Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–8

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Pseudo first order kinetics and proposed transformation products pathway for the degradation of diclofenac using graphite–PVC composite as anode.

Zainab Haider Mussa[a,c], Fouad Fadhil Al-Qaim[b,c,*], Mohamed Rozali Othman[c,d], Md Pauzi Abdullah[c,d], Jalifah Latip[c], Zuriati Zakria[e]

[a] *Faculty of Pharmacy, University of Babylon, PO Box 4, Hilla, Iraq*
[b] *Department of Chemistry, Faculty of Sciences for Women, University of Babylon, PO Box 4, Hilla, Iraq*
[c] *School of Chemical Sciences and Food Technology, Faculty of Sciences and Technology, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia*
[d] *Centre for Water Research and Analysis (ALIR), Faculty of Sciences and Technology, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia*
[e] *Environmental and Green Technology, Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia*

ARTICLE INFO

Article history:
Received 18 July 2016
Revised 10 December 2016
Accepted 18 December 2016
Available online xxx

Keywords:
Electrochemical degradation
Diclofenac
Kinetics
ToF/MS
Transformation products
E. coli bacteria

ABSTRACT

The electrochemical degradation kinetics of diclofenac (DCF) using graphite–PVC composite as anode was assessed in pure water and effluent wastewater. Effects of initial concentration of diclofenac, chloride ion (Cl^-) loading, type of sample and applied voltage were determined to test and validate a kinetic model for the oxidation of diclofenac by the electrochemical oxidation process. The results revealed that the electrochemical oxidation rates of diclofenac followed pseudo first-order kinetics. The rate constant values ranged from 0.018 to 0.173 /min, depending on the operating parameters. However, 6 V and 4 g/L NaCl were selected for further experiments (96.9% removal of diclofenac and 0.0078 kWh/g diclofenac consumption energy) after 30 min and at 20 mg/L of diclofenac. High consumption energy (0.0303 kWh/g diclofenac) was accompanied with high applied voltage of 10 V so it was not considered in this study.

Liquid chromatography time-of-flight mass spectrometry (LC–ToF/MS) was used for the elucidation of the main transformation products (TPs) which are resulted from the degradation of diclofenac (DCF) during the application of graphite–PVC composite as anode in aqueous matrices. The toxicity of DCF and its TPs was assessed against *E. coli* bacteria at different incubation time.

1. Introduction

Diclofenac (DCF), a nonsteroidal anti-inflammatory (NSAID) drug, was one of the top most sold drugs in Malaysia in 2010 [1].

Pharmaceuticals are increasingly detected in surface water and other water matrices because they are not removed completely in the conventional wastewater treatment plants [2-4].

Diclofenac was detected in influent, effluent of sewage treatment plants and hospital, and surface water as reported by the previous studies [5-7]. The reason may be attributed to the fact that the conventional treatments of waste water are not suitable to degrade diclofenac and other pollutants efficiently. However, it is necessary to look for alternatives. The degradation of diclofenac is investigated by various advanced oxidation processes (AOPs) under different experimental conditions: photocatalysis (TiO_2 as catalyst or Fenton reagent), direct photolysis, ozonation and sonolysis either alone or combined with ultra-violet UV. [8-13]. Recently, electrochemical oxidation process is an alternative technology for the treatment of organic pollutants in water samples even its transformation products. Simply, it is called anodic oxidation, where the direct and indirect oxidation process could have occurred on the surface of anode and/or at the bulk solution as reviewed by Moreira et al. [14].

Furthermore, diclofenac was treated by electrooxidation process using boron doped diamond electrode [15] or direct oxidation by addition oxidizing agents such chlorine dioxide [16], manganese oxide [17] and permanganate solution [18].

Several studies have demonstrated the possible negative impact of the diclofenac in the aquatic environment. Diclofenac has

---

* Corresponding author at: School of Chemical Sciences and Food Technology, Faculty of Sciences and Technology, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

E-mail address: fouadalkaim@yahoo.com (F.F. Al-Qaim).

http://dx.doi.org/10.1016/j.jtice.2016.12.031

Please cite this article as: Z.H. Mussa et al., Pseudo first order kinetics and proposed transformation products pathway for the degradation of diclofenac using graphite–PVC composite as anode., Journal of the Taiwan Institute of Chemical Engineers (2017), http://dx.doi.org/10.1016/j.jtice.2016.12.031

affected significantly the growth of several bacterial and algae species [19,20]. An interested study showed that the ecotoxicity of diclofenac and its transformation products was more toxic than those from the other compounds on adult zebrafish (*Danio rerio*) [20].

The big challenge for the degradation of diclofenac is what are the transformation products generated after degradation and how to identify these unknown compounds. Actually, the TPs varied depending on the conditions of the experiment. Some chlorinated TPs were observed after the direct oxidation of diclofenac by chlorine dioxide [16]. In electrochemical oxidation process, the generation of TPs depends on the type of electrolyte in the solution. Brillas et al. [15] used BDD electrode with Na_2SO_4 electrolyte for the degradation of DCF. The main transformation products are derivatives of hydroxyl-diclofenac (2-Hydroxyphenyl acetic acid, 2,5-Dihydroxyphenylacetic acid, 2,6-Dichloroaniline, 2,6-Dichlorohydroquinone). Al-Qaim et al. [21] used graphite–PVC as anode with NaCl electrolyte for the degradation of caffeine. However, the main TPs are chlorinated compounds ($C_8H_{10}ClN_4O_2$, $C_6H_{16}ClN_3O_5$, $C_7H_8Cl_2N_3O_5$, $C_7H_7Cl_3N_2O_6$). According to the authors' knowledge, the degradation of DCF using graphite–PVC as anode in the presence of NaCl has not been addressed yet.

In the current study, the kinetics of DCF degradation by graphite–PVC composite in pure water and wastewater was investigated. The evaluation of the potential toxicity of DCF and its TPs was provided at different times of electrochemical oxidation and different exposure time for *E. coli* bacteria. The degradation pathway of DCF was schemed to illustrate the formation of transformation products.

2. Materials and methods

2.1. Chemicals and reagents

Sodium chloride (NaCl) used as supporting electrolyte was purchased from Merck with purities of more than 99.5%. Tetrahydrofuran (THF) (CAS No 109-99-9) which is used as a solvent to dissolve the polyvinylchloride, polyvinylchloride (PVC) were purchased from Sigma Aldrich which is used adhesive to make a pellet of graphite. Diclofenac (CAS no. 15,307-79-6) was obtained from Sigma-Aldrich (USA). Pure water was supplied by EASYPure RODI (U.S.A). HPLC-grade acetonitrile (ACN), HPLC grade acetone, HPLC grade methanol and formic acid (FA) were supplied by Merck (Germany). For toxicity experiments, *E. coli* bacteria was obtained from Laboratory of Microbiology, Faculty of Sciences and Technology, University Kebangsaan Malaysia, Bangi, Malaysia, Mueller Hinton broth (nutrient broth) was obtained from Merck, Germany.

2.2. Experimental procedure

The reaction was provided by using a 100 mL pyrex glass inserted into a Pyrex glass vessel with two points, namely, an inlet and outlet water stream to control the temperature. The Pyrex glass electrochemical cell (reactor) was placed on a magnetic stirring block to keep its contents well mixed during the experiment. The graphite–PVC pellet and Pt plate were used as anode and cathode, respectively. The distance between the electrodes was approximately 2.5 cm. The electrodes were then connected to a direct current power supply (DC) (CPX200 DUAL, 35 V 10 A PSU)

The experimental design and setup of the graphite-PVC–composite electrode were mentioned in details by Mussa et al. [22]. Fig. 1 shows an interesting imagination for the making of graphite–PVC electrode.

The Pt metal foil electrode was prepared by using a Pt metal foil (99.98% purity from Aldrich chemical company). A 0.5 mm thick Pt foil was cut into approximately 1 cm × 1 cm piece. The Pt foil was then connected to a silver wire with silver conducting paint and then sealed to a glass rod. Subsequently, epoxy gum was applied to cover the silver wire connecting surface.

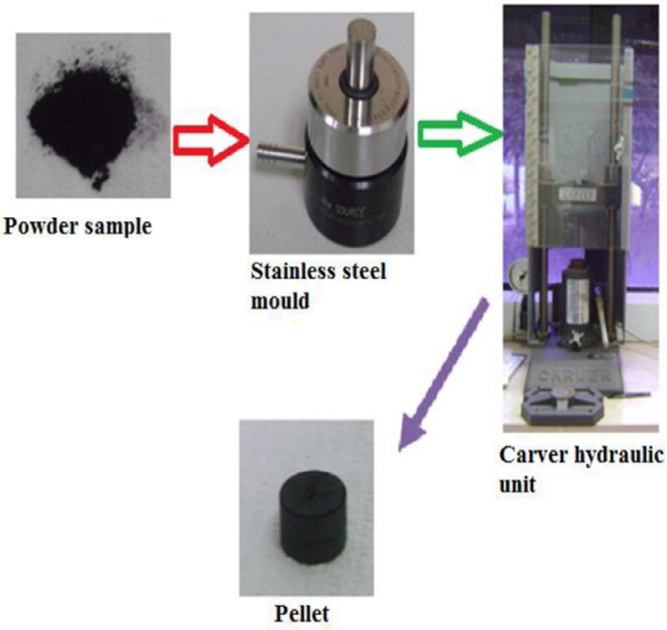

Fig. 1. A full diagram for making a graphite–PVC composite pellet.

The graphite–PVC electrode was prepared by mixing a weighed portion of graphite powder (100 mesh in size and 99.9% purity from Aldrich Chemical Company) and PVC in 4 mL tetrahydrofuran solvent. The graphite–PVC electrode was then swirled flatly to homogeneous consistency followed by drying in an oven at 50 °C for 3 h The mixture was placed in 1 cm diameter stainless steel mold and pressed at 10 ton/cm^2 by using hydraulic machine. A typical pellet contained approximately 95% of graphite and 5% of PVC. The total weight of the pellet was approximately 1.5 g. The graphite–PVC pellet was connected to a silver wire with silver conducting paint and sealed to a glass rode. Subsequently, epoxy gum was applied to cover the silver wire connecting surface.

Comparative electrochemical degradations of 50 mL solutions of diclofenac (5, 20, 50 and 100 mg/L) were made for graphite–PVC. Solutions were always kept between 22 °C and 24 °C, which was the maximum temperature that can be used in the cell without significant water evaporation during prolonged electrolysis.

2.3. Analytical methods

The evaluation of removal% for DCF during electrochemical process was achieved by high performance liquid chromatography (HPLC), from a Waters Chromatograph (Miliford-MA 1,757, USA). HPLC is equipped with a Perkin Elmir 785 A UV–visible detector and a chromolith Rp-18e, C18 column (5 µm, 100 mm × 4.8 mm). The analysis was performed in a gradient mode with 0.1% formic acid (FA) in pure water as mobile phase A and methanol as mobile phase B, at flow rate of 0.9 mL/min and a column temperature of 22–25 °C. Detection of diclofenac was made at 273 nm wavelength. The retention time of diclofenac was around 4.25 min and the total run was 5 min. The treated solutions were withdrawn every 10 min for 40 min then filtered using 0.25 µm filter syringe before injection with HPLC.

The analysis of TPs is considered an issue in this field because the formed unknown compounds require an accurate and advanced technology to build the structure or at least the empiri-

Please cite this article as: Z.H. Mussa et al., Pseudo first order kinetics and proposed transformation products pathway for the degradation of diclofenac using graphite–PVC composite as anode., Journal of the Taiwan Institute of Chemical Engineers (2017), http://dx.doi.org/10.1016/j.jtice.2016.12.031