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Coupling electrooxidation and Oxone for degradation of 2,4-Dichlorophenoxyacetic acid (2,4-D) from aqueous solutions

Nematollah Jaafarzadeh[a,b], Farshid Ghanbari[c,*], Amir Zahedi[d,*]

[a] Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran
[b] Department of Environmental Health Engineering, School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran
[c] Department of Environmental Health Engineering, Abadan School of Medical Sciences, Abadan, Iran
[d] Student Research Committee, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

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ABSTRACT

2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the most applicable of herbicides in the world. The presence of 2,4-D in aquatic environment threatens the human health and ecosystem. In current study, a hybrid process was conducted based on the combination of electrooxidation (EO) and Oxone for integration of hydroxyl and sulfate radicals. The operational parameters were investigated and 91% of 2,4-D was removed under the best condition (pH = 4.0, Oxone = 3 mM and 30 mA/cm^2). The combination of Oxone and EO indicated a synergistic effect on 2,4-D removal. NaCl and Na_2SO_4 as supporting electrolyte demonstrated similar results while $NaNO_3$ reduced the removal efficiency. The presence of Co^{2+} and Fe^{2+} enhanced 2,4-D removal through Oxone activation. EO/Oxone/Co^{2+} could completely degrade 2,4-D during 90 min reaction time while 68.9% of total organic carbon was eliminated within 3 h. Scavenging experiments showed that the contribution of sulfate and hydroxyl radicals was nearly the same in 2,4-D degradation in EO/Oxone while sulfate radical was prevailing species in EO/Oxone/Co^{2+}. The performance of EO/Oxone was also examined on a real matrix.

1. Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is a herbicide with potential toxicity for humans and animals which is widely applied in gardens and farming to control weeds. 2,4-D is a low cost, easily available and effective herbicide which is often used in all countries [1,2]. Accordingly, 2,4-D has recently become a considerable environmental problem due to its chemical stability and resistance. 2,4-D is identified as moderately toxic (Class II) to human beings and animals based of the report of WHO and maximum permissible concentration (MPC) in drinking water is recommended as 70 μg/L [3]. 2,4-D may be an endocrine disruptor which is classified in plant hormones (auxin). In addition, residual 2,4-D have been reported in aquatic environment and receiving waters [4,5]. Several methods have been suggested for 2,4-D degradation in aqueous solutions. Most of them are based on chemical oxidations since the biodegradability of 2,4-D is poor [6]. Advanced oxidation processes (AOPs) have been broadly used for degradation of persistent organic pollutants in which hydroxyl radical as main oxidative agent is produced in the solution for destruction of organic molecules [7,8]. Hydroxyl radical may be generated through electrochemical, chemical and photochemical processes [9]. Electrooxidation (EO) is a green procedure for the production of hydroxyl radical because its reactive agent is electron [10,11]. The mechanism of EO process is the generation of hydroxyl radical through oxidation of water molecule at the surface of anode which is well-known as anodic oxidation [11,12]. In anodic oxidation, the generated hydroxyl radical can directly react with the organic compounds. Different high overvoltage anodes (IrO_2, PbO_2, Pt, graphite and boron doped diamond) have been used in anodic oxidation process to generate hydroxyl radical [13]. Moreover, dechlorination may happen in electrochemical processes for chlorinated organic compounds.

$$MO_x + H_2O \rightarrow MO_x(HO^\bullet) + H^+ + e^- \quad (1)$$

Nowadays, hybrid processes have received a significant attention for rapid degradation of organic pollutants. In hybrid processes, one or some chemical oxidation processes are coupled for synergistic degradation of organic pollutants [14]. These processes often have several mechanisms for degradation of pollutants. In last decade, the use of Oxone® salt ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) has been increased for environmental remediation. The presence of peroxymonosulfate anion (HSO_5^-) in Oxone® salt induces the generation of sulfate radical ($SO_4^{\bullet -}$) in which an activator is used [15–17]. Oxone as source of peroxymonosulfate (PMS) is activated by transition metal, ultraviolet, ultrasound, carbon-based catalyst etc. The combination of Oxone and

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[*] Corresponding authors.
E-mail addresses: Ghanbari.env@gmail.com (F. Ghanbari), Azahedi89@gmail.com (A. Zahedi).

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electrooxidation has been rarely considered for degradation of persistent organic pollutants [18,19]. Indeed, this hybrid process is coupling electrooxidation process and sulfate radical-based process, in which Oxone can be activated through electron transfer according to Eq. (2) [18].

$$HSO_5^{-} + e^{-} \rightarrow SO_4^{\bullet -} + OH^{-} \qquad (2)$$

Several hybrid electrochemical processes have been used for 2,4-D degradation including electro-peroxone [20], electro-Fenton [21], and sono-electrooxidation [22]. Compared to hybrid Fenton-based processes, electrooxidation/Oxone is a free metal catalyst process in which sulfate and hydroxyl radicals are simultaneously generated at the solution to enhance the degradation of organic pollutants. Moreover, there is a little information related to integration of sulfate radical based processes and electrochemical process as a novel hybrid process. It should be also noted that no study has been conducted on 2,4-D degradation via combination of electrooxidation and Oxone.

In this study, combination of electrooxidation with PbO_2 anode and Oxone was studied for the first time. The operational parameters, mechanism, reaction kinetic and mineralization of 2,4-D were investigated. Moreover, the effects of some homogenous transition metals were also studied on 2,4-D degradation. Finally, the effects of some electrolytes were studied on the degradation rate of 2,4-D.

2. Materials and methods

2.1. Chemicals and reagent

2,4-D ($C_8H_6Cl_2O_3$) was purchased from Merck Inc. with purity of 98%. Oxone salt ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) was purchased from Sigma-Aldrich (1 mM Oxone is equal with 1 mM PMS). Sodium chloride (NaCl), sodium nitrate ($NaNO_3$), sodium nitrite ($NaNO_2$), sodium sulfate (Na_2SO_4) and sodium bicarbonate ($NaHCO_3$) were purchased from Fluka Company. Hydrogen peroxide (35%), sodium hydroxide, iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), potassium iodide (KI), cobalt (II) sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), and sulfuric acid (98%) were obtained from Merck Company. Sodium persulfate was purchased from Acros-organic Company. Ethanol (EtOH) and *tert*-butyl alcohol (TBA) were provided from Razi Company and Merck Inc. respectively. Sodium sulfate (Na_2SO_4) was purchased from Alfa Aesar Inc. Acetonitrile and water with HPLC grade were provided from Samchun Inc.

2.2. Electrooxidation experiments

Electrooxidation experiments were carried out an undivided cell at room temperature. A cylindrical reactor (Plaxi-glass) with the height of 10 cm and diameter of 6 cm was used as electrochemical cell. A PbO_2 electrode (2 × 4.9 × 0.1 cm) was used as anode while a stainless steel (2 × 4.9 × 0.3 cm) was used as cathode. PbO_2 anode is a non-active and high O_2-overvoltage electrode which has been classically used in EO. Moreover, it is available and inexpensive compared to Pt and BDD. 250 mL of 2,4-D solution was introduced to the electrochemical cell. In all experiments, the concentration of 2,4-D was 40 mg/L. 10 mM Na_2SO_4 was applied as supporting electrolyte. In order to apply electrical current, a digital DC power (30.0 V, 3000 mA) was used. The mutual distance of 3 cm between the anode and the cathode was maintained. The solution was mixed by a magnetic stirrer. The solution pH was adjusted by sulfuric acid and sodium hydroxide (0.1 M). Before starting the electrolysis, a certain amount of Oxone was added to the solution. With turning on DC power, the electrooxidation process was begun. The sampling was carried out every 15 min from the solution for 2,4-D analysis. The effects of pH, current density and Oxone concentration were investigated on 2,4-D removal. All experiments were in triplicate and the average of them was used for presentation of data. The standard deviation was less than 3.2%.

2.3. Analytical method

2,4-D concentration was measured by a high-performance liquid chromatography (HPLC) (KNAUER, Germany) with a 2500 ultraviolet (UV) detector at 280 nm wavelength as the absorption maximum of 2,4-D. The isocratic mobile phase was a mixture of acetonitrile and water with a ratio of 50:50. The flow rate of mobile phase was 0.5 mL/min. The stationary phase was a C8 (100-5) column (250 mm × 4.6 mm). The temperature of column was set at 30 °C. Analysis time was continued up to 10.0 min whereas the retention time was 3.4–3.7 min for 2,4-D peak. 2,4-D removal (%) was calculated based on 2,4-D concentration at different reaction time. The Oxone concentration (PMS) was measured based on iodometric titration. Chemical oxygen demand (COD) was determined by COD ampoules (HACH Chemical) using a spectrophotometer (HACH, DR6000). Total organic carbon (TOC) was measured by TOC analyzer (Shimadzu). Potassium hydrogen phthalate (KHP) was used for accuracy of COD and TOC measurements. Total dissolved solids (TDS), 5day-biochemical oxygen demand (BOD) (5210B) and chloride ions were determined according to Standard Methods [23].

3. Results and discussion

3.1. The effect of operational parameters

The effect of pH was explored on 2,4-D removal under the condition of 20 mA/cm^2 and 2 mM Oxone. Fig. 1a shows the 2,4-D removal at pH values of 3.0, 7.0 and 10.0. As can be seen, in the alkaline condition (pH = 10.0), the degradation efficiency was remarkably reduced. This issue can be attributed to the self-decomposition of Oxone at alkaline condition. PMS as major source of sulfate radical was decomposed to water, oxygen and sulfate ions [24].

$$2HSO_5^{-} + 2OH^{-} \rightarrow 2SO_4^{2-} + O_2 + H_2O \qquad (3)$$

2,4-D removals were 70.1% and 60.4% for pH = 4.0 and pH = 7.0 respectively. As shown, pH of 4 indicated high performance for EO process compared to neutral condition (pH = 7.0). It has been reported in literature that redox potential of free radicals in acidic condition is higher than that in alkaline condition [25,26]. This issue can be influential on 2,4-D degradation. In addition, pK_a of 2,4-D is 2.87 [27], hence at pH values more than 2.87, its anionic form might be degraded on the surface of anode.

In electrochemical process, current density is a vital factor for degradation reaction of organic pollutants. The effect of current density was investigated in the range of 10–40 mA/cm^2 under the conditions of pH = 4.0, 2 mM Oxone and 90 min reaction time. Fig. 1b demonstrates the effect of current density on 2,4-D removal. One can see that increasing in current intensity enhanced the 2,4-D removal. 2,4-D removals were 53.3, 70.1, 82.6 and 83.1% for 5, 10, 15, 20 mA/cm^2 respectively. Higher current density resulted in more generation of hydroxyl radical at the anode. This phenomenon led to increase of electron transfer to activate Oxone for generation of sulfate radical. However, after 30 mA/cm^2, removal efficiency did not change significantly. In anodic oxidation, parasite reactions usually occurs at higher current density in which non-oxidizing reactions take place at the surface of anode. In this way, oxygen evolution occurs at the surface of PbO_2 and consequently reduces the hydroxyl radicals (Eq. (4)) [28–30].

$$2PbO_2(HO^{\bullet}) \rightarrow 2PbO_2 + O_2 + 2H^{+} + 2e^{-} \qquad (4)$$

The Oxone concentration affects the amount of sulfate radical and degradation of pollutant. Fig. 1c demonstrates the effect of Oxone dosage on 2,4-D removal when current density was 30 mA/cm^2 and the solution pH was 4.0. One can see that in the presence of 1 mM Oxone, degradation was relatively slow and removal efficiency reached 57% during 90 min electrolysis. With increase of Oxone concentration to 2