increase in the active groups such as H_2O_2 (strong oxidizer) and HO· formed at the anode with increasing applied voltage below 30 V.

Moreover, it is also because the elemental palladium has a saturated active hydrogen storage concentration in which volume ratio of H/Pd equals to 500–2,800:1. Therefore the dechlorination rate on Pd/MWCNT electrode is also restricted by the saturated active hydrogen storage concentration. At low voltages, it takes a certain time to reach the saturation concentration which leads to the low dechlorination efficiency. On the contrary, as the voltage increases, the active hydrogen concentration at the electrode interface is quickly saturated and then provide the active hydrogen required for dechlorination. While the voltage is beyond 30 V, the reaction rate is no longer restricted by active hydrogen, but the mass transfer of diclofenac which decelerates the removal efficiency. Another reason may be the bubbles formed at high voltages hindered the direct contact between diclofenac and electrode. Similar results were observed for the electrocatalytic hydrogenolysis dechlorination of chlorinated phenols using a Pd-modified Ti cathode by the Scott group [46]. So the effective electrode area became the new limiting factor for electrolysis above 30 V. The effective area was selected such that the removal efficiency and dechlorination could increase gradually. The higher applied voltage could lead to an energy loss, and could promote a side reaction. Therefore, we chose 30 V as the optimum applied voltage.

In a small experiment, we found that the wet potassium iodide-starch test paper turned blue next to the anode generating a pungent smell, which is characteristic of Cl_2. During the dechlorination process, chloride ions in the solution above certain concentration could oxidize to Cl· atoms at the anode followed by the formation and release of Cl_2.

3.4. Effect of pH

The pH of the solution was adjusted to a value between 8 and 12 using NaOH and H_2SO_4. The results of the pH study are shown in Fig. 6.

The H^+ or OH^- concentration plays an important role in the degradation process [35]. The pH range of 8–12 was chosen because diclofenac is readily soluble under alkaline than acidic conditions. Fig. 6 shows that the removal efficiency of diclofenac increased rapidly with increase in a pH value from 8 to 10, and the increase was more gradual at a pH above 10. OH^- density can drastically promote the electrocatalytic dechlorination process. This positive effect of OH^- probably originates from its neutralization towards the adsorbed HCl produced by a catalytic hydrogenation step between adsorbed diclofenac and chemisorbed hydrogen. The adsorbed HCl would block the reaction sites if it was not quickly removed from the cathode surface [47,48].

The initial rapid increase was because diclofenac has Cl groups and formed ClO^-, which is the dominant oxidant species under the alkaline conditions. However, under alkaline conditions, dechlorination is suffocated because the production of active hydrogen keeps low. Meanwhile, the –NH– bond is difficult to break under the highly alkaline condition, which slowed down the removal rate.

The Pd/MWCNTs electrode showed the best removal efficiency at pH 10 compared with that of the graphite and MWCNTs electrodes.

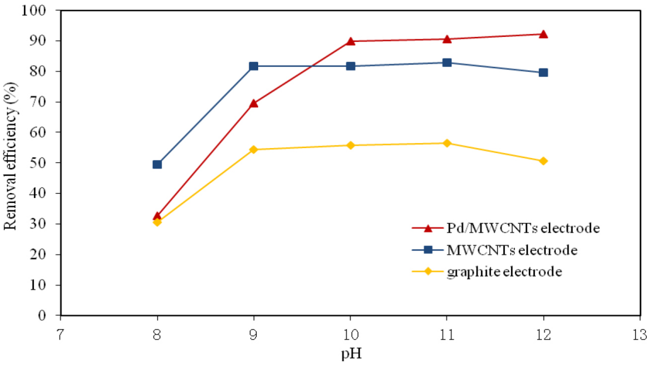


Fig. 6. Effect of pH on diclofenac removal efficiency.

3.5. Effect of electrolyte concentration

To investigate the effect of electrolyte concentration, Na_2SO_4 was selected as the supporting electrolyte in this experiment (Fig. 7). The electrolysis conditions were as follows: 50 mg·L^{-1} diclofenac, 30 V, and pH 10 for 2 h.

The removal efficiency of diclofenac greatly increased with increasing Na_2SO_4 concentration from 500 to 1,000 mg·L^{-1} and then showed a gradual increase with further increase in the concentration from 1,000 to 4,000 mg·L^{-1}. The use of Na_2SO_4 solution as the supporting electrolyte provided a large number of conductive free ions, which increased the ionic strength and solution conductivity at higher concentration. However, when the Na_2SO_4 concentration was too high, some of the electric energy was converted into heat, thereby increasing the temperature of the solution and resulting in some energy loss.

As a result, 1,000 mg·L^{-1} was determined as the optimal Na_2SO_4 concentration and it is close to the salt concentration in the tap water.

3.6. Effect of electrolysis time

Batch experiments were carried out to determine the optimal electrolysis time. The electrolysis conditions were as follows: 50 mg·L^{-1} diclofenac, 30 V, pH 10, and 1,000 mg·L^{-1} Na_2SO_4. The results of the degradation study as a function of electrolysis time for all the electrodes are shown in Fig. 8.

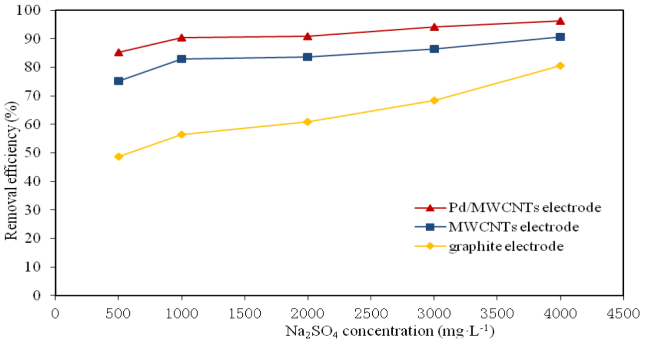


Fig. 7. Effect of electrolyte concentration on diclofenac removal efficiency.

The removal efficiency and dechlorination efficiency increased with increase in the electrolysis time. Fig. 8 shows that the removal efficiency of diclofenac increased significantly in first few hours for the MWCNTs and the Pd/MWCNTs electrodes but the increase slowed down over time. This could be attributed to the increase in the concentration of oxidant ClO^- due to dechlorination in first 2 h, which promoted the degradation of diclofenac. Nevertheless, the ClO^- concentration decreased after 2 h, affecting the removal efficiency and producing a large number of intermediates. Although removal efficiency of 98% can be achieved after 8 h, the 2-h electrolysis with a removal efficiency of 90.6% was considered as the optimal electrolysis time for the sake of time and cost saving.

3.7. Kinetics of diclofenac degradation

The kinetics of diclofenac degradation using the Pd/MWCNTs electrode was investigated at pH 10 and 30 V for 2 h. The simulation results are shown in Table 1.

Linear fit results showed that the electrochemical reductive degradation of diclofenac was pseudo-first-order reaction, which indicated that the degradation of diclofenac occurred at the electrode surface. This agrees well with the related result by using Pd/PPy–SLS/Ti electrode [49].

3.8. Analysis of degradation process

The intermediates and final degradation products were analyzed using HPLC-MS. The possible degradation mechanism is proposed in Fig. 9.

Two paralleled possible degradation pathways for diclofenac were detected. The first removal pathway was initiated by cleavage diclofenac into phenylacetic acid and 2,6-dichloroaniline because the –NH– bond was easily broken. Then, intermediates could be further hydroxylated to replace the chlorine atoms of the benzene ring and yield phenylamine at the cathode. The second pathway was originated from dihydrogen process to form $C_{14}H_9Cl_2NO$, followed by cleavage on the unstable N-heterocyclic rings to form C_8H_9NO or $C_7H_5Cl_2NO$. Compound $C_7H_5Cl_2NO$ was first hydroxylated into C_7H_9N and oxidized into phenylamine together with C_8H_9NO. The accumulation of phenylamine in the mixed electrolyte is responsible for the slower mineralization which control the degradation rate to some extent. Altogether, the dechlorination of diclofenac was achieved at the Pd/MWCNTs interface similar to the dechlorination of 4-chlorophenol [43].

The Cl· atoms derived from diclofenac tend to form Cl_2 at the anode electrode. The acceleration attributed from chloride and chlorine oxides was paid much attention because toxic by-products are very likely to form. To investigate the mineralization of diclofenac, concentrations of chloride ions significantly increased as the electro-reduction proceeded, and reached 93% of initial diclofenac concentration after 2 h. Significant release of chloride ions indicates mineralization of diclofenac to HCl and CO_2 in this system. Similar degradation process was also analyzed in pyrite Fenton system and electro-Fenton system [50,51].

3.9. Stability of Pd/MWCNTs electrode

MWCNT is proved in previous studies as stable material both physically and chemically. Sn-Sb/MWCNT, Ce/MWCNT, Pd/Graphene, etc. were fabricated and showed

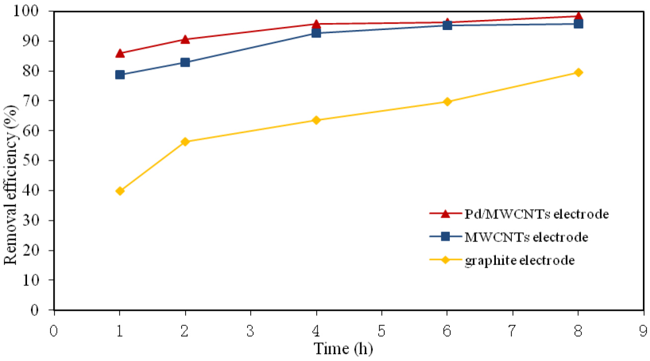


Fig. 8. Effect of electrolysis time on diclofenac removal efficiency.

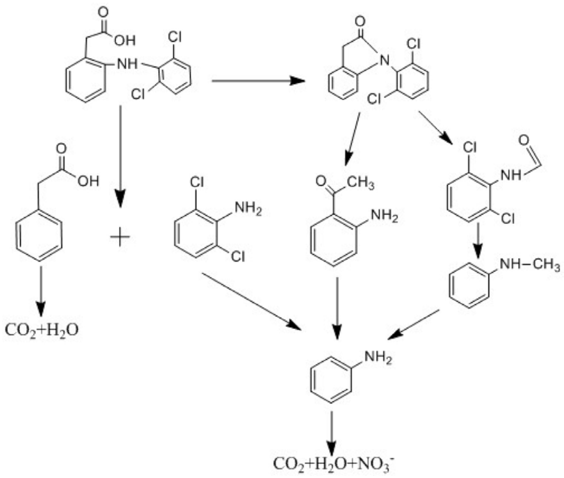


Fig. 9. Electrochemical degradation mechanism of diclofenac.

Table 1
Kinetics of diclofenac degradation

Kinetic models	Kinetic equations	Rate constant	R^2
Pseudo-zero-order	$q_t = k_0 t + q_e$	0.0013	0.9668
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	0.3656	0.9961
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	0.0211	0.9595

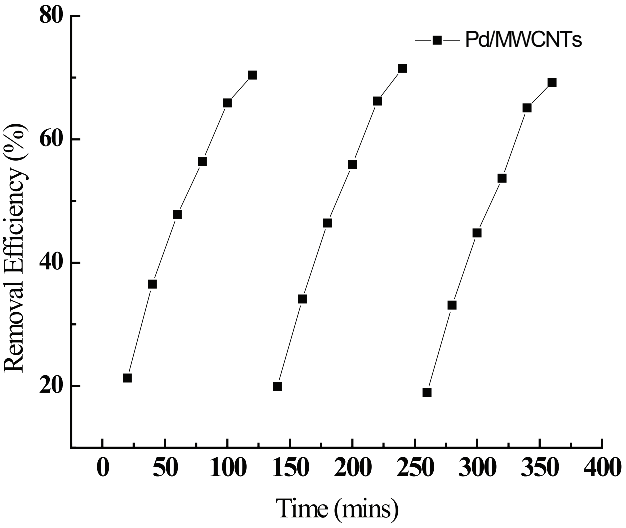


Fig. 10. Successive electrolysis of diclofenac on Pd/MWCNTs electrode.

great performance in electro-oxidation and stability [25,29,52]. As shown in Fig. 10, the stability of Pd/MWCNT electrode was evaluated with three cycles under reaction with initial concentration of 10 mg/L, voltage of 30 V, Na_2SO_4 dosage of 1,000 mg/L, reaction time of 2 h, respectively. It is indicated that 70.4%, 71.5%, and 69.2% of removal efficiency were achieved during the first, second, and third cycles, suggesting a good stability and reusability of the novel Pd/MWCNT electrode.

4. Conclusion

Electrochemical reductive degradation of diclofenac in aqueous solution was investigated in this study. The Pd/MWCNTs electrode was used as the cathode. Physical characterization, such as SEM, XRD, and CV, demonstrated fine partial sizes and distribution were achieved. Batch experiment results showed that the removal efficiency of diclofenac was above 90% under the following conditions: the diclofenac concentration of 50 mg·L^{-1}, the applied voltage of 30 V, the pH of 10, the Na_2SO_4 concentration of 1,000 mg·L^{-1}, and the electrolysis time of 2 h. Degradation of diclofenac was found to follow pseudo-first-order kinetics. Moreover, the two possible degradation pathways of diclofenac were proposed, and stability of the electrode was proved reliable.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (Project Nos. 51278022 and 51178022) for financial support. Additionally, the analytical work was supported by the Water Pollution Control Laboratory of Beijing University of Chemical Technology.

References

[1] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: agents of subtle change, Environ. Health Perspect., 107 (1999) 907–938.

[2] G. Ghasemzadeh, M. Momenpour, F. Omidi, M.R. Hosseini, M. Ahani, A. Barzegari, Applications of nanomaterials in water treatment and environmental remediation, Front. Environ. Sci. Eng., 8 (2014) 471–482.

[3] M.L. Hedgespeth, Y. Sapozhnikova, P. Pennington, A. Clum, A. Fairey, E. Wirth, Pharmaceuticals and personal care products (PPCPs) in treated wastewater discharges into Charleston Harbor, South Carolina, Sci. Total Environ., 437 (2012) 1–9.

[4] Y.U. Fei, M.A. Jie, W.U. Yanqing, Adsorption of toluene, ethylbenzene and xylene isomers on multi-walled carbon nanotubes oxidized by different concentration of NaOCl, Front. Environ. Sci. Eng., 6 (2012) 320–329.

[5] W. Xu, W. Yan, W. Huang, L. Miao, L. Zhong, Endocrine-disrupting chemicals in the Pearl River Delta and coastal environment: sources, transfer, and implications, Environ. Geochem. Health, 36 (2014) 1095–1104.

[6] D.J. Lapworth, N. Baran, M.E. Stuart, R.S. Ward, Emerging organic contaminants in groundwater: a review of sources, fate and occurrence, Environ. Pollut., 163 (2012) 287–303.

[7] J. Roberts, A. Kumar, J. Du, C. Hepplewhite, D.J. Ellis, A.G. Christy, S.G. Beavis, Pharmaceuticals and personal care products (PPCPs) in Australia's largest inland sewage treatment plant, and its contribution to a major Australian river during high and low flow, Sci. Total Environ., 541 (2016) 1625–1637.

[8] M. Carballa, F. Omil, J.M. Lema, M. Llompart, C. GarcíA-Jares, I. RodríGuez, M. Gómez, T. Ternes, Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant, Water Res., 38 (2004) 2918–2926.

[9] G. Dai, J. Huang, W. Chen, B. Wang, G. Yu, S. Deng, Major pharmaceuticals and personal care products (PPCPs) in wastewater treatment plant and receiving water in Beijing, China, and associated ecological risks, Bull. Environ. Contam. Toxicol., 92 (2014) 655–661.

[10] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, S. Liang, X.C. Wang, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, Sci. Total Environ., 473–474 (2014) 619–641.

[11] S. Weigel, J. Kuhlmann, H. Hühnerfuss, Drugs and personal care products as ubiquitous pollutants: occurrence and distribution of clofibric acid, caffeine and DEET in the North Sea, Sci. Total Environ., 295 (2002) 131–141.

[12] N. Nakada, K. Kiri, H. Shinohara, A. Harada, K. Kuroda, S. Takizawa, H. Takada, Evaluation of pharmaceuticals and personal care products as water-soluble molecular markers of sewage, Environ. Sci. Technol., 42 (2008) 6347–6353.

[13] K. Kuroda, M. Murakami, K. Oguma, Y. Muramatsu, H. Takada, S. Takizawa, Assessment of groundwater pollution in Tokyo using PPCPs as sewage markers, Environ. Sci. Technol., 46 (2012) 1455–1464.

[14] L.H. Heckmann, A. Callaghan, H.L. Hooper, R. Connon, T.H. Hutchinson, S.J. Maund, R.M. Sibly, Chronic toxicity of ibuprofen to *Daphnia magna*: effects on life history traits and population dynamics, Toxicol. Lett., 172 (2007) 137–145.

[15] N.H. Tran, J. Hu, S.L. Ong, Simultaneous determination of PPCPs, EDCs, and artificial sweeteners in environmental water samples using a single-step SPE coupled with HPLC–MS/MS and isotope dilution, Talanta, 113 (2013) 82–92.

[16] J.W. Kim, H. Ishibashi, R. Yamauchi, N. Ichikawa, Y. Takao, M. Hirano, M. Koga, K. Arizono, Acute toxicity of pharmaceutical and personal care products on freshwater crustacean (*Thamnocephalus platyurus*) and fish (*Oryzias latipes*), J. Toxicol. Sci., 34 (2009) 227–232.

[17] F. Pomati, S. Castiglioni, E. Zuccato, R. Fanelli, D. Vigetti, C. Rossetti, D. Calamari, Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic cells, Environ. Sci. Technol., 40 (2006) 2442–2447.

[18] S. Bae, D. Kim, W. Lee, Degradation of diclofenac by pyrite catalyzed Fenton oxidation, Appl. Catal., B, 134 (2013) 93–102.

[19] H. Faber, D. Melles, C. Brauckmann, C.A. Wehe, K. Wentker, U. Karst, Simulation of the oxidative metabolism of diclofenac by electrochemistry/(liquid chromatography/)mass spectrometry, Anal. Bioanal. Chem., 403 (2012) 345–354.

[20] C. Adams, M. Asce, Y. Wang, K. Loftin, M. Meyer, Removal of antibiotics from surface and distilled water in conventional water treatment processes, J. Environ. Eng., 128 (2002) 253–260.

[21] P.E. Stackelberg, J. Gibs, E.T. Furlong, M.T. Meyer, S.D. Zaugg, R.L. Lippincott, Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds, Sci. Total Environ., 377 (2007) 255–272.

[22] O.A. Arikan, Degradation and metabolization of chlortetracycline during the anaerobic digestion of manure from medicated calves, J. Hazard. Mater., 158 (2008) 485–490.

[23] Q. Liu, J. Yu, Y. Xu, J. Wang, L. Ying, X. Song, G. Zhou, J. Chen, Bioelectrocatalytic dechlorination of trichloroacetic acid at gel-immobilized hemoglobin on multiwalled carbon nanotubes modified graphite electrode: kinetic modeling and reaction pathways, Electrochim. Acta, 92 (2013) 153–160.

[24] J. Hirose, F. Kondo, T. Nakano, T. Kobayashi, N. Hiro, Y. Ando, H. Takenaka, K. Sano, Inactivation of antineoplastics in clinical wastewater by electrolysis, Chemosphere, 60 (2005) 1018–1024.

[25] Q. Shi, H. Wang, S. Liu, Z. Bian, Electrocatalytic degradation of 2,4-dichlorophenol using a Pd/graphene gas-diffusion electrode, RSC Adv., 4 (2014) 56263–56272.

[26] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, Chem. Rev., 109 (2009) 6541–6569.

[27] S.K. Smart, A.I. Cassady, G.Q. Lu, D.J. Martin, The biocompatibility of carbon nanotubes, Carbon, 44 (2006) 1034–1047.

[28] Z. He, M. Dai, K. Lin, C. Wu, M. Qian, J. Chen, S. Song, Kinetic model for electrochemical hydrodechlorination of 2-chlorobiphenyl on a palladium-modified nickel foam electrode in a plug flow reactor, Int. J. Electrochem. Sci., 9 (2014) 6059–6067.

[29] X. Hu, Y. Yu, Z. Sun, Preparation and characterization of cerium-doped multiwalled carbon nanotubes electrode for the electrochemical degradation of low-concentration ceftazidime in aqueous solutions, Electrochim. Acta, 199 (2016) 80–91.

[30] W. Wu, Z.H. Huang, Z. Hu, C. He, T.T. Lim, High performance duplex-structured SnO_2 anode modified by SnO_2-Sb-CNT composite for bisphenol A removal: electrochemical oxidation enhanced by adsorption, Sep. Purif. Technol., 179 (2017) 25–35.

[31] D. Deng, F. Deng, B. Tang, J. Zhang, J. Liu, Electrocatalytic reduction of low-concentration thiamphenicol and florfenicol in wastewater with multi-walled carbon nanotubes modified electrode, J. Hazard. Mater., 332 (2017) 168–175.

[32] H. An, L. Pan, H. Cui, D. Zhou, B. Wang, J. Zhai, Q. Li, Y. Pan, Electrocatalytic performance of Pd nanoparticles supported on TiO_2-MWCNTs for methanol, ethanol, and isopropanol in alkaline media, J. Electroanal. Chem., 741 (2015) 56–63.

[33] K.A. Wepasnick, B.A. Smith, K.E. Schrote, H.K. Wilson, S.R. Diegelmann, D.H. Fairbrother, Surface and structural characterization of multi-walled carbon nanotubes following different oxidative treatments, Carbon N. Y., 49 (2011) 24–36.

[34] Y.C. Chiang, W.H. Lin, Y.C. Chang, The influence of treatment duration on multi-walled carbon nanotubes functionalized by H_2SO_4/HNO_3 oxidation, Appl. Surf. Sci., 257 (2011) 2401–2410.

[35] Y. Fu, Z.D. Wei, S.G. Chen, L. Li, Y.C. Feng, Y.Q. Wang, X.L. Ma, M.J. Liao, P.K. Shen, S.P. Jiang, Synthesis of Pd/TiO_2 nanotubes/Ti for oxygen reduction reaction in acidic solution, J. Power Sources, 189 (2009) 982–987.

[36] K. Jukk, N. Alexeyeva, C. Johans, K. Kontturi, K. Tammeveski, Oxygen reduction on Pd nanoparticle/multi-walled carbon nanotube composites, J. Electroanal. Chem., 666 (2012) 67–75.

[37] Z.Q. Liu, J. Ma, Y.H. Cui, Carbon nanotube supported platinum catalysts for the ozonation of oxalic acid in aqueous solutions, Carbon N. Y., 46 (2008) 890–897.

[38] T. Onoe, S. Iwamoto, M. Inoue, Synthesis and activity of the Pt catalyst supported on CNT, Catal. Commun., 8 (2007) 701–706.

[39] C.L. Lee, Y.C. Huang, L.C. Kuo, Y.W. Lin, Preparation of carbon nanotube-supported palladium nanoparticles by self-regulated reduction of surfactant, Carbon N. Y., 45 (2007) 203–206.

[40] T. Das, S. Banerjee, K. Dasgupta, J.B. Joshi, V. Sudarsan, Nature of the Pd–CNT interaction in Pd nanoparticles dispersed on multi-walled carbon nanotubes and its implications in hydrogen storage properties, RSC Adv., 5 (2015) 41468–41474.

[41] R.D. Morgan, A. Salehi-Khojin, R.I. Masel, Superior formic acid oxidation using carbon nanotube-supported palladium catalysts, J. Phys. Chem. C, 115 (2011) 19413–19418.

[42] Y. Lu, M. Wang, C. Yuan, J. Zhao, J. Yu, Cyclic voltammetry for synthesizing carbon supported Pt-Cu alloy with superior oxygen reduction activity, Int. J. Electrochem. Sci., 10 (2015) 2825–2838.

[43] I.F.C. Quintus Fernando, N. Korte, Electrochemical dechlorination of 4-chlorophenol to phenol, Environ. Sci. Technol., 31 (1997) 1074–1078.

[44] A.I. Tsyganok, I. Yamanaka, K. Otsuka, ChemInform Abstract: Electrocatalytic Dehalogenation of Chloroaromatics on Palladium-Loaded Carbon Felt Cathode in Aqueous Medium, Chem. Lett., 4 (1998) 303–304.

[45] B. Yang, G. Yu, D. Shuai, Electrocatalytic hydrodechlorination of 4-chlorobiphenyl in aqueous solution using palladized nickel foam cathode, Chemosphere, 67 (2007) 1361–1367.

[46] H. Cheng, K. Scott, P.A. Christensen, Electrochemical hydrodehalogenation of chlorinated phenols in aqueous solutions I. Material aspects, J. Electrochem. Soc., 150 (2003) D17–D24.

[47] C. Ma, H. Ma, Y. Xu, Y. Chu, F. Zhao, The roughened silver–palladium cathode for electrocatalytic reductive dechlorination of 2,4-Dichlorophenoxyacetic acid, Electrochem. Commun., 11 (2009) 2133–2136.

[48] H.X. Ying, Q.C. Qian, X.M. Hong, H. Yan, Z. Hong, C.A. Ma, Optimisation of electrocatalytic dechlorination of 2,4-dichlorophenoxyacetic acid on a roughened silver-palladium cathode, Electrochim. Acta, 96 (2013) 90–96.

[49] Z. Sun, X. Wei, X. Hu, K. Wang, H. Shen, Electrocatalytic dechlorination of 2,4-dichlorophenol in aqueous solution on palladium loaded meshed titanium electrode modified with polymeric pyrrole and surfactant, Colloids Surf., A, 414 (2012) 314–319.

[50] J. Hofmann, U. Freier, M. Wecks, S. Hohmann, Degradation of diclofenac in water by heterogeneous catalytic oxidation with H_2O_2, Appl. Catal., B, 70 (2007) 447–451.

[51] W. Wu, Z. Huang, Z. Hu, C. He, T. Lim, High performance duplex-structured SnO_2-Sb-CNT composite anode for bisphenol A removal, Sep. Purif. Technol., 179 (2017) 25–35.