DEGRADATION OF GLYPHOSATE HERBICIDE BY AN ANODIC OXIDATION PROCESS

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ABSTRACT

Glyphosate is occasionally detected as water contaminants in agriculture areas where the herbicide is used extensively. The removal of glyphosate in synthetic solution using advanced oxidation process (AOP) is a possible approach for remediation of contaminated waters. Here, the ability of anodic oxidation for the degradation and mineralisation of glyphosate herbicide was investigated using Ti/PbO_2 anode in batch mode. The experimental results provided that the current intensity, treatment time, pH and initial concentration are the influent parameters on the glyphosate degradation. At the optimal condition, 16.9 mgL^{-1} of glyphosate decreased up to 0.6 mg L^{-1}, i.e the removal efficiencies were 95 ± 16 %. This work demonstrates that electrochemical oxidation is a promising process for degradation and mineralization of glyphosate.

Keywords: anodic oxidation, glyphosate, Ti/PbO_2, electrochemical, herbicide removal.

1. INTRODUCTION

Glyphosate is a non-selective, post-emergence organophosphorus herbicide used to control annual, perennial grasses and broad leaved weeds [1]. In particular, glyphosate is among the most widely used pesticides worldwide; according to the statistic forecast, the global market for glyphosate is expected to use 1.35 million tons annually [2]. The WHO (World Health Organization) has set the recommended level of glyphosate alone or in combination with AMPA of 0.9 mg L^{-1} for drinking water [3]. The presence of glyphosate in the aquatic environment has led to the need to develop techniques for its removal from water sources. Conventional methods frequently used in water treatment, such as physicochemical, biological are often not significantly decomposed or ineffective for removing herbicide [1, 4]. Advanced oxidation processes (AOPs) have been proposed as alternative methods for the removal of many toxic and bio-recalcitrant compounds in wastewater [5]. AOPs are characterized by the generation of the

hydroxyl radical species (•OH). These radicals are short-lived, highly reactive and able to selectively oxidize organic pollutants.

In the present study, the electrochemical oxidation of glyphosate was proposed. The destruction and mineralization of glyphosate in waters using the DSA anodes has been reported in the literature. However, to the best of our knowledge, this is the first time the electrochemical oxidation has been applied to tackle the challenging problem of efficient degradation of glyphosate without the presence of chloride (as electrolyte) which can lead to forming toxic by-products such as organochlorinated compounds. Thus the aims of this study are: (a) to evaluate the feasibility of using this approach to degradation and mineralisation of glyphosate from water without adding chloride as electrolyte; (b) to use statistical methodology for optimal treatment.

2. MATERIALS AND METHODS

2.1. Preparation of the synthetic solution

The water samples used throughout this study were prepared synthetically by dissolving glyphosate ($C_3H_8NO_3P$; CAS #1071-83-6) (Sigma Aldrich, NY, USA, purity $\geq$ 96 %) in ultrapure water. The stock solution of glyphosate was prepared by dissolving 1.69 g glyphosate in 1.0L of ultrapure water. Solubilisation was carried out at 250 rpm for 20 min. The sample solutions were prepared by taking desired amounts of stock solution in glass beakers and mixing with ultrapure water to reach final concentrations of 0.025 - 0.2 mmol L^{-1}. The sodium salt (Na_2SO_4 0.01 mol L^{-1}) was added to increase electrical conductivity.

2.2. Electrolytic reactor set-up

The electrochemical treatment of GP was carried out in batch mode with a single-compartment electrolytic cell made of Plexiglas with a dimension of 20 mm (width) $\times$ 150 mm (length) $\times$ 180 mm (height). The electrode sets consisted of one anode and one cathode with a distance between the electrodes of 10 mm. The anode studied was Ti/PbO_2 (lead oxide coated on titanium, 100 $\times$ 110 mm). The rectangular cathode plate electrode (100 mm $\times$ 110 mm) was made of Ti. The electrical current was applied using a digital DC generator VSP4030 (B&K Precision, CA, US). In all tests, a total volume of 1.0 L of contaminated water was used.

2.3. Electrochemical treatment of the glyphosate solution

2.3.1. Preliminary experiments

The first set of electrochemical experiments was used to carry out different tests to investigate the effects of the main factors (current, treatment time, pH and initial pollutant concentration) in treating water contaminated by glyphosate. During these tests, the residual TOC concentrations and residual concentrations of glyphosate were measured to evaluate the performance of the experimental unit. The current intensities varied from 0.5 A to 10.0 A (current densities from 4.55 mA cm^{-2} to 90.9 mA cm^{-2}). The treatment times of 0 - 360 min were tested. The effect of the initial glyphosate concentration was evaluated by using initial concentrations ranging from 3 to 30 mg L^{-1}. Different initial concentrations of glyphosate were studied which employed solutions of glyphosate at concentrations of 3, 5, 10, 15 and 30 mg L^{-1}. Likewise, the pH effect was investigated in the range 3–10 for fixed glyphosate concentration (16.9 mg L^{-1}) and their effectiveness was compared with initial pH (solution without pH control).

2.3.2. Experimental design

The removal of glyphosate by electrochemical was optimization using response surface methodology (RSM). A central composite design (CCD) methodology was employed to describe and optimize the glyphosate treatment using the electro-oxidation process. Two independent variables were used in this study based on preliminary experiments: treatment time and current intensity. A two-factorial design (at two-levels) completed by a central composite design, with five replicates at the center of the experimental region for each numeric factor, led to a total number of thirteen experiments employed for response surface modeling. The experimental range and levels of independent variables investigated for CBZ degradation with the coded values are shown in Table 1.

Table 1. Experimental range and levels of independent variables.

Coded variables (X_i)	Factor (U_i)	Description	Experimental field		$UU_{i,0}$	$\Delta\Delta U_i$
			Min value (−1)	Max value (+1)		
X_1	U_1	Treatment time (min)	90	180	135	90
X_2	U_2	Current (A)	2	5	3.5	3

During these assays, the effectiveness of the process was evaluated by glyphosate removal efficiency. Experimental data were obtained from the average of at least of three treatment replicates. Uncertainties were removed and calculated at a significance level of $p \leq 0.05$. The analysis of variance (ANOVA) and other statistical results were calculated and generated using the Design Expert Software version 7.1 (Stat-Ease Inc., USA).
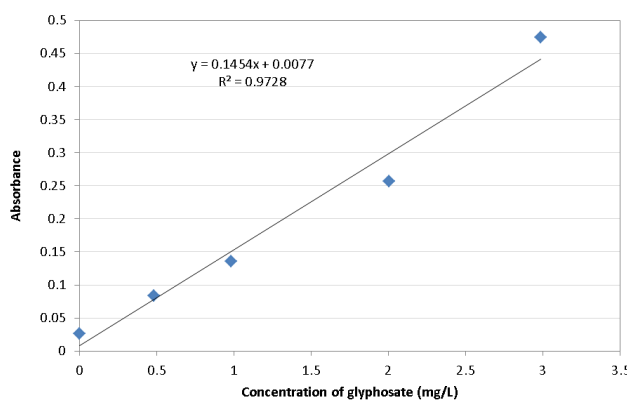
2.4. Analytical details

Figure 1. Calibration curve of glyphosate.

The residual concentrations of glyphosate (before and after the treatment) were firstly monitored by absorbance measurements using a spectrophotometer Carry UV 50 (Varian Canada Inc.). The test is based on the reaction of glyphosate with ninhydrin in presence of sodium molybdate in neutral aqueous medium to give a Ruhemann's purple product having the VIS absorption maximum at 570 nm. A stock 100 mg/mL solution was used to prepare eight samples containing different concentrations of the herbicide (1, 5, 10, 15, 25, and 35 mg L^{-1}). A

calibration curve of known glyphosate concentrations (0.0 - 3.5 mg L^{-1}) versus absorbance was used to calculate the residual glucosate concentration and define the effluent (Fig. 1). The detection limit of this method was 0.1 mg L^{-1}.

3. RESULTS AND DISCUSSION

3.1. Effect of the current intensity

The effect of the current density on the electrooxidation of glyphosate was evaluated by measuring the residual glyphosate concentration at current intensity of 0.5 A, 1.0 A, 1.5 A, 2.0 A, 3.0 A, 5.0 A and 10.0 A. The initial glyphosate concentration was 0.1 mmol L^{-1} (16.9 mg L^{-1}) and the treatment time was fixed at 180 min. Figure 2 shows degradation efficiency changes as a function of the current intensity imposed. The residual glyphosate concentration decreased with the current intensity imposed, the higher the current intensity, the more effective the process was for glyphosate oxidation. More than 96 % of glyphosate was removed for a current intensity higher than 1.5A
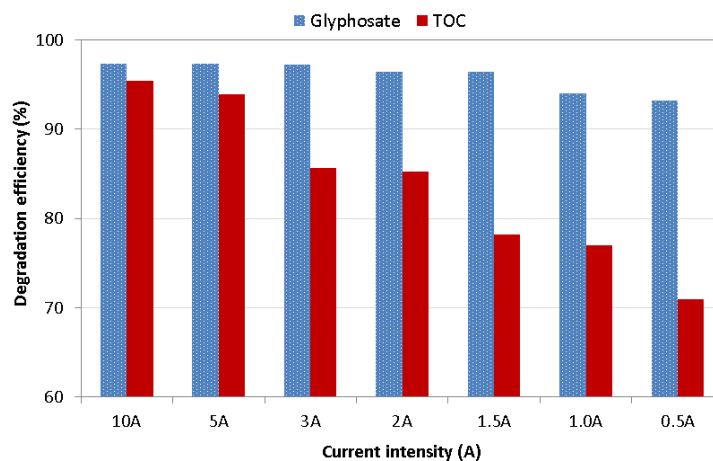

Figure 2. Effect of current intensity versus glyphosate degradation and mineralization rate (operating condition: I = 0.5 A – 10 A, Initial glyphosate conc. = 16.9 mg L^{-1}, t = 180 min).

However the efficiency of glyphosate degradation increased with current intensity until 3.0A and then remained quite stable around 97 % from 3.0A to 10.0A. It can be explained that the anodic oxidation of glyphosate occurs heterogeneously. It must be transported toward the anode surface, and then be oxidized there. As the glyphosate concentration was lowered to a certain level, only a fraction of current intensity supplied was used to oxidize pollutants, while the remaining charge loading was wasted for generation of oxygen. It was the reason for which the efficiency of glyphosate degradation remained stable in spite of high current applied. The same trend was also observed for TOC removal. As the current density increased, the mineralization rate became higher. Using a current intensity of 5.0 A, the rates of glyphosate degradation (97 %) were quite similar the rate of mineralisation (94 %), so the current intensity of 5.0 A was retained for the next step of the study.

3.2. Effect of treatment time

It has been established that the treatment efficiency is greatly affected by the operating conditions such as the reaction time and the cost of the electrochemical process [6, 7]. These tests were performed at a constant current intensity of 5A and various treatment times (5, 20, 30, 60, 120, 180 and 360 min). The initial glyphosate concentration was 0.1 mmol L^{-1} (16.9 mg L^{-1}) and the supporting electrolyte was Na_2SO_4 (0.01 mmol L^{-1}). The variation of residual glyphosate and TOC concentrations versus the retention time are shown in Fig. 3.
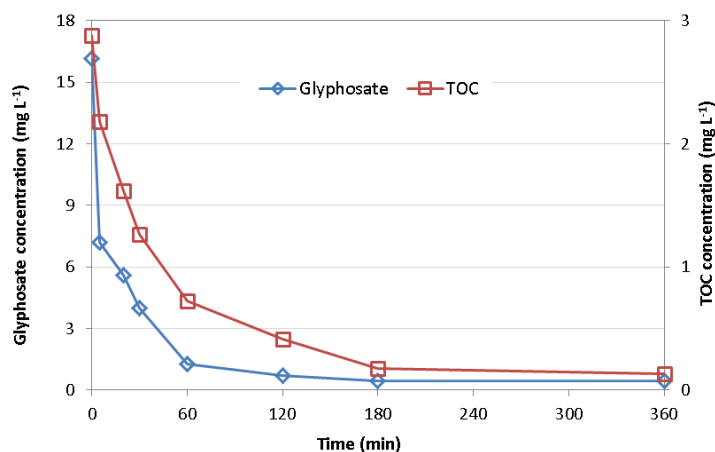

Figure 3. Variation of glyphosate and TOC concentrations versus treatment time (operating condition: I = 5A, Initial glyphosate conc. = 16.9 mg L^{-1}, t = 0 - 360 min).

The residual glyphosate concentration decreased rapidly during the first 60 min of treatment; then, it decreased slowly from 60 to 180 min and remained steady beyond 180 min. The TOC was more difficult to remove in the first region (0 - 60 min) owing to the complex of solution containing both glyphosate and its by-products. The relatively low high mineralisation rate (95 %) compare to 97 % of glyphosate indicated that major fraction of glyphosate was completely oxidized into water and carbon dioxide. From 180 min, the removal rate of glyphosate remained quite stable cause of competitive reactions can take place and limit hydroxyl radical formation. To reduce the energy consumption, the treatment time should be 120 min with the current applied of 5.0 A.

3.3. Effect of the pH

Manipulating the variation of pH is can be useful to increase the degradation rate and further optimize the treatment. To determine the effect of pH, various pH from 3-10 was investigated for fixed glyphosate concentration (0.1 mmol L^{-1}) and their effectiveness was compared with initial solution (without pH control).
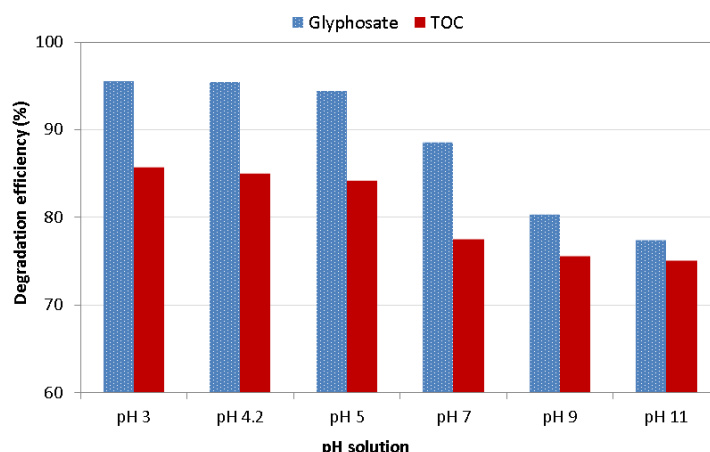
Figure 4. Effect of pH versus glyphosate degradation and mineralization rate (operating condition: I = 5A, Initial glyphosate conc. = 16.9 mg L^{-1}, t = 120 min).

Figure 4 shows that after 120 min of treatment, the glyphosate degradation and mineralisation rate is higher in acidic medium. The highest rates of glyphosate removal (95.5 %) and TOC removal (85.7 %) were recorded at pH = 3 compare to initial solution without pH control (pH = 4.22; 95 % of glyphosate and 80.2 % of TOC removal). These results are consistent with those obtained by Aquino Neto and de Andrade [8] while treating glyphosate (1000 mg L^{-1} solution) using a electrochemical oxidation process. After 4 h of electrolysis (*i* =50 mA cm^{-2}, electrolyte = Na$_2$SO$_4$), the degradation rate of glyphosate decreases with the increased pH of solution. Thus solution without pH control was selected for the next step of the experiments.

3.4. Effect of the initial glyphosate concentration

It is well known that the initial contaminant concentration can influence electrochemical oxidation processes. To verify these assumptions, complementary experiments with different initial concentrations of glyphosate from 0.025 mmol L^{-1} to 0.2 mmol L^{-1} were studied. During these assays, a current intensity of 5.0 A was imposed without pH control for a period of 120 min. Residual glyphosate concentration and TOC concentrations were monitored.
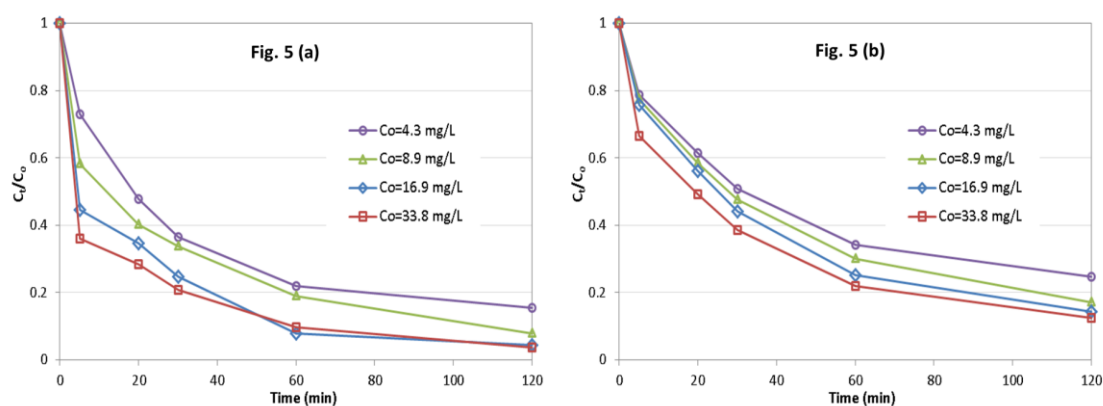

Figure 5. Effect of initial glyphosate concentration versus glyphosate degradation (5a) and mineralization rate (5b). (I = 5A, Initial glyphosate conc. = 4.3 - 16.9 mg L^{-1}, t = 0 - 120 min).

Figure 5 shows time course changes in the normalized concentration for glyphosate (5a) and TOC (5b). The results indicate that glyphosate electrochemical oxidation and mineralisation rate increases with higher initial concentration. The limiting values (0.8 mg L^{-1}) cannot be reached after 120 min of oxidation with initial concentration of 33.8 mg L^{-1}. However, the other initial concentration was able to reach a residual concentration of glyphosate below the acceptable level recommended for fresh water.

4. CONCLUSION

This study has shown the possibility of using an electrochemical technique to efficiently oxidise glyphosate (4 -16 mg L^{-1}) by the Ti/PbO$_2$ anode. These works demonstrated that the current intensity, treatment time, pH and initial concentration are the influent parameters. The electrochemical reactor operated at current intensity of 5 A and treatment time of 173 min was found to be the optimal conditions in terms of energy consumption/effectiveness. At this condition, glyphosate could be diminished by up to 95 % and 90 % of TOC could be removed in which the residual concentration of glyphosate (0.6 mg L^{-1}) in the treated water was below the acceptable level recommended for fresh water.

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