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Electrochemical degradation and mineralization of glyphosate herbicide

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Abstract

The presence of herbicide is a concern for both human and ecological health. 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 is a possible approach for remediation of contaminated waters. The ability of electrochemical oxidation for the degradation and mineralization of glyphosate herbicide was investigated using Ti/PbO_2 anode. The current intensity, treatment time, initial concentration and pH of solution are the influent parameters on the degradation efficiency. An experimental design methodology was applied to determine the optimal condition (in terms of cost/effectiveness) based on response surface methodology. Glyphosate concentration (C_0 = 16.9 mg L^{-1}) decreased up to 0.6 mg L^{-1} when the optimal conditions were imposed (current intensity of 4.77A and treatment time of 173 min). The removal efficiencies of glyphosate and total organic carbon were 95 ±16 % and 90.31 %, respectively. This work demonstrates that electrochemical oxidation is a promising process for degradation and mineralization of glyphosate.

Keywords: Glyphosate; herbicide; electrochemical; degradation, mineralization.

Introduction

Glyphosate is a broad spectrum, post-emergence organophosphorus herbicide used to control grasses and broad leaved weeds [1]. Recently, a widely use of the herbicides has raised increasing concern due to their enormous pollution of the environment. Data showed that less than 0.1% of the chemicals used for pest control will reach their target [2]. Thus, more than 99.9% of pesticides used has tendency move into the environment where they may adversely contaminate soil, water, and the atmosphere of the ecosystem [2]. In particular, glyphosate is among the most intensive used pesticides worldwide; according to the statistic forecast, the global market for glyphosate is expected to use 1.35 million tons annually [3]. Glyphosate can be found in surface and ground waters by direct use or by runoff or leaching from terrestrial applications. In Canada, glyphosate concentration as high as 5.153 mg L^{-1} were measured in runoff water after direct aerial application [4]. In the USA, pond water contained 0.09 – 1.7 mg L^{-1} of glyphosate and 2–35 μg L^{-1} of amino methyl phosphonic acid (AMPA) has been detected [5]. Several countries, including the United States, Canada, and Brazil have recorded some negative effects on human and animal health due to the glyphosate contamination in water [6-10]. Some studies reported that herbicides are entering the aquatic system, although in extreme low concentrations may introduce a potential hazard for human, in particular where no advanced water treatments facility are used [11]. The WHO (World Health Organization) has set the recommendation concentration of glyphosate alone or in combination with AMPA of 0.9 mg L^{-1} for drinking water [12] and the Environment Canada also set a limit of 0.8 mg glyphosate L^{-1} for the protection of aquatic life [13]. The existence of glyphosate in the aquatic environment requires developing methods for its removal from water. Conventional methods often used in water treatment plant, such as physicochemical, biological are sometime ineffective for removing herbicides [1, 14]. Existing advanced water treatment techniques include filtration using sand, ultra filtration, reverse osmosis, adsorption by activated charcoal and biological degradation are expensive and require large infrastructure investments and some are specific to particular contaminants [10]. Advanced oxidation processes (AOPs) can be proposed to remove from water and wastewaters many refractory and toxic contaminants [15]. During AOPs, hydroxyl radical species (·OH) are used as powerful oxidizing agents. These species are short-lived, highly reactive and able to oxidize many organic pollutants in water. Recent studies show that glyphosate treatment can be degraded through some other AOPs such as UV radiation, photocatalytic (UV/TiO_2) and electrochemical oxidation. The treatment using UV alone can be ineffective for glyphosate and AMPA oxidation. The combination of UV with H_2O_2 induced a good degradation of glyphosate, but not effective for AMPA, [11]. For instance, herbicide glyphosate was removed from water using UV/H_2O_2 system: after 5h of UV irradiation (40W), Manassero, Passalia, Negro, Cassano and Zalazar [16] has found a glyphosate degradation rate approximately of 80 % and a percentage of mineralization of 29 % were recorded (with an initial concentration of 41 mg glyphosate L^{-1} in the presence of 83 mg L^{-1} of hydrogen peroxide) [16]. Likewise, glyphosate can be significantly oxidized using UV/TiO_2 system, but it requires a long treatment time. Kongsong, Sikong, Niyomwas and Rachpech [17] have studied glyphosate degradation using photocatalytic by N-Doped SnO_2/TiO_2 thin-film-coated glass fibers. It took approximately 11 h to degrade glyphosate from 16.9 mg L^{-1} to 0.7 mg L^{-1} using a power of UV-lamp of 110 W (black light), a wavelength ranging between 310 and 400 nm with a distance between light source and substrate of 32 cm. In spite of the high oxidation rate of glyphosate, longer treatment time and the relatively higher treatment costs hamper the development of photocatalytic processes at large scale applications [18]. Therefore, research has focused on electrochemical oxidation process, which has several advantages such as easy control, no chemical added and highly effective removal of organic and inorganic compounds. Electrochemical oxidation process generates a very efficient oxidizing environment by forming hydroxyl radicals, providing effective water purification for elimination of persistent organic pollutants. Electrochemical oxidation is also able to oxidize organic pollutants into CO_2 and H_2O. This allows avoiding the problem of pollutant transfer from one phase to another. Neto and De Andrade [7] has studied glyphosate oxidation by using dimensionally stable anodes in chloride medium. After 4h of electrolysis with anode $Ti/Ir_{0.30}Sn_{0.70}O_2$, a complete glyphosate removal from the electrolyzed solution ($C_0 = 1000$ mg L^{-1}) was achieved. In the chloride matrix, application of 50 mA cm^{-2} leads to nearly total mineralization (release of phosphate ions=91%). However, chlorination will be inappropriate, notably from the associated risk of forming toxic by-products such as organochlorinated compounds.

In this study, the electrochemical oxidation of glyphosate is proposed. The destruction and mineralization of herbicides in waters using the electrochemical oxidation has been presented in the literature. However, to the best of our knowledge, this is the first time that the electrochemical oxidation has been applied without the presence of chloride (as supporting electrolyte) to solve the challenging problem of efficient degradation of glyphosate. Thus the aims of this study are: *i*) to evaluate the feasibility of using this approach for degradation and mineralization of glyphosate from water without adding chloride as supporting electrolyte; *ii*) to use statistical methodology approach in order to determine the optimal conditions for glyphosate degradation and; *iii*) to propose a reaction pathway (mechanism) for glyphosate degradation based on the identified by-products.

Materials and methods

Sample Preparation

The synthetic solution was prepared by dissolving glyphosate powder ($C_3H_8NO_3P$; CAS #1071-83-6) in ultrapure water (18 MΩ.cm^2). Glyphosate (Sigma Aldrich, NY, USA) used in this study was a reagent grade with purity ≥ 96% (Table 1).

[Table 1 near here]

The stock solution of glyphosate was prepared by dissolving 1.69 g of glyphosate in 1.0 L of ultrapure water. Solubilisation was carried out at 500 rpm for 10 min. The synthetic sample were prepared by taking desired amounts of stock solution in glass beakers and mixing with ultrapure water to reach final concentrations ranging between 4.3 and 33.8 mg L^{-1} in which a sodium salt (Na_2SO_4 0.01 mol L^{-1}) was added to increase electrical conductivity.

Electrochemical reactor set-up

The electrochemical oxidation of glyphosate was performed in batch mode with operation using an electrolytic reactor made of Plexiglas having a dimension of 21 mm (width)×150 mm (length)×180 mm (height). A schematic view of the experimental unit can be seen in Fig. S1 (*Supplementary data*). The electrode sets was comprised of one cathode and one anode with a distance between the electrodes of 10 mm. The electrodes were vertically installed inside the reactor. The anode used in this study was Ti/PbO_2 (lead oxide coated on titanium) and cathode was made of Ti. The preparation of this anode was described elsewhere (Didier et al, 2003). Both electrodes were in form of rectangular mesh with a dimension of 100 mm × 110 mm. A digital DC power supply VSP4030 (B&K Precision, CA, US) was used to apply the current intensity.

The agitation inside the electrolytic cell was carried out by recirculating water through the reactor in a continuous mode by means of a pump (operated at a constant speed of 1000 mL min^{-1}). In all experiments, a total volume of 1.0 L of sample was used. The working volume of the reactor was 550 mL, compared to 450 mL required in the recycling tank.

Electrochemical oxidation of the glyphosate solution

Preliminary experiments

The first step of electrochemical oxidation experiments was used to investigate the effects of the main factors (current applied, pH, treatment time and initial pollutant concentration) in treating water contained glyphosate. During these tests, the residual concentrations of glyphosate and residual TOC concentrations were measured to examine the performance of the electrochemical unit. The current intensities ranged from 0.5 A to 10.0 A (current densities from 4.55 mA cm^{-2} to 90.9 mA cm^{-2}). The treatment time up to 360 min was tested. The effect of the initial glyphosate concentration (4.3, 8.9, 16.9 and 33.8 mg L^{-1}) was studied. Likewise, the effect of pH value was tested in the range 3–10 using a glyphosate concentration of 16.9 mg L^{-1} and their effectiveness was compared with the initial pH (solution without pH adjustment).

Experimental design

The degradation of glyphosate by electrochemical was carried out using response surface methodology (RSM). A central composite design methodology (CCD) was used to optimize the glyphosate degradation using the electro-oxidation process. Two major independent variables were used in this study based on preliminary experiments: treatment time and current intensity.

A two-factorial design completed by a central composite design (at two-levels), 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 glyphosate degradation with the coded values are shown in Table 2.

[Table 2 near here]

The values of the variables and their variation limits were selected based on preliminary experiments. During these experiments, the glyphosate removal efficiency was used to evaluate the effectiveness of the process. Experimental data were collected from the average of at least of three replicates. Uncertainties were removed and calculated at a significance level of $p \leq 0.05$. The analysis of variance and other statistical data were calculated and generated using the Design Expert Software version 7.2 (Stat-Ease Inc., USA).

Solution Analyses

Glyphosate measurements

The concentrations of glyphosate (before and after the treatment) were firstly monitored by absorbance measurements using a spectrophotometer Carry UV 50 (Varian Canada Inc.) for ease of analysis during preliminary and optimization step. The method used to analysis glyphosate was described previously [19]. The test is based on the reaction of ninhydrin with glyphosate in presence of sodium molybdate in neutral aqueous medium to make a Ruhemann's purple product (having the VIS absorption maximum at 570 nm). A stock of 100 mg mL^{-1} solution was used to prepare standard sample containing different concentrations of the glyphosate (1.0, 5.0, 10.0, 15.0, 25.0, and 35.0 mg L^{-1}) which were then added to separate test tubes containing 1 mL of ninhydrin (5%, m v^{-1}) and 1 mL of sodium molybdate (5%, m v^{-1}). The mixtures were placed in a water bath at 100°C for 5 min and cooled naturally to ambient temperature, and made up to 10 mL in volumetric flasks. A calibration curve of known glyphosate concentrations (0.0-3.5 mg L^{-1}) versus absorbance was used to calculate the residual glyphosate concentration and define the effluent (Fig. S2, *Supplementary data*). The detection limit of this technique was 0.1 mg L^{-1}. However, when the optimal conditions were determined and repeated in triplicate to verify the effectiveness and the reproducibility of the electrooxidation process, the residual concentration of glyphosate and its by-products were analyzed by liquid chromatography/mass spectrometry technique (LC-MS) rather than UV-VIS spectroscopic. The analyses of glyphosate and AMPA were carried out using a Thermo Scientific Finnigan™ LC/MS system. The separations were performed using 50 x 2.1mm chromatographic columns; 5 µm particle size Thermo Scientific Hypersil™ BDS C18 and 5 µm particle size Hypercarb. Two mobile phases (A and B) were used during analysis: 0.1% formic acid in water (Phase A) and 0.1% formic acid in acetonitrile (Phase B). The injection of the two mobile phases was gradient programmed as follows 5 to 100% (Phase B) in 10 min and the injection flow rate was 0.3 ml min^{-1}. The formation of reaction intermediates was monitored by using TSQ Quantum Access mass spectrometry (Thermo Scientific, USA) equipped with an electrospray ionization source operated in the positive ion mode. Analysis was performed in Selected Ion Monitoring (SIM) mode. Nitrogen was used as a sheath and auxiliary gas. Working conditions were as followed: spray voltage was 4500 V and capillary temperature was 450°C. Calibration standards were prepared by serial dilution of the intermediate solutions (1 ppm) in water at concentrations of 2µg L^{-1} - 100 µg L^{-1} with sulfamethazine C_{13} was used as internal standard. The limit of detection was 1.0 µg L^{-1}.

Operating parameters and other measurements

The pH and conductivity were monitored using a pH/Cond meter (Accumet Research model AR 25) equipped with a pH and conductivity probe. Total organic carbon was measured using a Shimadzu TOC-V_{CPH} analyser (Shimadzu Scientific Instruments, Kyoto, Japan). Ammonium ions were measured by ammonium ion selective electrodes (Cole Parmer) using a pH/ion-meter (Accumet Research model AR 25 Dual Channel pH/Ion meter, Fisher Scientific). The ionic strength adjuster (5M NaCl) was added (2ml to every 100 ml of sample) to keep a constant background ionic strength present in the solution. Concentrations were measured with an incertitude of ± 5mg/L. Nitrate ions were measured by nitrate ion selective electrodes (Cole Parmer) using a pH/ion-meter (Accumet Research model AR 25). The ionic strength adjuster (2M $(NH_4)_2SO_4$) was also added at rate of 2ml to every 100 ml of sample. Concentrations were measured with incertitude of ± 5 mg L^{-1}. Phosphate ions were quantified by plasma emission spectroscopy (ICP-AES) with a Varian apparatus (Vista AX model, Alto, California).

Economic aspect

The economic study included the consideration of chemical and energy consumption. The electric cost was estimated to be approximately 0.06 US$ kWh. The energy consumption, E_C (kWh), calculated by multiplying the current applied, I (A), by the cell voltage, U_C (V), and taking into account the treatment time t (h), can be expressed by the following equation:

$$E_C(kWh) = \frac{U_C.I.t}{1000} \qquad (1)$$

The unit cost of the electrolyte (Na_2SO_4 industrial grade) was 0.30 US$ kg^{-1}. The total cost was evaluated in terms of US$ spent per m^3 of treated solution.

Results and discussion

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 10A, 5A, 3A, 2A, 1.5A, 1A and 0.5A. The initial glyphosate concentration was 0.1 mmol L^{-1} (16.9 mg L^{-1}) and the treatment time was fixed at 180 min. Fig. 1 shows degradation efficiency as a function of the current intensity imposed. The degradation efficiencies were 93.3%, 94.1%, 96.5%, 96.6%, 97.3%, 97.4% and 97.4% for 0.5A, 1 A, 1.5 A, 2 A, 3 A, 5 A and 10 A, respectively. The efficiency of glyphosate degradation increased with the current intensity imposed, the higher the current intensity, the more effective of removal and the lower residual glyphosate concentration. More than 96% of glyphosate was degraded for a current intensity higher than 1.5A and the residual concentration of glyphosate was below the limiting values (0.8 mg L^{-1}) recommended for the fresh water by Environment Canada[12]. 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 occurred heterogeneously. Glyphosate must be moved to the electrode surface (anode) 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 [20]. It was the reason for which the efficiency of glyphosate degradation remained stable in spite of high current applied. The residual glyphosate concentrations recorded at the end of the treatment varied from 0.43 mg L^{-1} to 1.14 mg L^{-1}, compared with 16.9 mg L^{-1} initially imposed in the raw effluent. The same trend was also obtained for TOC removal. As the current intensity increased, the mineralization rate became higher. The residual TOC concentrations recorded at the end of the treatment varied from 0.129 mg L^{-1} to 0.833 mg L^{-1}, compared to 2.878 mg L^{-1} initially measured. The percentage of oxidizable carbon (mineralised C-CO_2) for the total carbon in the final solution after 180 min at 0.5A, 1 A, 1.5 A, 2 A, 3 A, 5 A and 10 A were 71.1%, 77.0%, 78.2%, 85.3%, 85.7%, 94.0% and 95.5%, respectively. This confirmed that as the current intensity increased, the degradation efficiency also increased. When high current intensities were applied (i.e., 5 and 10 A), the mineralization of oxidizable carbon was relatively high, compared to the percentages of mineralization (TOC abatement) recorded for low current intensities (0.5A-3A). This suggests that as the glyphosate concentration was lowered to a certain level, its by-products were formed. The degradation of glyphosate and its by-products pursued until total mineralization occurred due to the electrophilic attack of oxidising species which are generated electrochemically. It is well known that those generated species react favourably with electron-rich compounds [20]. In fact, hydroxyl radicals species break the bonds (-C-N- and -C-P-), which are the major component of glyphosate and its by-product leading to higher oxidation rates and possible mineralization of organic matter. Using a current intensity of 5.0A, the rates of glyphosate degradation (97%) were quite high similar to the percentage of TOC removal (94%), so the current intensity of 5.0 A was used for the next experiments.

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 [20, 21]. In order to reduce the energy consumption and further optimize the process, additional experiments were conducted by testing various retention times. These tests were performed at a constant current intensity of 5A and different 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 against the retention time are shown in Fig. 2. Three regions could be observed in the (residual glyphosate concentration, time) and (residual TOC concentration, time) planes. In fact, the residual glyphosate concentration decreased rapidly during the first 60 min of treatment; then, it decreased slowly with a relatively low slope from 60 to 180 min and remained steady beyond 180 min. During these experiments, an initial glyphosate concentration of 16.9 mg L^{-1} was imposed compared to 0.43 mg L^{-1} recorded at 360 min (glyphosate removal of 97.5%). The TOC was more difficult to remove in the first region (0-60 min) owing to the complexity of both glyphosate and its by-products. The TOC concentrations obtained at the end of electrooxidation were 0.13 mg L^{-1}, whereas the initial TOC concentration was 2.9 mg L^{-1}. The experimental data were well fitted with the first-order kinetic (with a correlation coefficients ranging from 0.88 to 0.95; Fig. S3, *Supplementary data*) predicting a linear variation against time (t) of the –Ln (C/C_0)

$$-Ln\left(\frac{C}{C_0}\right) = k.t \qquad (2)$$

where C is the concentration of glyphosate at time t, C_0 is the initial concentration of glyphosate k is the pseudo-first-order degradation rate constant. The reaction rate apparent constants obtained were the followings: 0.044 min^{-1} (for glyphosate removal) and 0.024 min^{-1} (for TOC removal). The relatively high mineralization rate (95%) confirmed that a non-negligible part of glyphosate compound was oxidized into water (H_2O) and carbon dioxide (CO_2). It is worth noting that, during electrolysis, organic pollutants can be subjected to two different paths in anodic oxidation: electrochemical conversion or electrochemical combustion [21, 22]. Electrochemical conversion only transforms the organic pollutants into biodegradable compounds, whereas electrochemical combustion oxidised the organic pollutants to form H_2O and CO_2 and no further treatment is then required. When the treatment time was increased, hydroxyl radical concentrations generated at the surface of anode increased and it contributed to glyphosate degradation. After 180 min of treatment time, the percentage of glyphosate removal remained quite stable owing to competitive reactions (parasitic reactions) and hydroxyl radical formation was limited. A treatment time of 120 min was required to reach a residual glyphosate concentration below the limiting values (0.8 mg L^{-1}) recommended by the Canadian Environment Agency. Therefore 120 min of treatment time was selected for the next step of the study.

Effect of the pH

The change in initial pH can be useful to enhanced the degradation efficiency and further optimize the treatment. To examine the effect of pH, various pH from 3-10 was investigated for a fixed glyphosate concentration (0.1 mmol L^{-1}). The electro-oxidation experiments were applied at a current intensity of 5.0A. NaOH and H_2SO_4 were used to adjust the pH values of the solutions. Fig. 3 shows that after 120 min of treatment, the glyphosate degradation and mineralization rate was higher in acidic medium. The highest rates of glyphosate removal (95.5%) and TOC removal (85.7%) were recorded at pH = 3 compared to the initial solution without pH control (pH=4.22; 95% of glyphosate and 80.2 % of TOC removal). It is worth noting that, in all cases with pH < 5, residual glyphosate concentrations were below the limiting values (0.8 mg L^{-1}). Glyphosate compound has the characteristics of a ternary acid, which has four ionization constants pK_{a1} =0.8 (1st phosphonic), pK_{a2} =2.6 (carboxylate), pK_{a3} =5.6 (2nd phosphonic) and pK_{a4} =10.6 (amine) [8]. This molecule has an electrical charges in function of pH of solution. These results are consistent with those obtained by Aquino Neto and de Andrade [23] while treating glyphosate (1000 mg L^{-1} solution) using an electrochemical oxidation process. After 4 h of electrolysis (i =50 mA cm^{-2}, electrolyte = Na_2SO_4), the degradation rate of glyphosate decreased with the increase of pH. The highest degradation rate (34%) was obtained at approximately pH = 2, compared to 18% recorded for pH=11. Thus, to easily reach a residual concentration of glyphosate below the acceptable level recommended for fresh water and to avoid adding chemical during electrolysis, a treatment without pH control was selected for the next step of the experiments.

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: 4.3, 8.9, 16.9 and 33.8 mg L^{-1} (from 0.025 mmol L^{-1} to 0.2 mmol L^{-1}) were studied. During these assays, a current intensity of 5 A was applied without pH adjustment during 120 min. Residual glyphosate concentration and TOC concentrations were measured. Fig. 4 presents the changes in the normalized concentration for glyphosate (4a) and TOC (4b) in function with time. This result indicated that glyphosate electrochemical oxidation and mineralization rate increased when the initial glyphosate concentration increased. The limiting values (0.8 mg L^{-1}) recommended by the Canadian Environment Agency could not be reached after 120 min of oxidation with the initial concentration of 33.8 mg L^{-1}. However, for the other initial concentrations, the limiting value recommended by the Canadian Environment

Agency could be reached. A minimum of 0.68 mg L^{-1} of glyphosate was recorded when the initial concentration imposed was 4.3 mg L^{-1}. Additionally, the maximum percentage of mineralization of 87.4% was obtained (at an initial concentration of 33.8 mg L^{-1}) compared to those recorded: 85.6% (C_0 = 16.9 mg L^{-1}), 83.0% (C_0 = 8.9 mg L^{-1}) and 75.2% (C_0 = 4.3 mg L^{-1}).

Optimization of glyphosate degradation and economical aspect

CCD was used to optimize the electrochemical process for glyphosate degradation. A two-level central composite experimental design, with five replicates at the center point leading to a total number of thirteen experiments was used for response surface modelling (Table 3).

[Table 3 near here]

The CCD matrix is comprised of three parts: factorial matrix (assays 5, 6, 12, 13), a star matrix (assays 1, 3, 8, 11) and a group of points at the center of the experiments (assays 2, 4, 7, 9, 10). The response was described by a second-order model in the form of quadratic polynomial equation given below:

$$Y = b_0 + \sum_{i=1}^{k} b_i.X_i + \sum_{i=1}^{k} b_{ii}.X_i^2 + \sum_j \sum_{i=2}^{k} b_{ij}.X_i X_j + e_i \qquad (3)$$

where Y is the experimental response; X_i and X_j are the independent variables; b_0 is the average of the experimental response; b_i is the estimation of the principal effect of the factor i on the response Y; b_j is the estimation of the second effect of the factor j on the response Y; b_{ij} is the estimation of the interaction effect between i and j on the response Y and e_i represents the error on the response Y. All coefficients are calculated using the least square method [24].

The coefficients of the polynomial model (quadratic model) were calculated using the Design-Expert® Program Software; the regression model has been presented by the following equation for each response (residual glyphosate concentration and mineralization efficiency, respectively) in terms of coded variables:

$$Y_{glyph.} = 1.28 - 0.23X_1 - 032X_2 + 0.11X_1X_2 - 0.16X_1^2 - 0.12X_2^2 \qquad (4)$$

$$Y_{TOC} = 81.84 + 5.43X_1 + 7.43X_2 - 2.28X_1X_2 + 0.56X_1^2 - 1.61X_2^2 \qquad (5)$$

The analysis of variance indicates that the model is significant for glyphosate and TOC removal (Section S3, *Supplementary data*). The value of the correlation coefficient for glyphosate removal ($R^2 = 0.9219$) indicates that only 7.81% of the total variation could not be explained by the empirical model. The agreement between actual and predicted values of glyphosate removal is satisfactory and consistent with the statistical significance of the quadratic model. To rigorously determine the optimal conditions for glyphosate degradation in terms of cost and effectiveness, the criteria selected for the optimization condition for glyphosate degradation are the following: *i*) treatment time and current intensity have to be minimized with a relatively high importance (3/5 weighting factor) in order to reduce the treatment cost (including the energy cost); *ii*) the percentage of TOC degradation must be maximized with the high importance (3/5 weighting factor); *iii*) the final concentration of glyphosate degradation must be lowered than recommend value (0.8 mg L^{-1}) with the highest importance (5/5 weighting factor). Based on these criteria, the Design Expert Program Software proposed several interesting solutions to obtain a high degradation of glyphosate. The optimal conditions for glyphosate degradation in terms of cost/effectiveness were established as follows: 173 min of treatment using a current intensity of 4.77A and the theoretical response proposed for TOC degradation was 90.28 % whereas the residual concentration was 0.69 mg L^{-1} for the glyphosate.

According to the results mentioned above, the electrolytic reactor that carried out at a current applied of 4.77A for 173 min of treatment with initial concentration of 16.9 mg L^{-1} glyphosate gave the best performance of electro-oxidation of glyphosate. It was now important to determine whether the results of these tests are reproducible. Thus, the optimal assay (determined in terms of effectiveness and cost) was repeated in triplicate to verify the effectiveness and reproducibility of electro-oxidation performance in treating waters contaminated by glyphosate in the presence of Na_2SO_4 as electrolyte. Table 4 compares the untreated and the electro-oxidation-treated water. An average glyphosate concentration of 12.4 ± 0.5 mg L^{-1} was measured in influent water (control assay).

[Table 4 near here]

The control assay consisted only of agitating the synthetic glyphosate solution in the electrolytic cell without imposing any current density. By comparison, the application of electrochemical treatment reduced the concentration of glyphosate to an average value of 0.6 mg L^{-1} (with a standard deviation of 0.25 mg L^{-1}) which means that it can be supposed as accuracy constant of 7.81 %. Finally, the glyphosate removal efficiency had a mean value of 95.16% at the optimal conditions (I=4.77A, t=173 min) given a treatment cost of \$6.33 m^{-3} (\$1.08 per gram of glyphosate removed).

Conclusions

This study has shown the possibility of using an electrochemical technique to efficiently oxidize glyphosate (4 -16 mg L^{-1}) using Ti/PbO_2 anode. The first part of these works showed that the current intensity, treatment time, pH and initial concentration are the most influent parameters. The used of Na_2SO_4 as a supporting electrolyte was useful to take away the risk of formation of toxic by-products during electrolysis compared to other sodium salts (e.g., NaCl). Moreover, a CCD was employed to define the optimal operating conditions for glyphosate degradation. The electrochemical reactor operated at current intensity of 4.77 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 by the Canadian Environment Agency. Likewise, glyphosate decomposition based on the identified by-products exhibited that total mineralisation has been achieved. The total treatment cost was estimated to $1.08 per gram of glyphosate removed which showed a potential technology that can be used as advanced treatment to remove herbicides and other contaminants from water.

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Supplementary material

Additional tables and figures associated with this article can be found in the online version.

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Figure list

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

Fig. 2. Variation of glyphosate and TOC concentrations versus treatment time (operating condition: I= 5A, Initial glyphosate conc. = 16.9 mg L^{-1}, t= 0-360min)

Fig. 3. Effect of pH versus glyphosate degradation and mineralization rate (operating condition: I = 5A, Initial glyphosate conc. = 16.9 mg L^{-1}, t = 120 min).

Fig. 4. Effect of initial glyphosate concentration: normalized glyphosate concentration (4a) and normalized TOC concentration (4b). (Operating condition: I = 5A, Initial glyphosate conc. = 4.3-16.9 mg L^{-1}, t =0-120 min).

Table 1

Properties of glyphosate

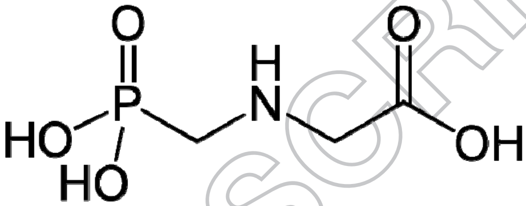
Herbicide	**Glyphosate**
Molecular structure	
Molecular weight, g mol^{-1}	169.07
Solubility, g L^{-1}	10.1
Log K_{ow}	-3.2
LD_{50}, mg kg^{-1}	4230
Maximum acceptable concentration in fresh water, mg L^{-1}	0.8

Table 2

Experimental range and levels of independent variables.

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

Table 3

Central composite matrix and experimental results

Assay	**Experimental design**		**Experimental plan**		**Response** (degradation results)	
	X_1	X_2	U_1 (A)	U_2 (min)	Glyphosate (mg L^{-1})	TOC removal (%)
1	0	+1.7	3.50	198.6	0.78	87.0
2	0	0	3.50	135.0	1.28	82.02
3	-1.7	0	1.38	135.0	1.43	77.45
4	0	0	3.50	135.0	1.3	82.71
5	+1	+1	5.00	180.0	0.44	93.95
6	+1	-1	5.00	90.0	0.99	80.26
7	0	0	3.50	135.0	1.25	81.46
8	0	-	3.5	71.	1.48	70.77

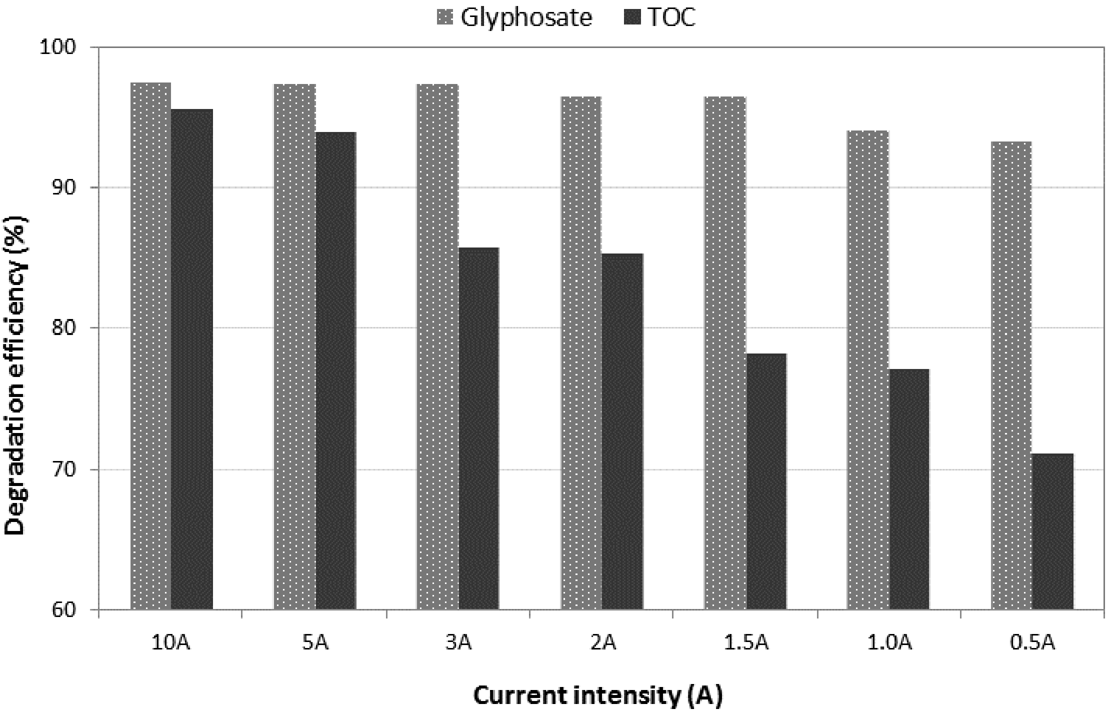
		1.7	0	36		
9	0	0	3.50	135.0	1.32	81.0
10	0	0	3.50	135.0	1.26	82.1
11	+1.7	0	5.62	135.0	0.68	89.0
12	-1	+1	2.00	180.0	0.59	85.3
13	-1	-1	2.00	90.0	1.58	62.51

Table 4

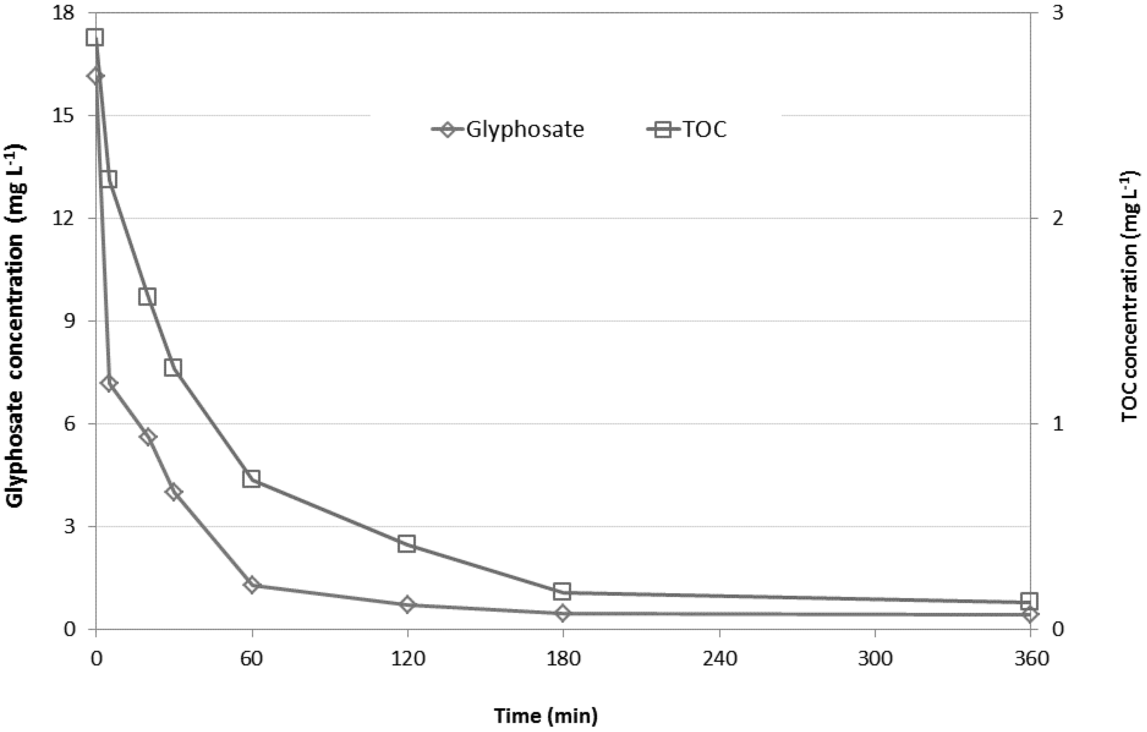
Optimum operating conditions and experimental results.

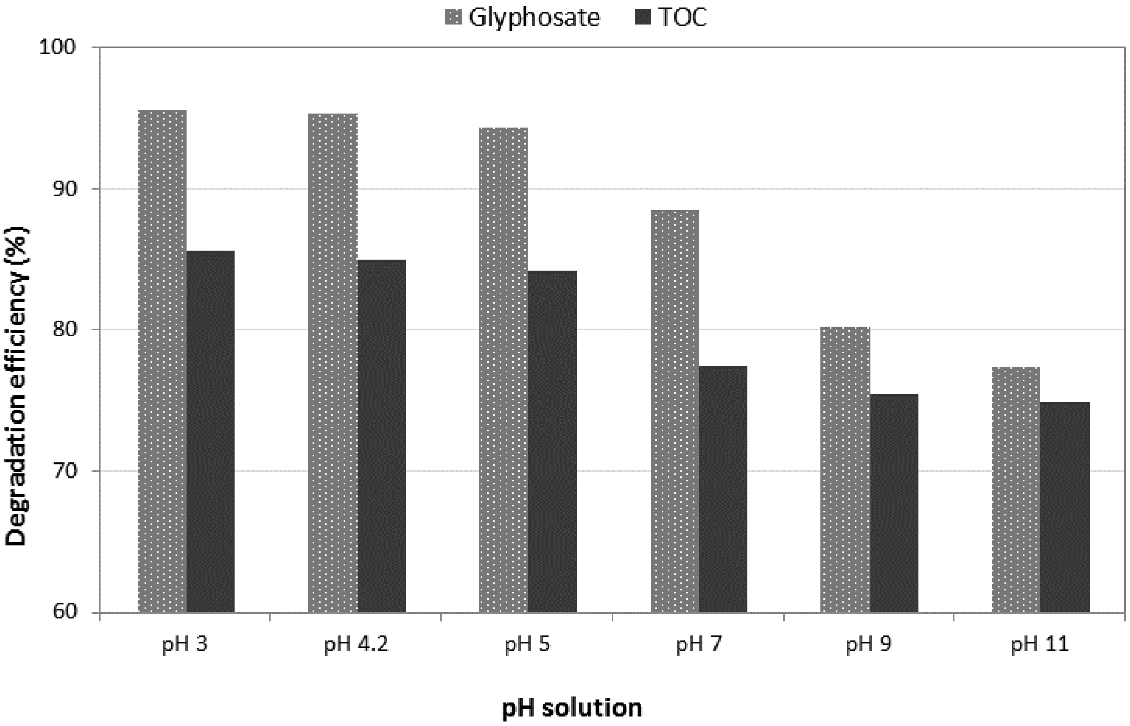
Parameter	**Optimal value and results**
Operating condition	
Treatment time, min	173
Current intensity, A	4.77
Glyphosate concentration, mg L^{-1}	16.9
Theoretical response:	
• Glyphosate concentration, mg L^{-1}	0.69
• TOC removal, %	90.28
Experimental results:	
Influent(before treatment)	
• pH	4.2 ± 0.5
• Glyphosate, mg L^{-1}	12.4 ± 0.5
• TOC, mg L^{-1}	2.007 ± 0.05
• P_{PO4}, mg L^{-1}	< 0. 1
• N_{NO3}, mg L^{-1}	0.048 ± 0.02
• N_{NH4}, mg L^{-1}	< 0.01
Effluent (after treatment)	
• pH	4.0 ± 0.5
• Glyphosate, mg L^{-1}	0.60 ± 0.25
• TOC, mg L^{-1}	0.1945 ± 0.02
• P_{PO4}, mg L^{-1}	1.911 ± 0.1

• N_{NO3}, mg L^{-1}	0.775 ± 0.04
• N_{NH4}, mg L^{-1}	0.364 ± 0.01
Experimental response:	
• Glyphosate removal, %	95.16
• TOC removal, %	90.31



Glyphosate
TOC
Degradation efficiency (%)
100
90
80
70
60
10A
5A
3A
2A
1.5A
1.0A
0.5A
Current intensity (A)


18
15
12
9
6
3
0
Glyphosate concentration (mg L-1)
3
2
1
0
TOC concentration (mg L-1)
Glyphosate
TOC
0
60
120
180
240
300
360
Time (min)


Glyphosate
TOC
Degradation efficiency (%)
100
90
80
70
60
pH 3
pH 4.2
pH 5
pH 7
pH 9
pH 11
pH solution

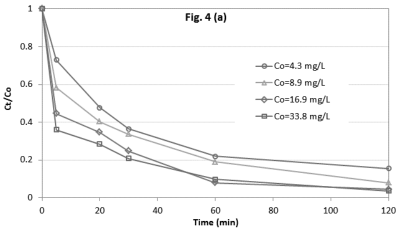


Fig. 4 (a)
Ct/Co
Time (min)
Co=4.3 mg/L
Co=8.9 mg/L
Co=16.9 mg/L
Co=33.8 mg/L
0
0.2
0.4
0.6
0.8
1
0
20
40
60
80
100
120

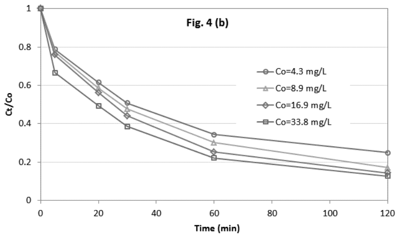


Fig. 4 (b)
Ct/Co
Time (min)
Co=4.3 mg/L
Co=8.9 mg/L
Co=16.9 mg/L
Co=33.8 mg/L
0
0.2
0.4
0.6
0.8
1
0
20
40
60
80
100
120