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Full Paper

Combined Electro-Fenton and Biological Process for Treatment of Antidepressant Sertraline: Performance Enhancement and By-Products Monitoring

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Abstract- In this work, we evaluated the potential of combining Fenton's reagent and biological treatment to remove persistent pharmaceutical pollutants, specifically sertraline hydrochloride (SER-HCl) with a view to mineralizing it in an economical and ecological way. A single-compartment batch reactor containing a carbon felt cathode and a platinum anode was used to perform the electro-Fenton pretreatment of SER-HCl. GC-MS and LC-MS were used to identify the intermediate by-products and thus to suggest a probable path of degradation. In addition, tracking of inorganic ions as well as the nitrogen and chloride molecules liberated during SER-HCl electrolysis was determined by ion chromatography. Then, the continuous aerobic degradation of SER-HCl, was studied for a period of 21 days at around 25 °C. A complete degradation of SER-HCl (0.1 mM) was noted at 400 mA after 5 min of electrolysis. In addition, an improvement in the BOD5/COD ratio was observed from an initial value of

0.042 to 0.33 and 0.47 over 1.5 and 2 hours of electrolysis respectively. The solution should be biodegradable after 1.5 hours of electro-Fenton pretreatment, from which the pharmaceutical product oxidized to readily biodegradable compounds, mostly short-chain carboxylic acids, which are available for uptake by microorganisms. In this point, a biological process of the electrolysis co-products after 1 h and 30 min, and 2 h was then performed aiming at biodegrading the remaining products. As a result, the COD yield increased slightly throughout the 21 days to 90.7% and 94.2% for 1 h30min and 2 h, respectively, showing the suitability of the proposed coupled process.

Keywords- Antidepressant Sertraline; Bio-Electro Fenton; Biodegradability; Electro-Fenton; Biological treatment

1. INTRODUCTION

Pharmaceutical pollutants include a set of stable active components which is persistent against degradation by microorganisms which leads to contamination of the aquatic environment [1,2]. In fact, hospital effluents are usually thrown into the ecosystem without any prior pretreatment, leaving behind an accumulation of effluents containing non-biodegradable persistent organic pollutants such as psychiatric drugs [3,4].

One of the major antidepressant pollutants that have been detected in aquatic samples in various countries with undesirable effects on aquatic organisms [3,5] is a selective serotonin reuptake inhibitor, called sertraline hydrochloride (SER-HCl). This molecule is hydrolytically stable and poorly biodegradable [5]. This results in bioaccumulation at the level of aquatic organisms, such as invertebrates, fish, and aquatic beetles [1]. In addition, the toxicological effect of sertraline bioaccumulation on some microbial aquatic organisms has been reported in several studies, citing growth inactivation in *Pseudo-kirchneriella subcapitata* and *Simulium vittatum*, gene transcription inhibition in *Danio rerio*, and reproductive toxicity in *Pimephales promelas* [1,6]. The environmental problem caused by the presence of this antidepressant drug SER-HCl in wastewater and surface water is a challenge to develop effective and economical methods to remove completely this persistent organic pollutant.

Currently, several technologies have been implemented to eliminate sertraline hydrochloride (SER-HCl) in water [5], including photodegradation, gamma radiation and biological treatment [7-11]. However, this type of process, although effective, but requiring a long time to completely remove the persistent pollutant, as well as the transformation of the parent molecule into a toxic by-product becomes incapable of being easily degraded.

On the other hand, Advanced Oxidation Processes (AOPs) have appeared as successful high-performance technologies to completely oxidize persistent organic pollutants (POPs) existing in water. Among the various advanced oxidation processes, the electro-Fenton (EF) process is the most applied electrochemical advanced oxidation process (EAOP) [12,13] due to its remarkable advantages, such as high yields, ability to operate under mild conditions, economic feasibility, ease of automation and environmental friendliness [13,14]. This electrochemical process is based on the non-selective generation of potent active species such

as $^{\bullet}OH$ [2,14] formed by the reaction of H_2O_2 with Fe^{2+} (eq.1), on the one hand, this equation is made by a simultaneous generation of H_2O_2 according to a cathodic reduction of two electrons of dissolved oxygen (eq.2), otherwise, Fe^{2+} ions are regenerated electrocatalytically by the reduction of Fe^{3+} ions (eq.3) formed in the Fenton reaction. This procedure proved to have a good potential to degrade and mineralize various species of contaminants persistent, such as pesticides, pharmaceuticals and antidepressants [2,12,13,15].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$

$$O_2 + 2H^+ + 2\,e^- \rightarrow H_2O \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

In spite of their strong oxidization capacity, however, electro-Fenton (EF) requires a high additional consumption of energy [2,13,15] for the mineralization experiments, which limits its practical application. On the positive side, performing biological treatment immediately after a solution pretreated by the electro-Fenton process can substantially minimize the operational costs [13,16]. This approach is particularly useful when the microorganisms existing in the activated sludge are not capable of analyzing the native substance, that is to say, they must not be biodegradable [16].

Indeed, by using the EF process as a pretreatment step, the solution becomes biodegradable, from where, the parent drug is transformed into easily biodegradable and less toxic compounds [16,17]. Because, during the degradation of the electro-Fenton process, oxidation reactions open the aromatic rings of the molecule and subsequently form aliphatic molecules, including short-chain carboxylic acids [18]. These latter are considered as biodegradable substances. This clarified the importance of performing electro-Fenton as a pre-treatment before the conventional biological process [13,15-17,19, 20,21].

In previous work, we carried out the electro-Fenton process to degrade and completely remove the sertraline hydrochloride molecule (SER-HCl), also we investigated the possibility of combining this electrochemical (EF) process with a bioprocess to achieve a cost-effective approach, while determining the influence of different parameters affecting the process, such as the initial drug concentration, the current intensity and the Fe^{2+} catalysis dose. Now, this paper aims to apply the coupling between the electro-Fenton process as a pretreatment station followed by an anaerobic treatment in order to mineralizing this type of pollutant (SER-HCl) in an economic condition. In this purpose, a monitoring of SER-HCl mineralization, biodegradability of electrolysis by-products was examined, as well as the identification of by-products via EF application was followed in terms to better comprehend the degradation pathway of SER-HCl.

2. EXPERIMENTAL METHODS

2.1. Chemical and reagent

The pollutant treated; Sertraline hydrochloride ($C_{17}H_{17}NCl_2$, HCl) (>98% purity) was acquired from laboratory Polymedic (Casablanca, Morocco). Ferrous sulfate hepta-hydrated $FeSO_4.7H_2O$ was selected as a catalyst. Potassium chloride KCl was procured from Shanghai chemicals (Shanghai, China) and Na_2SO_4 (99% purity) was obtained from Fluka Analytical. All solutions were made with pure ultrapure milliQ water (Millipore) possessing a resistivity > 18 MΩ cm. pH adjustment of the solutions was made by the addition of sulfuric acid (96% purity) provided from Sigma-Aldrich (Saint-Quentin Fallavier, France).

2.2. Electrochemical procedure

Pretreatment of SER-HCl was realized with an electrochemical cell at volume of 250 mL. The delivery of the current intensity during the electrolysis was done with a potentiostat-galvanostat type PGZ 100 from VoltaLab in an electrochemical cell composed of a cathode of a carbon-lorraine felt (6 cm×5 cm×0.5 cm) and an anode of a platinum sheet (2.5 cm×2 cm). Before performing the electrolysis, the solution containing SER-HCl antidepressant was saturated with oxygen by air bubbles for 10 minutes. On the other hand, a 0.05 M concentration of Na_2SO_4 support electrolyte was added to keep the ionic strength constant [2,10,13]. A catalyst concentration of $FeSO_4,7H_2O$ was introduced in the solution before starting the electrolysis. Throughout the experiment, the solution was controlled at pH=3 by sulfuric acid (H_2SO_4) [2,13,15]. However, all the experiences were realized at room temperature under vigorous agitation.

2.3. Determination of the biological oxygen demand (BOD_5)

To evaluate the biodegradability of the SER-HCl molecule and its by-products, the BOD analysis was performed with an Oxitop IS6 (from WTW, Alès, France) at 20 °C, in the dark for 5 days with an adjustment of the solution at pH=7. For inoculation, the initial microbial concentration required in the solution is 0.05 g L^{-1} [13,22].

Table 1. Different reagents used in BOD_5

	Reagents	Concentration (mg/L)
Mineral Basis	$MgSO_4$, $7H_2O$	22.5
	$CaCl_2$	27.5
	$FeCl_3$	0.15
	NH_4Cl	2
Buffer Solution	Na_2HPO_4	6.80
	KH_2PO_4	2.80

A pilot sample consisting of glutamic acid (150 mg L^{-1}) and glucose (150 mg L^{-1}) was performed to estimate the suitability of activated sludge. To evaluate the BOD linked to the respiratory activity of endogenic bacteria, it is necessary to prepare a blank solution in which the sample has been substituted with water. Table 1 summarizes the reagents used as a mineral base, nitrification inhibitor, and buffer solution for all experiments.

2.4. Biological treatment

A mineralization of Sertraline hydrochloride (SER-HCl) by-products were performed under aerobic operating conditions utilizing activated sludge collected at a local sewage plant (Ain el Ouda) which was used as received without prior purification. For all biological experiments, the cultures were performed in 500 mL Erlenmeyer flasks capped with a cellulose cover permitting the aeration. The flask includes 250 mL of non-treated Sertraline hydrochloride or electrolyzed solutions by electro-Fenton for 1h30min or 2h at 25°C with a shaker device of 150 rpm. The pH was regulated to 7.0. The culture media containing 0.5 g L^{-1} of activated sludge [12] and we used the following mineral base (mg/L): KH_2PO_4 43.8, Na_2HPO_4 33.4, $CaCl_2$ 27.5 $MgSO_4.7H_2O$ 22.5, NH_4NO_3 3.0 with 0.5 mL of trace elements was included in all solutions (mg L^{-1}): $FeSO_4.7H_2O$ 1.36, $CuSO_4.2H_2O$ 0.24, $ZnSO_4.5H_2O$ 0.25, $NiSO_4.6H_2O$ 0.11, $MnSO_4.H_2O$ 1.01 [19]. A 5 mL sample was withdrawn periodically, filtered through a 0.45 μm syringe filter and injected for COD measurement.

2.5. Biosorption test

The culture middle was inoculated with two genres of inoculums: the first is an inactivated sludge, it was autoclaved at 120°C for 20 min to prevent the biodegradation phenomena and to assess only the biosorption, while the second is the activated sludge. The sertraline hydrochloride molecule and its by-products were incubated at a concentration of 0.5 g L^{-1} in a volume of 500 mL in the presence of the trace minerals used similarly in the biological process, under conditions of 25°C and stirred at 200 rpm. The samples were collected for 300 min and analyzed by COD-meter [12,23].

2.6. Analytical Procedure

2.6.1. Chemical Oxygen Demand (COD) measurement

The spectrophotometer method DR/125 (Hach Company, USA) was utilized to determine the COD removal value. The oxidation of samples was performed by incubation for 2 h at 148°C with potassium dichromate $K_2Cr_2O_7$ in acid solution (99%, Panreac quimica) [2,12,14].

2.6.2. Chromatography methods

To identify the various by-products resulting from electrolysis, two chromatographic methods were used, one is liquid chromatography combined with mass spectrometry (LC/MS) and the other is Gas Chromatography linked with Mass Spectrometry (GC/MS).

2.6.2.1 Liquid Chromatography Coupled with Mass Spectrometry (LC/MS)

In LC-MS, the determination of transformation products (TPs) of SER-HCl was performed with strong pressure liquid chromatography Ultimate 3000 with a Diode Array Detector (PDA) combined with an ESI source and a LTQ-orbitrap mass spectrometer (Thermo Scientific, Bremen, Germany). Chromatographic separation was performed with a C18 column in inverse phase (BDS Hypersil C18 (150×4.6mm×5µm)). The elution gradient was performed in two mobile phases A and B. The first was ultrapure water with 0.1% formic acid and the second was acetonitrile.

2.6.2.2. Gas Chromatography Coupled with Mass Spectrometry (GC/MS)

GC-MS analyze was realized utilizing an MSD analyzer (Agielent technologies-USA) fitted with a column (30 m length, 0.25 mm, film thickness 0.25 m). The initial temperature of the gas chromatography instrument was 40 °C, held for 2 minutes, after that increased to 300 °C at 25 °C/min and maintained for 6 minutes. The total execution time was 16 minutes. The MS detector was a single quadrupole that was operated in the 70 eV electron ionization mode and using a single ion monitoring mode. Helium was chosen as the transport gas at a flow rate of 1.5 mL/min. The sample requires first a proper preparation with solid phase extraction on SPE C18 column (6 mL) of silica using ethyl acetate as solvent [5].

2.6.2.3. Ionic chromatography (CI)

The quantification of ions was done in a DIONEX-ICS 3000 ion chromatography system equipped with a conducting sensor with a heated cell to 35 °C. NO_3^- and Cl^- ions were analyzed on an anion interchange column AS9-HC (4×250 mm). The gradient elution modality was used to make all the analyses. 9mM Na_2CO_3 was used as mobile phase for the analysis of anions.

2.6.3. Determination of ammoniac nitrogen

The determination of ammoniac nitrogen is achieved using an automated colorimetric analyzer. The color produced during the formation of the complex between the ammonium ion and salicylate, nitroferricyanide and dichloroisocyanuric acid is measured at 660 nm [24].

3. RESULTS AND DISCUSSIONS

3.1. Electro-Fenton process pretreatment

The influence of the electro-Fenton procedure on the decay and total mineralization of SER-HCl were determined in a previous study [2]. Electrolysis was performed at an initial

amount of SER-HCl of 0.1 mmol L^{-1} by applying a current of 400 mA with 0.1 mmol L^{-1} Fe(II) and 0.05 mol L^{-1} Na_2SO_4 . Such conditions were considered as optimal in our work. In fact, after 5 min of electrolysis, a complete SER-HCl degradation was detected with an apparent kinetics (k_{app}) of 0.9 min^{-1}; whereas a total mineralization of SER-HCl was achieved after 5h of electrolysis (99% COD removal) by electro-Fenton process (Figure 1) [2].

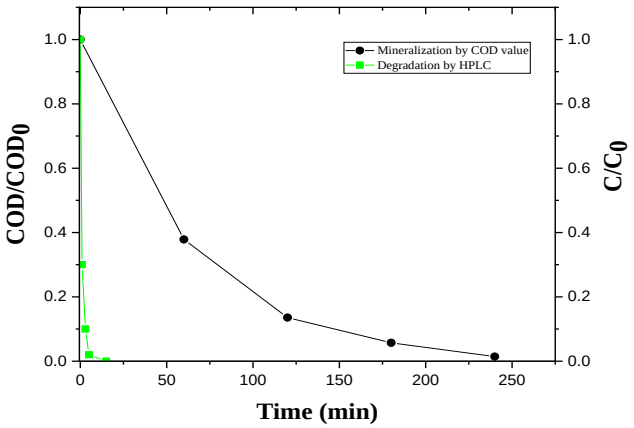


Figure 1. Monitoring of degradation and mineralization of SER-HCl under favorable conditions: [SER-HCl]= 0.1 mM; [$FeSO_4$]= 0.1 mM; [Na_2SO_4]= 0.05M; pH=3, I=400 mA

In this process, oxygen is conveyed in solution by bubbling, so that two electrons from the oxygen are constantly reduced at the cathode, resulting the electrochemical production of hydrogen peroxide (H_2O_2) at acidic conditions. Afterwards, the produced H_2O_2 responds with ferrous iron to generate $^{\bullet}OH$ causing a mineralization of the SER-HCl antidepressant into CO_2, water and mineral salts [2,13,14]. In spite of its advantages, this method involves high operational expenses, which limits its applicability in practice, such as the energy consumption rises according to the electrolysis time, which makes the mineralization kinetics slower because of the acceleration of parasitic reactions and the formation of intermediates not easily oxidizable [2]. This emphasizes the important relationship between improved efficacy and a reduce cost of treatment.

In this point, several scientists tested to combine this process with a bio-treatment system; which requires the determination of the time of this coupling [2,13,17,25-27]. In this case, before the biological treatment, a preliminary study by electro-Fenton process was performed for the antidepressant Sertraline hydrochloride (SER-HCl), in order to ensure a solution in organic compounds that could be biodegraded by activated sludge.

3.2. SER-HCl biodegradability study

In order to evaluate the biodegradability of the electrolyzed solution, a BOD_5/COD ratio was studied, considering that a solution is biodegradable when it reaches a value equal or superior to 0.33 [2,13,28].

The objective of this estimate is to evaluate the favorable time to make a coupling with the solution pretreated by the electro-Fenton process with the biological treatment, while the SER-HCl molecule becomes less toxic and more biodegradable. From a previous study [2], the initial BOD_5/COD ratio being only 0.042, this value shows that the molecule (SER-HCl) is poorly biodegradable and indicates the need to pre-treat it before subjecting it to biological treatment.

In contrast, the BOD_5/COD ratio was increased to 0.33 and 0.47 after 1.5 h and 2 h of electrolysis (Figure 2), accordingly, while the COD reduction efficiency (initial amount of 140 mg O_2 L^{-1}) also augmented from 75% to 86% during 1.5h to 2 h of electrolysis, respectively. It can be inferred that after 120 min of electrolysis, a significant portion of the persistent by-products was previously oxidized by hydroxyl radicals. On the other hand, after 90 min of electrolysis, the solution is transformed into a biodegradable medium (BOD_5/COD=0.33) [13,19]. At this point, the solution becomes rich in aliphatic components such as short carbon chain carboxylic acids, which are capable of being degraded by microorganisms, easily biodegradable, and least toxic. These results prove the importance of doing the pretreatment by the EF process, which could be a good benefit to combine it with an aerobic treatment to save energy costs [2,29]. Indeed, 1.5h of electrolysis was more cost-effective from an energetic viewpoint, admitting a fairly moderate mineralization yield (75%); while 2h electrolysis provided a higher level of biodegradability.

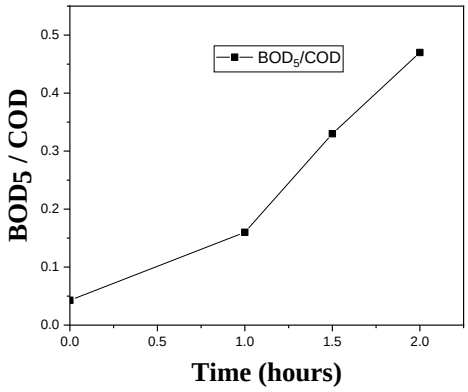


Figure 2. Time courses of the BOD_5 on COD ratio during electrolysis in conditions: [SER-HCl] = 0.1 mM, 400 mA, [Fe^{2+}] = 0.1 mM, pH = 3, [Na_2SO_4] =0.05 M

3.3. Biosorption tests for SER-HCl and its by-products

To fully understand the biosorption and/or biodegradability of the SER-HCl molecule and its intermediates during biological treatment, it is needed to determine the amount of organic matter adsorbed by the activated and inactivated sludge before biological treatment. The inactive microorganisms have a higher adsorption capacity than the active microorganisms, owing to their larger adsorption surface area [13,23,30].

It should be noted that COD_t /COD_0 number of inactive microorganisms remained steady (Figure 3), while a modest diminution was shown for the biosorption of by-products on

activated sludge. This result can be correlated with the strongly biodegradable constituents produced by the electro-Fenton pretreatment. Therefore, it can be assumed that the biosorption phenomenon is considered negligible with activated sludge. It is also observed that the COD_t /COD_0 values of sertraline hydrochloride solution with inactive sludge remain constant (Figure 3), so there was no biosorption of SER-HCl on the inactivated sludge.

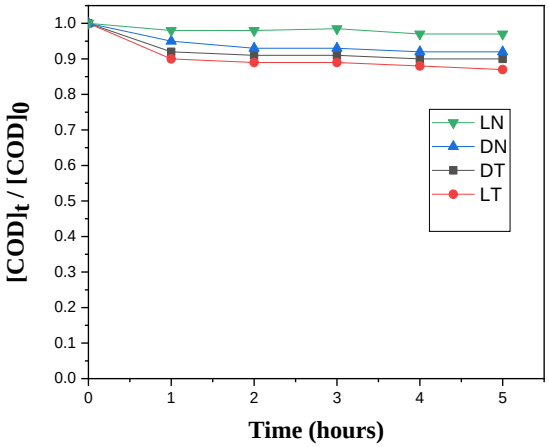


Figure 3. Evolution of biosorption on living (L) and dead (D) cells sludge of 0.1 mM non-treated SER-HCl (N) and SER-HCl solutions electrolyzed for 2 h (T), at 25 °C, pH 3, 400 mA, $[Na_2SO_4] = 0.05M$ and $[FeSO_4] = 0.1$ mM

LN: Non-treated SER-HCl solution processed by living cells sludge

DN: Non-treated SER-HCl solution processed by dead cells sludge

DT: Solution electrolyzed for 2h treated by dead cells sludge

LT: Solution electrolyzed for 2h treated by living cells sludge

3.4. Biological treatment

To confirm the importance of coupling between the electro-Fenton method and aerobic process, an activated sludge rearing of the by-product solutions was performed after 1.5 h or 2 h of electrolysis. A biological monitoring of two pretreated and untreated solutions was carried out in duplicate for 21 days. Figure 4 shows that COD value decreased slightly during the first ten days to return constantly, when the SER-HCl molecule is used as the sole carbon source in the biological treatment. Actually, in the absence of pretreatment of SER-HCl with the electro-Fenton method, a decrease of 18% was noted only after 21 days of culture by activated sludge. This result suggests that sorption by activated sludge is responsible for the initial decrease in the concentration of SER-HCl [9,17,30]. Indeed, we can suppose that at the start of the culture, the microorganisms were not capable of assimilating the Sertraline hydrochloride molecule (SER-HCl).

In the case where the pretreatment was performed by EF, it is observed that the value of the COD_t/COD_0 ratio decreases rapidly in the first two days of culture for the solutions

electrolyzed for 1.5 h and 2 h from 1 to 0.13 and 0.07 respectively. In this stage, it must be noted that the mineralization rate of the SER-HCl by-products pretreated by activated sludge is almost rapid following 2 days of culture, namely a mineralization rate of 86.4% and 92.85% for 1.5h and 2h respectively. The evolution of these values showed that most of the by-products of electrolysis were rapidly biodegraded, as well as it may be due to the conjunction between two activities, one is the biosorption of intermediate compounds generated on activated sludge and the other is their biodegradation through activated sludge [12,16,31]. Also, it should be noted that no significant increase was detected until 14 days, this is probably due to a period of acclimatization of the most resistant microorganisms SER-HCl by-products. Afterward, from 14 h to the completion of the culture, the COD value was slightly increased to 90.7% and 94.2% for 1.5 h and 2 h respectively.

The pretreatment performed by the electro-Fenton process in 1.5 h and 2 h leads to a difference in the mineralization rate during the biological treatment. As a function, the solution pretreated in 2h had a higher removal rate than the solution pretreated in 1.5h; which is in accordance with the biodegradability results. The gain in mineralization during biological treatment for 1.5 h and 2 h of electrolysis is almost similar. It can be deduced that the advantage of coupling electrochemical pretreatment with biological treatment allows applying 1.5 h of electrolysis as a cost-effective and environmental time.

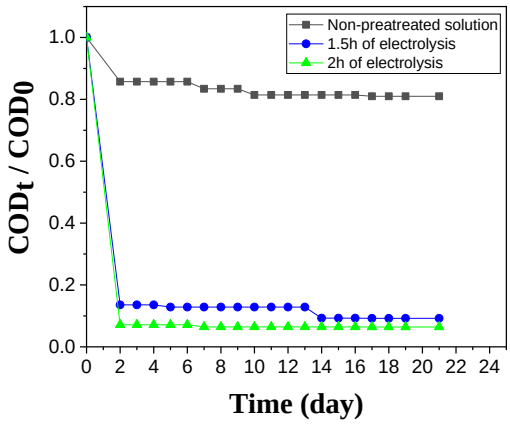


Figure 4. Evolution of the COD values during biological treatment on pretreated SER-HCl solutions for 2 h and 3h and non-pretreated solution SER-HCl; [Activated sludge] = 0.5 $g.L^{-1}$, 200 rpm, 25°C, pH = 7

3.5. Evolution of the generated inorganic ion

The Sertraline hydrochloride molecule includes the heteroatoms in the parent structure (one nitrogen atom on the ring and two substitutions of chloride) which becomes inorganic species during mineralization. Figure 5. illustrates the quantification of the inorganic ion revealed during electrolysis. We can observe that chlorine atoms are liberated more rapidly than nitrogen. In fact, the formation of nitrate was detected after 60 min of electrolysis, with low

concentrations, on the other hand, there is no formation of nitrite throughout the treatment [13]. The chlorine atoms reach the stoichiometric amount in 240 min by a concentration of 0.053 mmol L^{-1}, such that 53% of the chlorine atoms of the SER-HCl molecule are transformed in solution as chloride ions. On the other hand, the ammonium content was generated in solution since 60 min of electrolysis with a concentration 0.02139 mmol L^{-1}.

Moreover, the progressive increase of ammonium concentration reaches the maximum value of 0.0322 mmol L^{-1} at 120 min and then slightly decreases to 0.01007 mmol L^{-1} during 240 min of electrolysis. The drop of ammonium quantity can be owed to its oxidation and/or it's reduction at the electrodes (in particular the oxidation of NH^{4+} and NO_2 to NO_3^- at the anode) as well as by the reduction of NH_4^+ at the cathode or an oxidation reaction of Cl^- at the anode generating HClO [13,15].

It should be noted that 32% of the nitrogen atoms were converted into ammonium, whereas 9.6% were converted after 120 min of electrolysis in nitrates. It can be said that the remaining amount of undetected nitrogen may be linked to its existence in the nitrogen by-products in solution. Another observation that may be in agreement with the absence of nitrite is that some N can also be converted to gaseous products such as N_2, NO_2 or N_2O_5 [15,32].

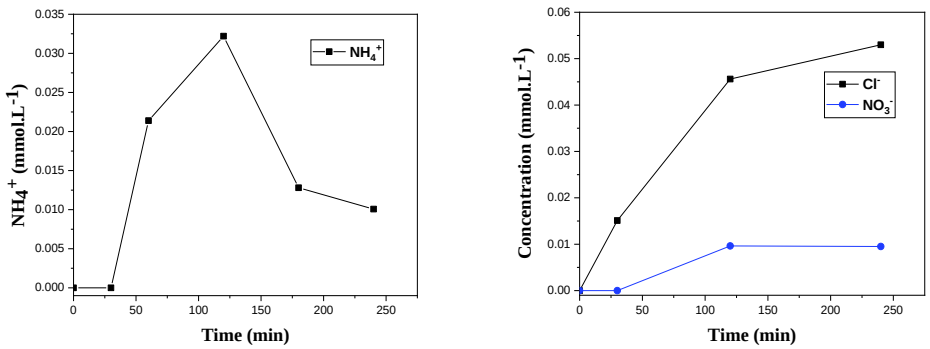


Figure 5. Evolution of inorganic ions via the treatment by electro-Fenton in operation conditions: I= 60 mA, [SER-HCl]= 0.1 mM, [Fe^{2+}]= 0.1 mM, [Na_2SO_4]=0.05M

3.6. Mechanism of SER-HCL hydrochloride

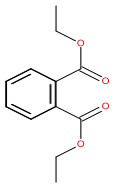
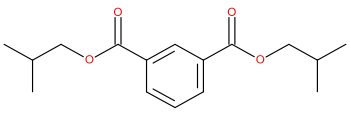
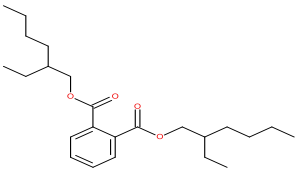
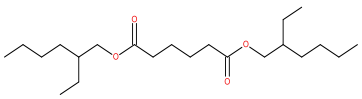
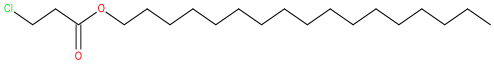
The identification of the by-products of Sertraline hydrochloride molecules produced by the electro-Fenton process was detected by GC/MS and LC/MS chromatographic methods. Compounds generated in electrolysis were identified using an MS library database. The masses of the by-products of the Sertraline hydrochloride molecule obtained throughout the electrolysis were established in the table above and the mechanism ways are proposed in the Figure 6.

It should be noted that once the aromatic compound opens, a large variety of ruptured compounds is expected. Thus, other chromatographic peaks were also detected but could not be successfully recognized (the mass spectrum match was below 90%) [21]. The

transformation products detected in the solution are formed as a result of hydroxylation, oxidation, dehydration, release of unstable elements, dichlorination, and cleavage of the molecule bonds by hydroxide attack.

It can be observed that the process starts with an attachment of the hydroxyl radical on the aromatic rings of the Sertraline molecule, creating two isomers supposed SER (A) and SER (B) (m/z=322.0760). They were detected in 2 min of electrolysis and disappeared in 5 min of electrolysis. This product has been reported similarly in the literature [5,8,9,33,34]. The decomposition of Sertraline molecule is also expected to other intermediates that can be related either by desmethylsertraline (m/z= 292) and/or a hydrolysis of SER that turns into SER-Ketone (SEK). A mono-dechlorination of the molecule Sertraline was detected in 7 min of electrolysis and disappeared completely and quickly after 10 min of electrolysis. The displacement of a chlorine atom in the hydrocarbon ring forms two isobaric species A and B at (m/z=272). The mode of appearance of this product might correspond to the oxidation of the parent molecule Sertraline to ketone function. These studies are in accordance with the existing data in literature [5,8,9]. The TPs with $[M + H]^+$ 194 are obtained by the breakdown of dichlorobenzene ring tracked by a mono (or di)hydroxylation. This structure can also be transformed to $[M + H]^+$ 144 by a demethylation and release of OH function. The fragment ion identified in m/z 159 resulted from an additional loss of the tetralin cycle [5]. Finally, we detected four TPs at $[M + H]^+$ 231, 214, 203 and 205 that involved partial detachment of the dichlorophenyl ring. The opening of TPs at 205 gives the hexanoic acid at m/z 143.

Table 2. By product results by mineralization of sertraline hydrochloride

Compound	Chemical Structure	Masse molaire	Retention time
Diethyl phtalate		222	10.6
Benzendicarboxylic Acide, 2-methylpropyle ester		278	13.7
Phtalic acide, bis (2-ethylhexyl) ester		390	28.3
Hexanedioic acide (Adipic acide)		370	26.3
3-Chloropropionic acide, heptadecyl ester		346	24

Phthalic, benzoic, and adipic acids (Table.2) were generated from the start of electrolysis and were accumulating for the primary 30 minutes, then gradually decayed over the course of the treatment. Hexanoic acid, being the only nitrogenous acid produced and accumulated more slowly. They persisted in the solution throughout the electrolysis. The detectable acids stayed even at the completion of the 5 h treatment.

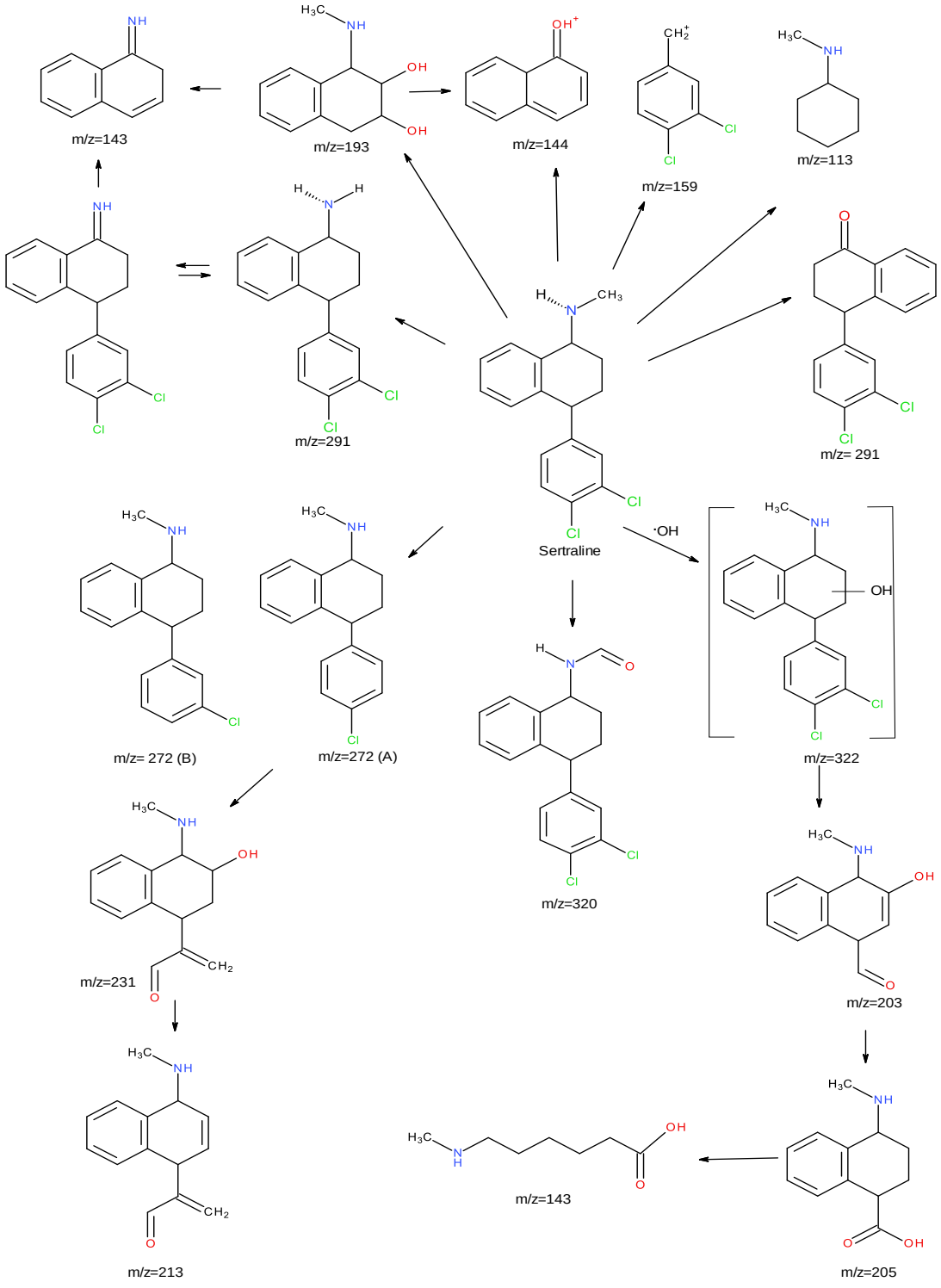


Figure 6. Mechanism pathway of degradation of sertraline

4. CONCLUSION

The pretreatment of SER-HCl by electro-Fenton is used to obtain the biodegradable solution. Thus, about 1.5h of EF electrolysis, the by-products formed can be characterized as being partially biodegradable (BOD_5/COD =0.33), therefore it is an optimal time to achieve the linkage between this process and the biological treatment. A biological treatment of the by-products of 1.5h and 2h of electrolysis were carried out, after having confirmed the absence of biosorption of the electrolysis by-products on the surface of the microorganisms existing in the activated sludge. The mineralization efficiency after 21 days of biological treatment by activated sludge of a 1.5h and 2h electrolyzed solution was 86.4% and 92.85% respectively. These findings indicate the effectiveness of linking an electro-Fenton procedure with an activated sludge biological treatment for the mineralization of sertraline hydrochloride (SER-HCl) with respect to environmental prevention. A degradation mechanism for SER-HCl was then suggested. From the detection of the by-products resulting from the electrolysis, explanations regarding the influence of their chemical structure on the degradation have been proposed.

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