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Elimination of bio-refractory chlorinated herbicides like atrazine, alachlor, and chlorbromuron from aqueous effluents by Fenton, electro-Fenton, and peroxi-coagulation methods

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ABSTRACT

Alachlor, atrazine (broad-leaf herbicides), and chlorbromuron (photosynthesis inhibitor) have been used worldwide to control weeds in crops. Their extensive use have led to widespread contamination of soils, and water which has consequently led to increasing concern about the environmental fate of these substances, since these herbicides are persistent in the environment and exhibit relatively slow rate of decomposition. Several advanced oxidation processes have been used to degrade such bio-refractory organic contaminants present in wastewater. The Fenton process is classified among these processes and has been used for the removal of many hazardous organics from wastewater efficiently. This study reports the removal of alachlor, atrazine, and chlorbromuron from aqueous effluents by classical Fenton, electro-Fenton, peroxi-coagulation, and photoperoxi-coagulation processes in slightly acidic aqueous solutions. A UV lamp was used to assist the peroxi-coagulation process. Herbicide concentration decrease during the oxidation processes was followed by HPLC and chemical oxygen demand (COD) analyses. The reaction for the removal of these herbicides follows apparent-first-order kinetics. Photoperoxi-coagulation was better than electro-Fenton process. The use of UV-light irradiation during the herbicide elimination by peroxi-coagulation achieved total COD removal at 75 min for all the three herbicides treated. In the absence of UV-light irradiation, COD removals of 96, 97, and 93% were achieved for 83.3 mg/L alachlor, 62.0 mg/L of atrazine, and 35.0 mg/L of chlorbromuron, respectively.

Keywords: Atrazine; Alachlor; Chlorbromuron; Fenton; Herbicides

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1. Introduction

Intensive use of pesticides in agricultural activities results in pollution of raw water resources. Because of the movement and dispersion of pesticides, these herbicides are easy to migrate in agricultural ecosystem causing the pollution of soil, groundwater, air, surface water, aquatic life in general, plants, animals, food, and human populations through run-off, drainage, interflow, and leaching [1,2]. Chlorinated pesticides such as alachlor and atrazine represent a major class of synthetic organic compounds commonly found in contaminated waters [3–5]. Alachlor and atrazine are herbicides widely used for pre- and post-emergence control of broadleaf and grassy weeds in maize and other crops [4,5]. Chlorbromuron is a typical methylmethoxyurea herbicide related to the family of phenylurea herbicides [6,7]. It is widely used to inhibit the photosynthesis process of weeds [8]. These herbicides are persistent, toxic, and classified as probable human carcinogen by the US EPA [9,10]. Several water treatment processes for the elimination of herbicides have been reported, among them some can be mentioned like adsorption [11], photolysis [12], Fenton [13], photocatalysis [14], ozonation [15], direct electrolysis [16], and electrochemical methods such as electrocoagulation [17], peroxi-coagulation [18], and electro-Fenton [6,17,19] among others.

Recently, the electrochemical techniques have become very important water treatment methods because of their effectiveness for the mineralization of toxic and recalcitrant (bio-refractory) organic compounds. The destruction of such pollutants is commonly carried out by direct electrolysis (anodic oxidation) and indirect electrolysis (generation of an oxidant like H_2O_2) since these methods can convert such pollutants into CO_2 and inorganic ions. These methods have in common the generation of highly oxidizing and non-selective hydroxyl radicals ($OH^{\bullet}$). In anodic oxidation, adsorbed $OH^{\bullet}$ are formed at the surface of a high-oxygen overvoltage anode from water oxidation [18,20], as per reaction (1).

$$H_2O \rightarrow OH^{\bullet}_{ads} + H^+ + e^- \qquad (1)$$

whereas, in the indirect electrolysis, the H_2O_2 oxidant can continuously be supplied in slightly acidic media from the two-electron reduction of oxygen on a cathode surface made of reticulated vitreous carbon (RVC) [21], graphite [22], O_2-diffusion [23], and carbon felt [24]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$

The oxidizing power of H_2O_2 is enhanced by the catalytic Fe^{2+} (classical Fenton's reaction) generating $OH^{\bullet}$ [25]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^- \qquad (3)$$

This catalytic reaction is propagated from ferrous ion regeneration mainly by the reduction of the produced ferric species with electrogenerated hydrogen peroxide from reaction (2) [25,26]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (4)$$

In this way, the Fenton's reagent is generated in an acidic solution contained in the cathodic compartment of a divided cell in which Fe^{2+} is added and H_2O_2 electrogenerated *in situ* by oxygen reduction on the cathode (reaction (2)). Thereafter, organic pollutants are mineralized by the action of $OH^{\bullet}$ generated from reaction (3). When the Fenton's reaction takes place in an undivided cell with a Pt anode and the catalytic Fe^{2+} is added to the initial solution, to mineralize the pollutants by the combined action of $OH^{\bullet}$ generated from reaction (1) at the anode and from reaction (3) in the medium, it is known as electro-Fenton process [27]. If a sacrificial iron anode is used instead then the process is known as peroxi-coagulation. The soluble ferrous ion is continuously supplied to the reacting solution, according to the anodic reaction (5):

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (5)$$

Fe^{2+} reacts with electrogenerated H_2O_2 and the excess of Fe^{3+} formed precipitates as $Fe(OH)_3$. Therefore, the organic pollutants are removed by the combined action of $OH^{\bullet}$ generated from reaction (3) and coagulation with the $Fe(OH)_3$ precipitate [27].

The efficiency of Fenton and peroxi-coagulation processes is improved by using UV or visible light illumination. In light, the rate of $OH^{\bullet}$ formation is increased in these processes by photoreactions of H_2O_2 ($\lambda < {\sim}360\,\text{nm}$) [28] and/or Fe(III) [29] that produce $OH^{\bullet}$ directly or regenerate Fe^{2+} to feed into reaction (3) [25]:

$$H_2O_2 \xrightarrow{h\nu} 2OH \qquad (6)$$

$$Fe^{3+} + OH^- \xrightarrow{h\nu} Fe^{2+} + OH^{\bullet} \qquad (7)$$

The aim of this work was to study the removal of alachlor, atrazine, and chlorbromuron from aqueous effluents by Fenton, electro-Fenton, peroxi-coagulation, and photoperoxi-coagulation processes in slightly acidic aqueous solutions.

2. Experimental

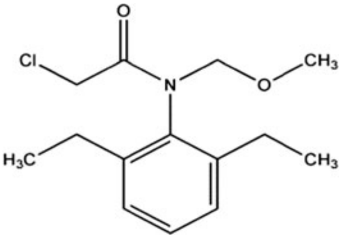
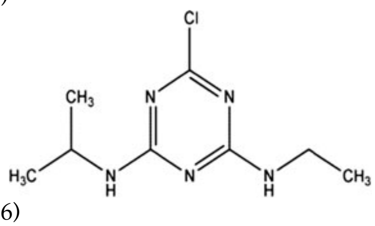
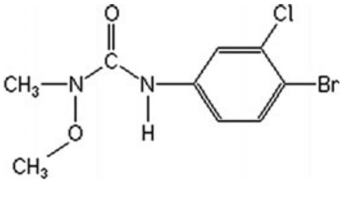
2.1. Chemicals

Pure compounds of alachlor (2-chloro-2-,6-diethyl-N-(methoxymethyl) acetanilide), atrazine (2-chloro-4-(isopropylamino)-6-(ethylamino)-s-triazine), and chlorbromuron (3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea) were of HPLC grade (99.9%). Sulfuric acid, sodium sulfate, and ferrous sulfate, were purchased from Sigma–Aldrich. Hydrogen peroxide (30%) was purchased from Hach. All solutions were prepared with distilled water and were saturated with oxygen (PRAXAIR, industrial grade). All the chemicals were used as received without further purification.

2.2. Procedures

Several molar ratios of H_2O_2:[Herbicide] solutions containing 1×10^{-3} M Fe^{2+}, 0.05 M Na_2SO_4 at pH 2 were tested varying the initial concentration of hydrogen peroxide while keeping constant the concentration of each herbicide: 3.09×10^{-4} M of alachlor, 2.89×10^{-4} M of atrazine, and 1.19×10^{-4} M of chlorbromuron. The degradation of herbicides was carried out by potential controlled electrolysis at -0.7 V vs. saturated calomel electrode (SCE) in the cathodic compartment using a potentiostat (PG590, Heka interfaced with a PC) in a three-electrode divided cell (0.19 L), and at constant cell voltage of 2.5 V using a power source (1627 A, Precision) in a two-electrode undivided cell (0.2 L). Details of the experimental set up can be found elsewhere [6]. Briefly, the three-electrode divided cell, comprised by a Pt gauze anode separated by a cation permeable membrane (Nafion® 117) using a (25 mm × 25 mm × 10 mm) RVC cathode (60 ppi, Electrolytic Inc., NY), was employed to electrogenerate hydrogen peroxide. The reference electrode was a SCE (Orion). The anodic compartment was filled up with 0.1 M H_2SO_4 solution; the electrolyses undertaken in the three-electrode undivided cell took place in the cathodic compartment where the membrane was substituted by an acrylic lid to keep similar experimental conditions [6]. Whereas, the undivided two-electrode cell, comprised of a stainless steel (316) anode (35 mm × 40 mm × 3 mm) and a RVC cathode, was employed to electrogenerate simultaneously the iron and the hydrogen peroxide in the solution. A UV lamp (15 W, 352 nm) was incorporated to the undivided two-electrode cell when needed. A constant

Table 1
Structural formula, molecular weight, and solubility of alachlor, atrazine, and chlorbromuron

Herbicide	Structural formula (molecular weight) (g/mol)	Solubility (mg/L)
Alachlor ($C_{14}H_{20}ClNO_2$)	 (269.8)	242
Atrazine ($C_8H_{14}ClN_5$)	 (216.06)	70
Chlorbromuron ($C_9H_{10}BrClN_2O_2$)	 (293.5)	35

stream of oxygen was flowing in the solution of the cathodic compartment (at pH 2) during the electrolyses carried out at room temperature (25°C). Samples were withdrawn during the electrolyses at timed intervals and reactions were quenched by addition of H_3PO_4 before the analyses of chemical oxygen demand (COD) and herbicide concentration by HPLC analysis. COD was analyzed using a Hach spectrophotometer (model DR 4000U), standard tubes, and standard methods [30] inside the concentration ranges of 0–20 mg/L COD and 0–150 mg/L COD. HPLC analysis was carried out using a Waters Resolve C18, 3.9 mm × 300 mm column, Waters 996 Photodiode Array Detector, and Waters 600 Pump and Controller. The maximum absorption wavelength of atrazine was selected as 238 nm, for alachlor 212 nm, and for chlorbromuron 204 nm. The mobile phase consisted of 70% acetonitrile with 30% distilled–deionized water, and was delivered at a flow rate of $1.0\,\mathrm{mL\,min^{-1}}$, which resulted in an atrazine peak at 3.2 min, alachlor peak at 5.5 min, and chlorbromuron peak at 4.4 min. Calibration curves were constructed by plotting the area under the peak *vs.* [herbicide] for each herbicide. Table 1 shows the features of the herbicides employed.

The current efficiency (CE, %) for the oxidation of the herbicides was calculated [31] as per Eq. (8):

$$\mathrm{CE}\,(\%) = \frac{(\mathrm{COD}_0 - \mathrm{COD}_f)}{\mathrm{O_{Eq}It}}\mathrm{FV}(100) \tag{8}$$

where COD_0 and COD_f (in $\mathrm{g_{O2}\,dm^{-3}}$) are the initial and final CODs, respectively. $\mathrm{O}_{\mathrm{E}q}$ is the oxygen equivalent mass ($8\,\mathrm{g\,eq^{-}}$), I is the current (A), t is the oxidation time (s), F is the Faraday constant (96,487 C/mol), and V is the volume of the electrolyte ($\mathrm{dm^3}$).

The specific energy consumption (EC, in $\mathrm{kW\,h\,m^{-3}}$) was calculated [6,32] by Eq. (9):

$$\mathrm{EC} = \frac{U_{\mathrm{cell}}\mathrm{It}}{3600\mathrm{V}} \tag{9}$$

where U_{cell} is the cell voltage (V), I is the current (A), t is the electrolysis time (s), and V is the volume of the treated solution ($\mathrm{dm^3}$).

3. Results and discussion

3.1. Degradation of the herbicides by the classical Fenton's reaction

The electrochemical oxidation reactions corresponding to the electrochemical mineralization process can be expressed according to reaction (10) for alachlor, reaction (11) for atrazine, and reaction (12) for chlorbromuron.

$$\text{Alachlor: } C_{14}H_{20}ClNO_2 + 26H_2O \rightarrow 14CO_2 + NH_3 + HCl + 68H^+ + 68e^- \tag{10}$$

$$\text{Atrazine: } C_8H_{14}ClN_5 + 16H_2O \rightarrow 8CO_2 + 5NH_3 + HCl + 30H^+ + 30e^- \tag{11}$$

$$\text{Chlorbromuron: } C_9H_{10}BrClN_2O_2 + 22H_2O \rightarrow 9CO_2 + HBr + HCl + 2HNO_3 + 50H^+ + 50e^- \tag{12}$$

These involve $68e^-$, $30e^-$, and $50e^-$ reactions for alachlor, atrazine, and chlorbromuron, respectively. The atom of nitrogen is considered to be converted into NH_3 in alachlor and atrazine, and HNO_3 in chlorbromuron. This is based on the degradation mechanisms of alachlor [33], atrazine [34,35], and phenylurea herbicides [7] proposed by several authors. Thus, the stoichiometric conversion of 1 mol of each herbicide to CO_2 requires 34, 15, and 25 mol of H_2O_2 for alachlor, atrazine, and chlorbromuron, respectively, as shown in Table 2. Fig. 1 shows the evolution of COD as a function of different molar ratios of $[H_2O_2]$:[Herbicide] for each herbicide in the presence of 1×10^{-3} M Fe^{2+} at pH 2. The stoichiometric molar ratio of $[H_2O_2]$:[Herbicide] for each herbicide did not produce a total oxidation of each herbicide, since COD removals of 97, 88, and 89% for alachlor, atrazine, and chlorbromuron,

Table 2
H_2O_2 stoichiometry (stq) for the conversion of 1 mol of herbicide to CO_2 and COD removal (for different molar ratios of $[H_2O_2]$:[herbicide] by classical Fenton's reaction using H_2O_2 + 1 mM Fe^{2+} at pH 2 at 75 min of reaction)

	$[H_2O_2]$:[Herbicide]			
Reactions for complete chemical oxidation of herbicides	= stq	COD (%)	> stq	COD (%)
$C_{14}H_{20}ClNO_2 + 34H_2O_2 \rightarrow 14CO_2 + NH_3 + HCl + 42H_2O$ (Alachlor)	34	97	51.0	100
$C_8H_{14}ClN_5 + 15H_2O_2 \rightarrow 8CO_2 + 5NH_3 + HCl + 14H_2O$ (Atrazine)	15	88	22.5	96
$C_9H_{10}BrClN_2O_2 + 25H_2O_2 \rightarrow 9CO_2 + HBr + HCl + 2HNO_3 + 28H_2O$ (Chlorbromuron)	25	89	37.5	100

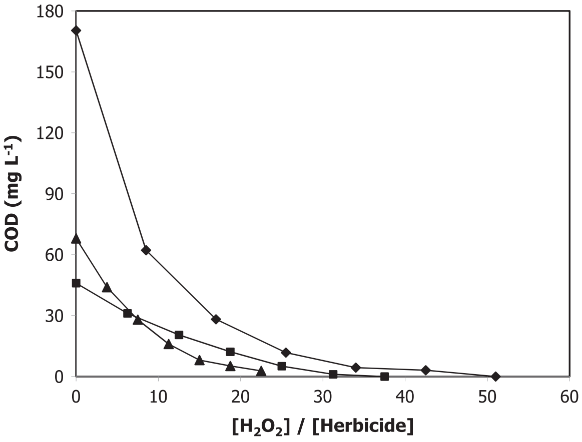


Fig. 1. Showing the evolution of COD profile as a function of several molar ratios of $[H_2O_2]$:[Herbicide] for ♦ alachlor (3.085×10^{-4} mol/L), ▲ atrazine (2.89×10^{-4} mol/L), and ■ chlorbromuron (1.19×10^{-4} mol/L) in the presence of 1×10^{-3} M Fe^{2+} at pH 2. The concentration of H_2O_2 varied: for alachlor $0 < [H_2O_2] < 15.75 \times 10^{-3}$ mol/L, for atrazine $0 < [H_2O_2] < 6.50 \times 10^{-3}$ mol/L, and for chlorbromuron $0 < [H_2O_2] < 4.46 \times 10^{-3}$ mol/L.

respectively, were achieved. Table 2, also indicates that a molar ratio of $[H_2O_2]$:[Herbicide] > stoichiometry were needed to completely remove the COD in alachlor and chlorbromuron, but for atrazine only a 96% of COD was removed. These figures indicate that the complete chemical oxidation of each herbicide is more complex than that shown by these chemical reactions, since the amount of H_2O_2 required depends on the degradation mechanism followed by each herbicide during the degradation process. Also, the by-products formed during the degradation of the herbicides also demand H_2O_2.

The effect of different initial concentrations of herbicides during their degradation by the classical Fenton's reaction, in the presence of the stoichiometric amount of H_2O_2 and 1×10^{-3} M Fe^{2+} at pH 2, is depicted in Fig. 2. This figure shows that the evolution of COD profile with time follows similar trend for all the initial concentrations of alachlor, atrazine, and chlorbromuron used.

3.2. Electro-Fenton

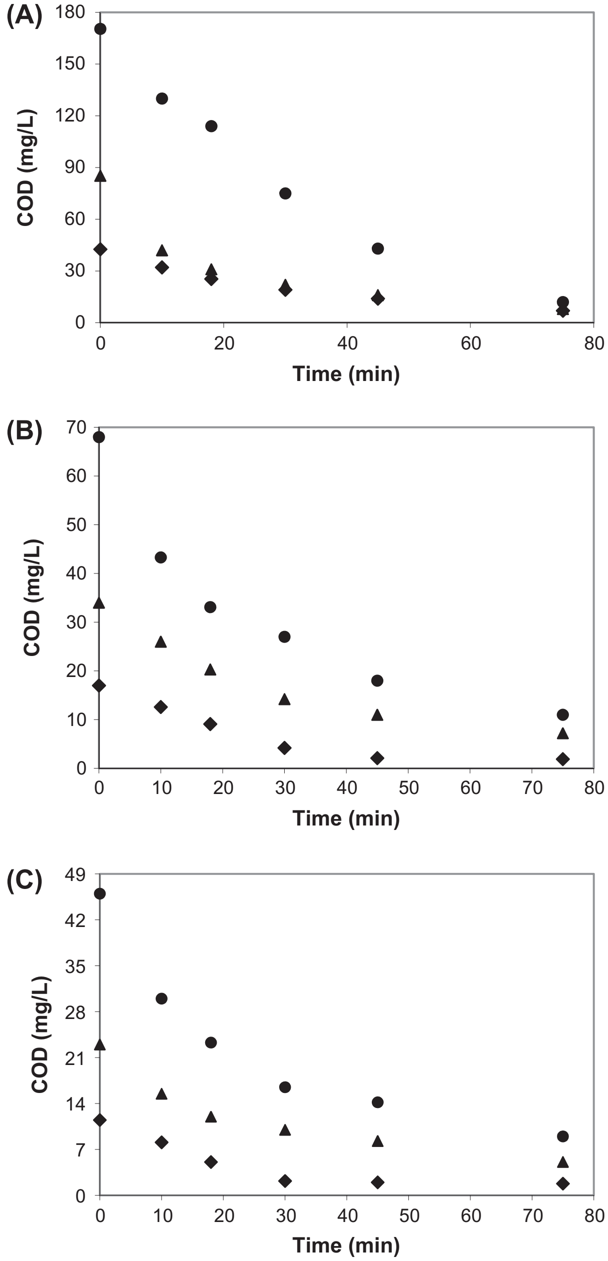


Fig. 2. Evolution of COD profile as a function of time for different initial concentrations of (A) alachlor, (B) atrazine, and (C) chlorbromuron in the presence of the stoichiometric amount of H_2O_2 and 1×10^{-3} M Fe^{2+} at pH 2.

The degradation of alachlor, atrazine, and chlorbromuron herbicides was carried out by the electro-Fenton reaction in which the hydrogen peroxide was continuously supplied by a two-electron reduction of oxygen reaction on the RVC cathode in acidic solutions [36], as per reaction (2). The oxidation power of H_2O_2 was enhanced by using ferrous ions (1×10^{-3} mol/L Fe^{2+}) which leads to the formation of highly oxidizing and non-selective $OH^{\cdot}$ radicals, as shown by reaction (3).

The H_2O_2 was electrogenerated in herbicide solutions (containing 1×10^{-3} M Fe^{2+}) using divided and undivided three-electrode cells by potential-controlled electrolysis applying 0.7 V vs. SCE to the cathode at pH 2 under a continuous stream of oxygen. Fig. 3

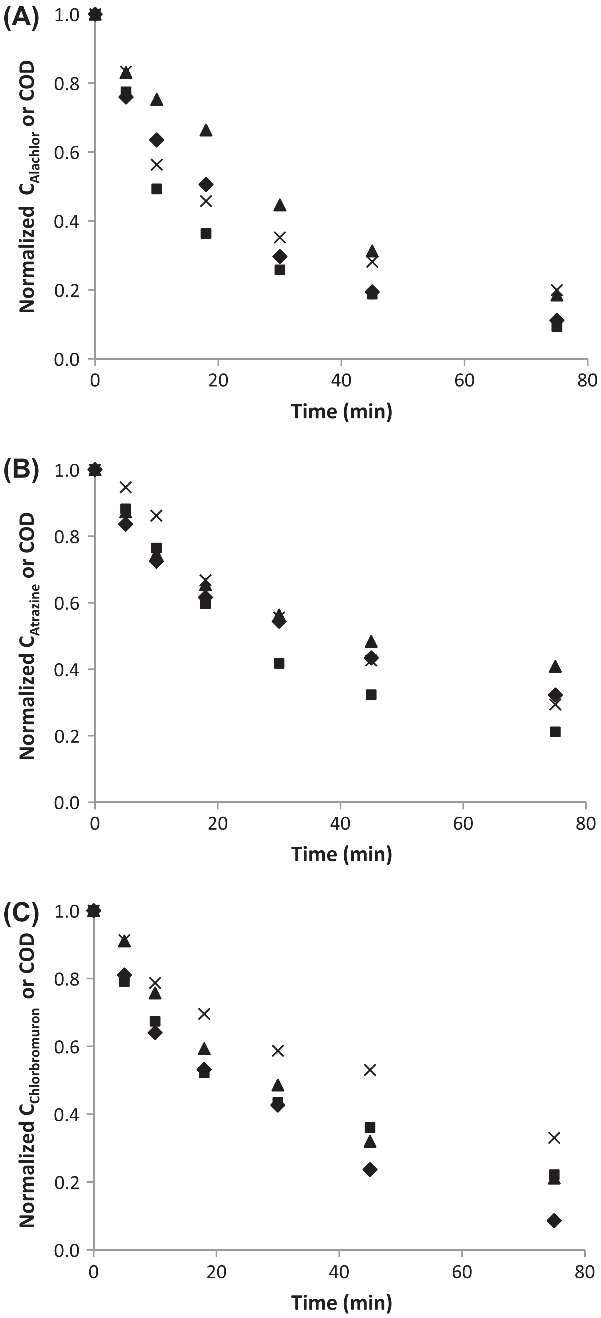


Fig. 3. Normalized concentration of herbicides (♦,▲) and normalized COD (■,×) as a function of time for (A) 41.2 mg/L of alachlor with COD = 85.2 mg/L, (B) 31 mg/L of atrazine with COD = 34 mg/L, and (C) 17 mg/L of chlorbromuron with COD = 23 mg/L in the presence of 1×10^{-3} M Fe^{2+} and electrogenerated H_2O_2 using a divided cell (♦,■) and undivided cell (▲,×) at pH 2.

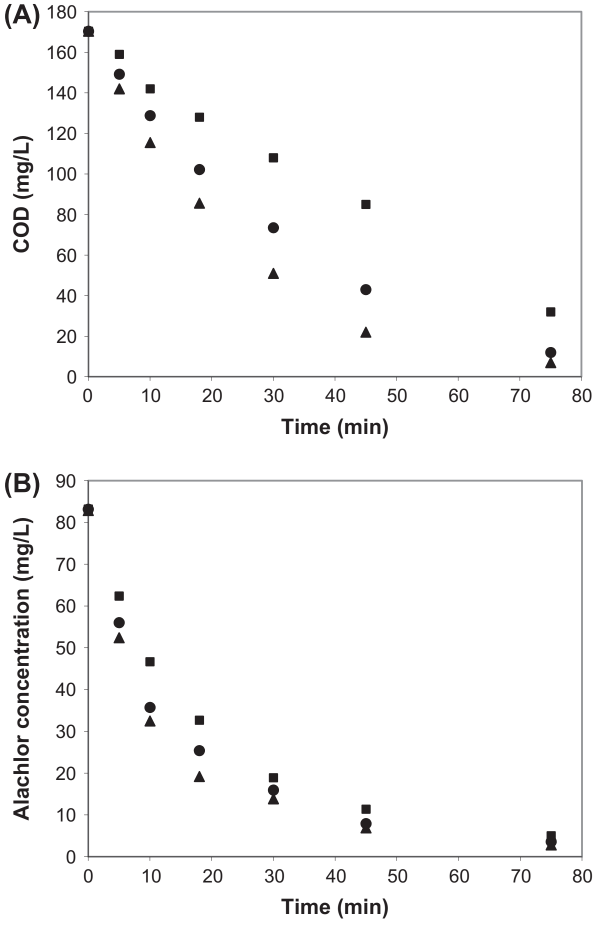


Fig. 4. Showing a comparison of the profile decay for the degradation of alachlor by Fenton reaction using a divided (•) and undivided (■) electrochemical cell, and peroxi-coagulation (▲) processes at pH 2. (A) COD removal and (B) alachlor concentration with time in the presence of 1×10^{-3} M Fe^{2+} in • and ■. All solutions contained 0.05 mol/L Na_2SO_4 with a constant stream of oxygen.

shows the evolution of normalized herbicide concentration and normalized COD during the degradation of (A) 41.2 mg/L of alachlor ($COD_0 = 85.2$ mg/L), (B) 31 mg/L of atrazine ($COD_0 = 34$ mg/L), and (C) 17 mg/L of chlorbromuron ($COD_0 = 23$ mg/L) by electro-Fenton. In the absence of the cationic membrane (undivided cell), only 80, 70, and 67% of COD depletion and 89, 60, and 79% of herbicide concentration decrease were achieved at 75 min of electrolysis for alachlor, atrazine, and chlorbromuron, respectively. This is because the H_2O_2 is oxidized on the anode surface decreasing the amount of $OH^{\cdot}$ radicals. Also, the ferrous ions can be oxidized on the anode and regenerated on the cathode. In contrast, in the divided cell (with membrane), the oxidation of the herbicides was accelerated because of the increased formation of $OH^{\cdot}$ radicals as per reaction (3) in the Fenton's reaction; thus, a final mineralization of 91, 79, and 79% of COD was achieved at 75 min of electrolysis for alachlor, atrazine, and chlorbromuron, respectively. A final herbicide concentration of 90, 68, and 92% was also achieved at 75 min of electrolysis for alachlor, atrazine, and chlorbromuron, respectively. Higher mineralization during herbicide oxidation by electro-Fenton was achieved in a divided electrochemical cell.

3.3. Oxidation of herbicides by Fenton, electro-Fenton, peroxi-coagulation, and photoperoxi-coagulation

A series of electrolyzes at constant voltage were carried out to oxidize alachlor, atrazine, and chlorbromuron at pH 2 by Fenton (in a divided cell), electro-Fenton (undivided cell), and peroxi-coagulation processes without and with UV light. In electro-Fenton process 1×10^{-3} M Fe^{2+} was added to the herbicide solutions and the pH practically was unchanged; while, in the peroxi-coagulation process the pH varied from 2 to 2.7 during the 75 min of oxidation but it was not regulated. Figs. 4–6 show the comparative COD abatement for a 170.4 mg/L of alachlor solution, a 68 mg/L of atrazine solution, and a 46 mg/L of chlorbromuron solution, respectively, of initial pH 2 treated for 75 min by Fenton (divided cell), electro-Fenton (undivided cell), and peroxy-coagulation processes. These figures also show the depletion of herbicide concentrations during these treatment methods. All herbicides were rapidly destroyed by all the three processes tested, and the degradation of all the herbicides follows the oxidation order of (▲) peroxi-coagulation > (•) Fenton (divided

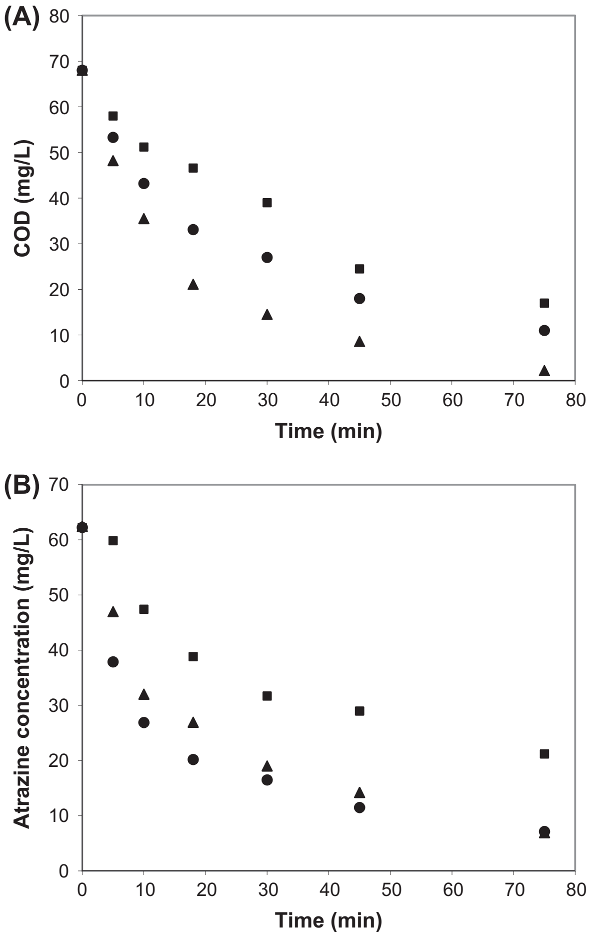


Fig. 5. Showing a comparison of the profile decay for the degradation of atrazine by Fenton reaction using a divided (•) and undivided (■) electrochemical cell, and peroxi-coagulation (▲) processes at pH 2. (A) COD removal and (B) atrazine concentration with time in the presence of 1×10^{-3} M Fe^{2+} in • and ■. All solutions contained 0.05 mol/L Na_2SO_4 with a constant stream of oxygen.

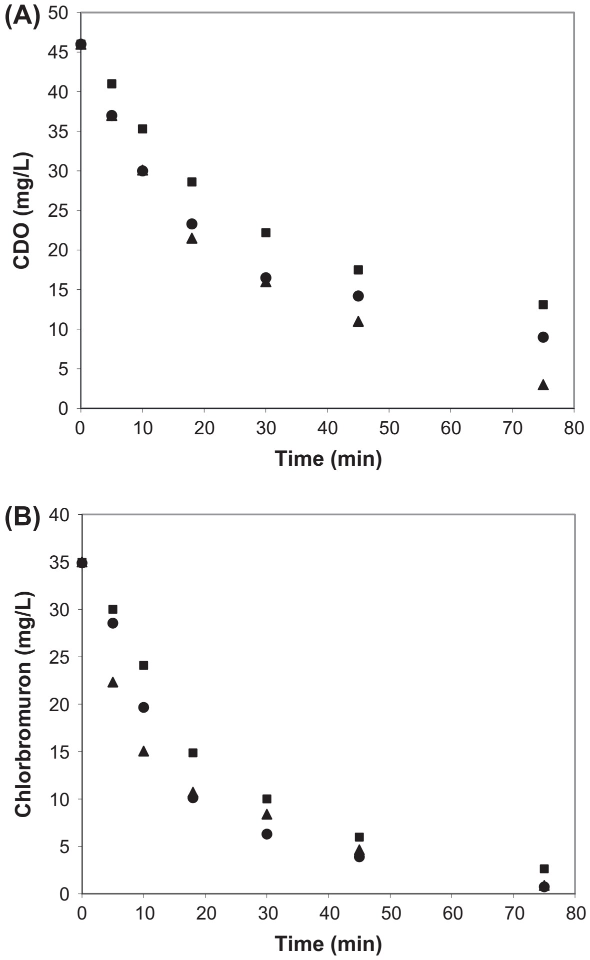


Fig. 6. Showing a comparison of the profile decay for the degradation of chlorbromuron by Fenton reaction using a divided (•) and undivided (■) electrochemical cell, and peroxi-coagulation (▲) processes at pH 2. (A) COD removal and (B) Chlorbromuron concentration with time in the presence of 1×10^{-3} M Fe^{2+} in • and ■. All solutions contained 0.05 mol/L Na_2SO_4 with a constant stream of oxygen.

cell) > (■) electro-Fenton (undivided cell), as reported in Tables 3 and 4.

COD reductions of 96, 97, and 93% for alachlor, atrazine, and chlorbromuron, respectively, were achieved by peroxi-coagulation process at 75 min. The rapid COD abatement under peroxi-coagulation conditions may be attributed to the higher generation of $OH^{\cdot}$ radicals by the continuous generation of Fe^{2+} from the oxidation of the anode [26], as per reaction (5). The high COD removal (mineralization) is also indicative of the formation of a large proportion of easily oxidable by-products with $OH^{\cdot}$ during the oxidation of all the three herbicides by the peroxi-coagulation process. Whereas, COD reductions of 93, 84, and 80% for alachlor, atrazine, and chlorbromuron, respectively, were achieved at 75 min of oxidation by Fenton (using a divided cell, with membrane). These results show that the peroxi-coagulation method is

Table 3
Apparent first order reaction for COD and Herbicide concentration removal: (a) Classical Fenton's reaction (CF) using the stoichiometry with addition of 1 mM Fe^{2+} at pH 2, (b) Fenton using a divided cell (F(d-cell)), (c) electro-Fenton (undivided cell) (EF(u-cell)) with addition of 1 mM Fe^{2+} at pH 2 and −0.7 V vs. SCE, and (d) Peroxi-coagulation (P-c) using pH 2 and 2.5 V of voltage cell. All solutions contained 0.05 mol/L Na_2SO_4 with a constant stream of oxygen

	Alachlor (83 mg/L)		Atrazine (62 mg/L)		Chlorbromuron (35 mg/L)	
Degradation process	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
COD						
CF	0.0356	0.986	0.0233	0.970	0.0211	0.941
F(d-cell)	0.0350	0.990	0.0236	0.969	0.0211	0.941
EF(u-cell)	0.0213	0.961	0.018	0.978	0.017	0.955
P-c	0.0435	0.997	0.044	0.989	0.0348	0.991
[Herbicide]						
F(d-cell)	0.0408	0.965	0.026	0.896	0.0502	0.988
EF(u-cell)	0.0373	0.979	0.0135	0.914	0.0351	0.984
P-c	0.0432	0.955	0.0276	0.962	0.0450	0.981

Table 4
COD removal and CE calculation obtained using several degradation processes: (a) Fenton using a divided cell (F(d-cell)), (b) electro-Fenton in undivided cell (EF(u-cell)) with addition of 1 mM Fe^{2+} at pH 2 and −0.7 V vs. SCE, and (c) peroxi-coagulation (P-c) using pH 2 and 2.5 V of voltage cell. All solutions contained 0.05 mol/L Na_2SO_4 with a constant stream of oxygen

		F(d-cell)		EF(u-cell)		P-c	
Herbicide	[Herbicide] (mg/L)	COD_{Rem} (%)	CE (%)	COD_{Rem} (%)	CE (%)	COD_{Rem} (%)	CE (%)
At 0.5 h							
Alachlor	83.3	57	100	37	100	70	100
	41.7	74	100	65	100	–	–
Atrazine	62.0	60	100	43	74	79	73
	31.0	58	50	44	39	–	–
Chlorbromuron	35.0	64	75	52	61	65	41
	17.4	57	33	41	24	–	–
At 1.25 h							
Alachlor	83.3	93	100	81	100	96	89
	41.7	91	78	80	69	–	–
Atrazine	62.0	84	58	75	52	97	36
	31.0	79	27	71	24	–	–
Chlorbromuron	35.0	80	38	72	34	93	24
	17.4	78	18	67	16	–	–

more effective for the oxidation of alachlor, atrazine and chlorbromuron.

Regarding to the depletion of the herbicide concentration (as shown in graphs (B) of Figs. 4–6 for alachlor, atrazine, and chlorbromuron, respectively), all herbicide solutions treated by Fenton (using a divided cell) and peroxi-coagulation methods exhibited the same COD removals under the conditions of these two processes: 97, 89, and 97% for alachlor, atrazine, and chlorbromuron, respectively.

COD abatement and herbicide concentration decrease followed a pseudo-first-order reaction during the oxidation of alachlor, atrazine, and chlorbromuron by these processes, as described by Eq. (13) [37]:

$$\ln\frac{\text{Parameter}_0}{\text{Parameter}_f} = kt \tag{13}$$

where Parameter_0 and Parameter_f are the initial COD or initial herbicide concentration and the final COD or final herbicide concentration, respectively. Table 3 shows a comparison of k values (pseudo-first-order rate constant) for COD depletion and herbicide concentration removal by: (a) classical Fenton's reaction (kCF) using the stoichiometry with addition of 1 mM Fe^{2+} at pH 2, (b) Fenton using a divided cell (kF(d-cell)), (c) electro-Fenton in an undivided cell (kEF(u-cell)) with addition of 1 mM Fe^{2+} at pH 2 and -0.7 V vs. SCE, and (d) peroxi-coagulation (kP-c) using pH 2 and 2.5 V of voltage cell. All solutions contained 0.05 mol/L Na_2SO_4 with a constant stream of oxygen. A comparison of k values obtained for the classical Fenton's reaction with those from the tested methods, indicate that $k\text{CF} < k\text{P-c}$, $k\text{CF} = k\text{F(d-cell)}$, and $k\text{CF} > k\text{EF(u-cell)}$; thus, the rate for COD removals is higher for the peroxi-coagulation method.

The increase of oxidation time and the decrease of herbicide concentration in bulk solution during the treatment caused a decrease of CE due to secondary reactions (Table 4). Table 4 shows that: (a) the lowest CE was observed for chlorbromuron removal, (b) lower current efficiencies were observed for the peroxi-coagulation process for the oxidation of all three herbicides, and (c) alachlor oxidation showed the highest current efficiencies for all the treatment processes.

Based on the better performance of the peroxi-coagulation process on herbicide elimination, a UV-lamp (352 nm) was incorporated to the cell configuration of the peroxi-coagulation process (photoperoxi-coagulation) using same conditions (cell voltage of 2.5 V, 0.2 L, pH 2, 50×10^{-3} mol/L Na_2SO_4 electrolyte and O_2 bubbling). Fig. 7 shows the normalized COD decay as a function of time for (■) 83.2 mg/L of alachlor with 170.4 mg/L of COD, (▲) 62.5 mg/L of atrazine with 68 mg/L of COD, and (•) 35.0 mg/L of chlorbromuron with 46.0 mg/L of COD obtained by the photoperoxi-coagulation method. As illustrated in Fig. 7, the use of UV-light irradiation during the herbicide elimination by peroxi-coagulation achieved total COD removal at 75 min for all the three herbicides treated. In the absence of UV-light irradiation, COD removals of 96, 97, and 93% were achieved for 83.3 mg/L alachlor, 62.0 mg/L of atrazine, and 35.0 mg/L of chlorbromuron, respectively. 100% of COD removals at 75 min by photoperoxi-coagulation increased the specific energy consumption.

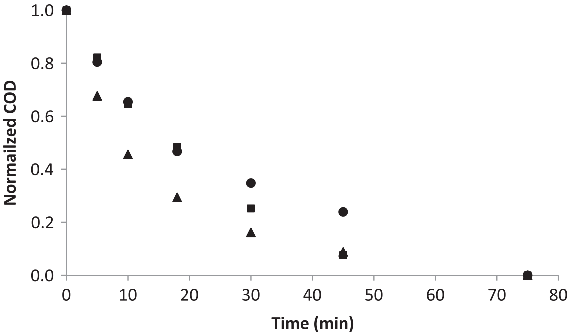


Fig. 7. Normalized COD decay as a function of time for (■) 83.2 mg/L of alachlor with 170.4 mg/L of COD, (▲) 62.5 mg/L of atrazine with 68 mg/L of COD, and (•) 35.0 mg/L of chlorbromuron with 46.0 mg/L of COD. Photoperoxi-coagulation processes (2.5 cell voltage and UV light 352 nm, at pH 2,). All solutions contained 0.05 mol/L Na_2SO_4 with a constant stream of oxygen.

3.4. Energy consumption

The specific energy consumption (EC, in kW h m^{-3}) was calculated by Eq. (9) for the peroxi-coagulation process which showed better performance on herbicide elimination. The cell configuration for the peroxi-coagulation process had a cell voltage of 2.5 V (0.098A) and a volume of 0.2 L. Thus, the specific energy consumption for COD removals at 75 min of electrolysis for herbicide oxidation is 1.53 kW h m^{-3}. This energy consumption accounts for a 96% of COD removal of 83.3 mg/L of alachlor (89% CE), 97% of COD removal of 62.0 mg/L of atrazine (36% CE), and 93% of COD removal of 35.0 mg/L of chlorbromuron (24% CE). Clearly, chlorbromuron is more difficult to eliminate from the solution than alachlor and atrazine since the same specific energy consumption is demanded for treating lower initial concentration. Its energy consumption may be related with the formation of more stable compounds and the decreasing of its initial low concentration in the bulk solution caused a decrease of CE and an increase of side reactions.

4. Conclusions

This study has shown that peroxi-coagulation with a sacrificial iron anode and RVC cathode assisted by an UV-light irradiation (photoperoxi-coagulation) was a very effective process for the elimination of alachlor, atrazine, and chlorbromuron herbicides in slightly acidic aqueous solutions at $pH < 3$.

The stoichiometric molar ratio of $[H_2O_2]$:[Herbicide] for each herbicide did not produce a total oxidation of each herbicide, since COD removals of 97, 88, and 89% for alachlor, atrazine, and chlorbromuron, respectively, were achieved. These results showed that the rate for COD removals was higher for the peroxi-coagulation method. The photoperoxi-coagulation method achieved total COD removal at 75 min for all the three herbicides treated. In the absence of UV-light irradiation, COD removals of 96, 97, and 93% were achieved for 83.3 mg/L alachlor, 62.0 mg/L of atrazine, and 35.0 mg/L of chlorbromuron, respectively.

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