

Combined photo-Fenton and biological treatment for Diuron and Linuron removal from water containing humic acid

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Abstract

A combined chemical (photo-Fenton) and biological treatment has been proposed for Diuron and Linuron degradation in water containing natural dissolved organic matter (DOM). Humic acid (HA) was used to simulate the DOM. During the photo-Fenton process ($[\text{Fe(II)}] = 15.9 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2] = 202 \text{ mg L}^{-1}$, 60 min of UVA irradiation time), the chemical oxygen demand (COD), total organic carbon (TOC), toxicity (EC_{50}^{153}) and biodegradability (BOD_5/COD) of the generated intermediates were assessed. A reduction of photo-Fenton efficiency was observed when HA was present in solution. This effect has been explained as the result of a UVA light screening as well as a OH^\bullet radical quenching process by the HA. After the photo-Fenton process, the initial toxic and non-biodegradable herbicides were transformed into intermediates suitable for a subsequent aerobic biological treatment that was performed in a sequencing batch reactor (SBR). Complete elimination of the intermediates in presence of HA was reached at the end of the chemical–biological coupled system. Biosorption of HA onto the aerobic biomass was characterized. The results indicate that the Freundlich model adequately describes the adsorption of HA, a phenomena that follows a pseudo second-order adsorption kinetic model.

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1. Introduction

Water shortage is an important environmental problem that could be ameliorated by using regenerated wastewaters [1,2]. Those are waters that after use are treated and disinfected for subsequent re-use. For example, water polluted with herbicides after agricultural practices would be a good candidate for wastewater regeneration.

Herbicides pollution is of main concern for the environment and public health due to the general toxic and non-biodegradable nature of the pollutants [3]. Among the herbicides used to prevent the growth of undesirable plants, phenylurea compounds have been widely employed since their discovery in 1950. Diuron and Linuron are two phenylurea herbicides that prevent weed growth by inhibiting the photosynthesis.

Traditional chemical methods for wastewater regeneration are, for instance, coagulation, precipitation [4] or adsorption [5].

The phase transference of pollutants, instead of their elimination, is the main disadvantage associated to those techniques. They require a post-treatment to remove the pollutant from the newly contaminated environment.

In the last decades, advanced oxidation processes (AOP) have been proposed as suitable degradation techniques for pesticide removal, since they are effective for degradation of water and soil soluble organic contaminants [6]. AOPs are based on the production of highly reactive hydroxyl radical (OH^\bullet) under mild experimental conditions. This radical oxidizes organic matter ($E_{\text{red}} = 2.8$ versus NHE) producing CO_2 as the final product.

Among all the AOP described, photo-Fenton is frequently preferred to others like ozonation [7] or heterogeneous photocatalysis with TiO_2 [8]. This AOP achieves high reaction yields with low treatment costs, mainly due to the possibility of using solar light as photon source [9]. In the Fenton process hydroxyl radical promoters are Fe(II) and hydrogen peroxide [10] (reaction (1), Fenton process):

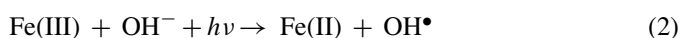


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Nomenclature

AOP	advanced oxidation process
b	energy of Lagmuir sorption constant (L mg^{-1})
BOD ₅	biochemical oxygen demand (mg L^{-1})
C_e	equilibrium TOC (HA) concentration (mg L^{-1})
COD	chemical oxygen demand (mg L^{-1})
DO	dissolved oxygen (mg L^{-1})
DOM	dissolved organic matter
EC ₅₀ ¹⁵	effective toxic concentration that causes a 50% bacteria reduction during 15 min contact (mg L^{-1})
HA	humic acid
HPLC	high-pressure liquid chromatography
HRT	hydraulic retention time
k_1	rate constant of first-order sorption (min^{-1})
k_2	rate constant of second-order sorption ($\text{g mg}^{-1} \text{min}^{-1}$)
K_F	Freundlich adsorption capacity (mg g^{-1})
n	Freundlich intensity constant
q_e	equilibrium sorption capacity (mg TOC/g TSS)
Q^0	maximum adsorption capacity Lagmuir constant (mg g^{-1})
TOC	total organic carbon (mg L^{-1})
TSS	total suspended solids (mg L^{-1})
SBR	sequencing batch reactor
VSS	volatile suspended solids (mg L^{-1})

Under irradiation of $\lambda < 410 \text{ nm}$, Fe(III) can be reduced to Fe(II) closing a loop mechanism where Fe species act as catalyst, producing additional OH^\bullet [11] (reaction (2), photo-Fenton process):



The main advantage associated with this AOP is not only the possibility of using solar light as the photon source, but also the environmental compatibility of reactants. At the end of photo-Fenton process any remaining hydrogen peroxide decomposes to H_2O . On the other hand, Fe(II) can be eliminated by raising the pH of the solution if its concentration exceeds the legal environmental disposal level.

Recently, the coupling of an AOP and a biological treatment has been proposed as a new approach to regenerate polluted effluents [12–15]. The objective of this strategy is the use of an AOP to convert initial toxic and non-biodegradable compounds into by-products that can be assimilated by the biomass. Accordingly, the economic cost and environmental impact, that are often associated with the chemical process, are substantially minimized.

A sequencing batch reactor (SBR), based on the biodegradation activity of an aerobic bacteria consortium, is used in this study after chemical treatment to completely remove organic matter. This biological treatment configuration has become popular for its efficiency and flexibility [16]. Also, it is considered

suitable as a biological system “model” due to the small volumes of effluent to be treated in a laboratory study, as well as the good control it offers. The conventional SBR operation is based on the principle of four sequential steps – i.e., fill, react, settle and draw – all them being operated in a single reactor [17,18].

Many efforts have been made by different research groups to eliminate phenylureas from synthetic wastewaters [19–22]. As real effluents also contain natural dissolved organic matter (DOM), it is important to study the degradation of those herbicides in the presence of humic substances. Humic substances generally constitute 30–50% of the dissolved organic carbon (DOC) of natural DOM in surface waters [23]. Zepp et al. [24] suggest that the phenolic humic substances, which are present in most inland waters, inhibit the free radical chain reaction that takes place in all AOPs. In addition of being a radical scavenger, humic acid (HA) may also trap photons during the photolysis process [25].

Previous studies have shown the optimal properties of chemical–biological coupled systems for the removal of Diuron and Linuron from water without interferences [22].

In this work, we study the Diuron and Linuron removal from water in the presence of HA. With this aim, COD, TOC, herbicide concentration, EC₅₀¹⁵ and BOD₅/COD of the intermediates generated at the end of the chemical step have been measured. Moreover, a SBR has been used to evaluate the feasibility of the coupled chemical–biological treatment for water containing those herbicides in the presence of high concentrations of HA.

Since adsorption of HA onto the biomass was observed, characterization of this process has been also required.

2. Experimental

2.1. Preparation of initial wastewater

Diuron (98.5% Aragonesas Agro S.A. technical grade), Linuron (92.6% Makhteshim Agan España, S.A.) and HA (Aldrich Co.) were used as target compounds in the experiments (see Fig. 1 for herbicides chemical structures). A unique solution of 42 mg L^{-1} of Diuron and 75 mg L^{-1} of Linuron in Millipore Milli-Q purified water was prepared. These values correspond to the maximum solubility of both herbicides in water at 25°C . A saturated initial solution was prepared and then filtrated by means of a $20 \mu\text{m}$ nylon filter (solution A). The initial features of the filtered solution A were as follows; pH 5.7, TOC = $50 \pm 2 \text{ mg L}^{-1}$, COD = $139 \pm 7 \text{ mg L}^{-1}$, BOD₅ < 5 (detection limit). The initial solution was transparent and colorless. The solution was non-biodegradable and TOC abatement,

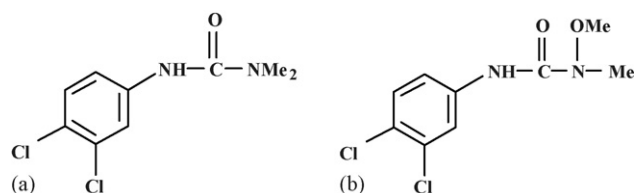


Fig. 1. Diuron (a) and Linuron (b) molecular structures.

due adsorption onto the biomass, was not observed after 28 days of Zahn–Wellens test [26].

A mixed herbicide–HA solution (solution B) was prepared by continuously stirring solid HA in the solution A. The initial features of solution B were as follows: 200 mg L^{-1} of HA, pH 8.3, $\text{TOC} = 123 \pm 6 \text{ mg L}^{-1}$, $\text{COD} = 342 \pm 10 \text{ mg L}^{-1}$, $\text{BOD}_5 < 5$ (detection limit). This solution was brown in color.

Finally, a HA solution (200 mg L^{-1}) was prepared as control sample (solution C). The initial features of solution C were as follows: pH 8.3, $\text{TOC} = 73 \pm 7 \text{ mg L}^{-1}$, $\text{COD} = 203 \pm 10 \text{ mg L}^{-1}$, $\text{BOD}_5 < 5$ (detection limit). TOC abatement due to HA adsorption onto the biomass was observed and characterized.

2.2. Experimental procedure

2.2.1. Humic acid adsorption studies

The activated sludge was directly obtained from the aerobic stage of a full-scale urban wastewater treatment plant (WWTP) in Manresa (Spain). Initial total suspended solids (TSS) value was around 3300 mg L^{-1} . A dilution was carried out to obtain a TSS value of 1000 mg L^{-1} in the final 1 L solution. The adsorption of HA by the living activated sludge was studied as a function of contact time. The adsorption kinetics were calculated by adding 200 mg L^{-1} of HA to the 1 L biological reactor (1000 mg L^{-1} TSS concentration). The reactor was agitated at a constant temperature (20°C). Samples were periodically collected from the reactor and the sludge was removed by centrifugation. In order to obtain the adsorption kinetic constant value, TOC in solution was measured during 400 min.

Isotherm adsorption experiments were conducted using 250 mL vessels that contained 10 mL of activated sludge (3300 mg L^{-1} TSS) and 90 mL of HA solutions of different concentration (from 100 to 1000 mg L^{-1}). pH was adjusted to 7. The vessels content was stirred at room temperature during 24 h (20°C). After that, TOC was measured.

In both experiments TOC measurements were also done in a blank run without HA (the same amount of biomass) in order to correct the final TOC values of each sample for desorbed organic matter. The final dissolved HA concentration (TOC) was calculated by subtracting the blank sample TOC values from the HA samples TOC values.

2.2.2. Photo-Fenton experimental procedure

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck) and H_2O_2 (Panreac, 33%, w/v) were used in the photo-Fenton experiments. Experiments were conducted at $25 \pm 0.2^\circ\text{C}$ in a cylindrical Pyrex thermostatic cell of 0.275 L capacity provided with a magnetic stirrer. A 6 W Philips black light was used as photon source. The intensity of the light entering the photo-reactor, measured by actinometry, was 0.21 mW cm^{-2} . The photo-Fenton reactor was protected from any external light with a dark cover. The photo-treatment time selected was 60 min. pH was adjusted to 2.8 in all solutions before starting the photo-Fenton reaction [27]. Samples were periodically taken from solution with a syringe. TOC, COD and hydrogen peroxide evolution were measured. At the end of the photo-treatment BOD_5/COD and toxicity were assessed.

2.2.3. Aerobic sequencing batch reactor experimental procedure

Three identical sequencing batch reactors of 1.5 L (SBR 1, SBR 2 and SBR 3) were used to simulate the activated sludge process. A dilution of biomass from the urban wastewater treatment plant was carried out to obtain a TSS value of 1000 mg L^{-1} in the final sequencing batch reactor.

SBR 1 was fed with Diuron–Linuron photo-treated solution (A). SBR 2 was fed with Diuron–Linuron and HA (200 mg L^{-1}) photo-treated solution (B). Finally, SBR 3 worked as a control and was fed with a HA (200 mg L^{-1}) solution (C). Prior to feed the SBR, hydrogen peroxide was removed from the photo-treated solutions by adding an excess of sodium sulphite. Aeration was then used to convert the remaining sulphite into sulphate [28]. When direct fed was not possible (several 250 mL chemical reaction batches were needed to fill the 1.5 L biological reactor) storage at around -8°C was required.

The procedure followed every day was: after the aeration–reaction period (22.5 h), agitation was stopped to let the biomass to settle down. After 1 h, the volume to be changed according to the hydraulic retention time (HRT) was decanted from the supernatant and replaced by the corresponding photo-treated solution (pH 7 previously adjusted). The HRT of the SBR experiments, that measures the average time that the effluent remains in the bioreactor, was two days. Thus, the volume of solution replaced after each batch was:

$$V_{\text{replaced}} = \frac{V_{\text{SBR}}}{\text{HRT}} \quad (3)$$

Minerals were also daily added to reach a constant nutrient concentration in the SBR: MgSO_4 (202 mg L^{-1}), CaCl_2 (73.4 mg L^{-1}), NH_4Cl (76.4 mg L^{-1}) and NaH_2PO_4 (1242 mg L^{-1}).

TOC measurement of the replaced solution was carried out. This process was repeated 16 cycles in each run in order to obtain repetitive results (i.e., a variation coefficient of TOC measurements lower than 4%). One cycle was achieved when the total SBR initial volume had been replaced with new solution. Volatile and total suspended solids (VSS and TSS) were measured daily.

The pH around 7 and dissolved oxygen (DO) – not lower than 3 mg L^{-1} – were daily controlled. The reactor was maintained at laboratory temperature (20°C) and mixed by a magnetic stirrer. Air was supplied by a gas diffuser.

2.3. Analytical methods

The initial herbicide concentration, TOC and COD data were recorded during the oxidation process. The HPLC system, used in the determination of herbicides concentration, was formed by a LC-10 AT VP pump (Shimadzu) and a UV–vis diode array detector (Agilent 1100 Series). Acetonitrile (Pobus, HPLC grade) was used to prepare the mobile phases in the HPLC system and a $5 \mu\text{m}$ Hypersil column ($250 \text{ mm} \times 0.46 \text{ mm}$) from Teknocrroma was used as stationary phase. TOC was analyzed with a Shimadzu TOC-V_CSH apparatus. 0–150 and 0–1500 mg L^{-1} range Aqualytic vials were used for chemical COD determination based on a close reflux

determination method [29]. This analysis was done in a COD reactor from HACH Co., and a HACH DR/2000 spectrophotometer was used for colorimetric measurement. The accuracy of the COD measurements was checked by preparing a potassium hydrogen phthalate standard. Correction for hydrogen peroxide interference on the standard COD test was carried out [30]. The concentration of H_2O_2 was analyzed by the iodometric method [31].

At the end of the oxidation process, toxicity (EC_{50}^{15}) and biodegradability (BOD_5/COD) were analyzed. The toxicity tests were performed with the BioTox[®] equipment (Lab-system) using the *Vibrio fischeri* bacteria to assess the effective concentration of a test sample that caused a 50% reduction in bacteria light emission during 15 min of bacteria-toxic contact (EC_{50}^{15}). A WTW OxyTop system was used for BOD_5 determinations. In those analyses, the data accuracy was checked by making BOD_5 measurements of a mixture of 150 mg L^{-1} of glucose and 150 mg L^{-1} of glutamic acid. In all the biological analysis hydrogen peroxide and iron were previously eliminated from solution to avoid interferences. Iron was eliminated by raising the pH to 8 and then filtering the solution. Hydrogen peroxide was eliminated by adding sodium sulphite.

When the SBR was used, VSS and TSS were determined according to Standard Methods [32]. All analytical measurements were repeated at least two times.

3. Results and discussion

3.1. Kinetic experiments of humic acid biosorption

In this paper Diuron and Linuron removal from water in the presence of HA by means of a coupled chemical and biological system is examined. Adsorption of HA onto de biomass was observed and its characterization was required.

Lagergren suggested a rate equation for the solutes adsorption onto a solid surface [33]. This pseudo-first-order rate linearized equation is

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

where k_1 is the rate constant of the pseudo-first-order sorption. The pseudo-first-order equation has been extensively used to describe the sorption kinetics [34,35]. Nevertheless, not complete regression adjustment was obtained when this model was used to fit biosorption of HA onto the biomass (i.e., $R^2 = 0.958$, $k_1 = 33 \times 10^{-4} \text{ min}^{-1}$).

Thus, a pseudo-second-order model was used to analyze the data. The resulting linearized rate law for this system was

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k_2 is the rate constant of the pseudo-second-order sorption. This model has been applied to analyze sorption kinetics in liquid–solid interfaces by Ho et al. [36,37]. Comparing both pseudo-first and pseudo-second-order models, a closer to 1.0 correlation coefficient is observed for the pseudo-second-order model (i.e., $R^2 = 0.999$). Thus, this model is better to describe

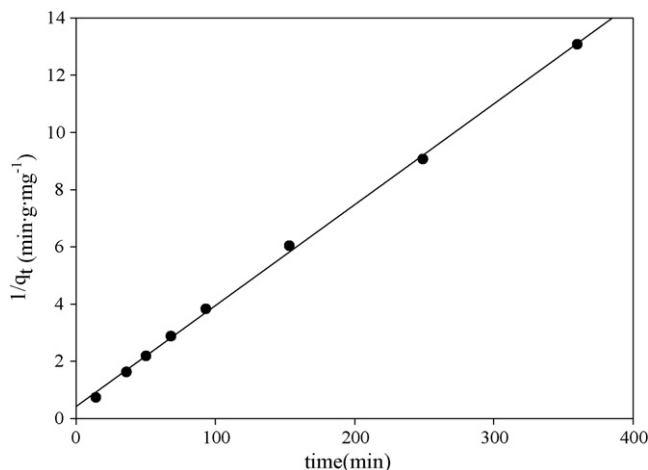


Fig. 2. Linearized pseudo-second-order kinetic model for the adsorption of humic acid onto alive aerobic biomass (initial humic acid concentration of 200 mg L^{-1}). $T = 20^\circ\text{C}$, $\text{pH} = 7$, $\text{VSS} = 1.05\text{ g L}^{-1}$.

the biosorption kinetics of HA (see Fig. 2) and, consequently, a pseudo-second-order rate constant of HA adsorption onto the biomass has been determined ($31 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$).

Azizian [38] concludes that the pseudo-second-order model is suitable for sorption kinetics when the initial substrate/adsorbent concentration ratio is low. On the other hand, when the initial ratio is high the pseudo-first-order model becomes more adequate. This is in agreement with the present experimental situation since a HA/biomass ratio used is 0.2 has been used, and this is considered a relatively low quantity of substrate for the available adsorption sites.

3.2. Isotherm study

The equilibrium of HA biosorption was modeled using Freundlich and Langmuir isotherms. The Langmuir isotherm is valid for a monolayer adsorption onto the surface with a finite number of identical sites. The linearized Langmuir equation is given as

$$\frac{C_e}{q_e} = \left(\frac{1}{bQ^0} \right) + \left(\frac{C_e}{Q^0} \right) \quad (6)$$

where Q^0 and b are the Langmuir constants characteristic of the system.

The linearized Freundlich equation, that attempts to incorporate the role of substrate–substrate interactions on the surface, is given as

$$\log q_e = \log K_F + \left(\frac{1}{n} \right) \log C_e \quad (7)$$

where K_F and n are the Freundlich constants characteristic of the system. These constants indicate the adsorption capacity and adsorption intensity, respectively.

Table 1 shows the parameters obtained for the Langmuir and Freundlich models. The closer to 1.0 correlation coefficient of the Freundlich suggests that this model better describes the biosorption equilibrium of HA (see Fig. 3). The Freundlich

Table 1
Langmuir and Freundlich isotherm constants of humic acid adsorption onto alive aerobic biomass

Parameters	
Langmuir	
Q^0 (mg g ⁻¹)	245
$1/b$ (mg L ⁻¹)	54.0
R^2	0.976
Freundlich	
K_F (mg g ⁻¹)	24.2
$1/n$	0.392
R^2	0.990

$T = 20^\circ\text{C}$; pH 7.

model describes a monolayer adsorption on a solid surface characterized by an asymmetrical energy distribution, for instance a biomass surface. Furthermore, the experimental data of the present work agrees with the results obtained in a previous work [39].

3.3. Photo-Fenton oxidation of Diuron and Linuron

Diuron and Linuron removal from water using a chemical–biological coupled system via photo-Fenton process has been previously studied in our research group [22]. Results showed that 202 mg L⁻¹ of H₂O₂ and 15.9 mg L⁻¹ of Fe(II) were required to convert initial toxic and non-biodegradable herbicides into by-products that could be assimilated by the biomass. The photo-treatment time was 60 min.

The mineralization of Diuron and Linuron herbicides in presence of HA has been carried out in order to evaluate the effects of DOM as interference. Thus, the Diuron–Linuron–HA solutions were treated with the same chemical reactant dose that rendered biocompatible photo-treated effluents when no HA was in the media (i.e., 202 mg L⁻¹ of H₂O₂ and 15.9 mg L⁻¹ of Fe(II)).

Preliminary experiments were performed in order to establish the adequate HA load. It was observed that in absence of

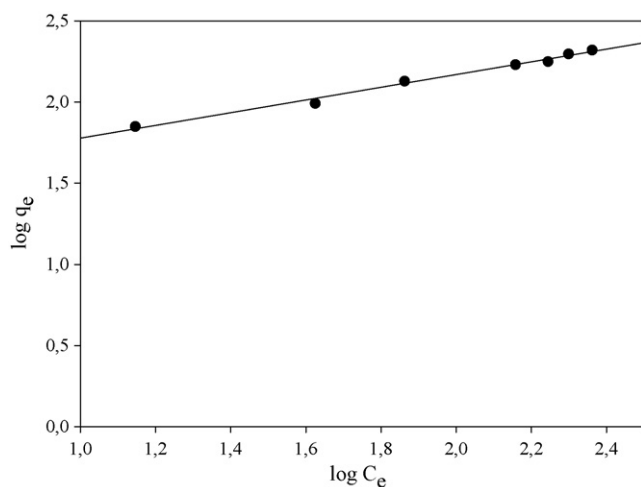


Fig. 3. Linearized Freundlich adsorption isotherm model at 20 °C. pH 7, VSS = 0.33 g L⁻¹.

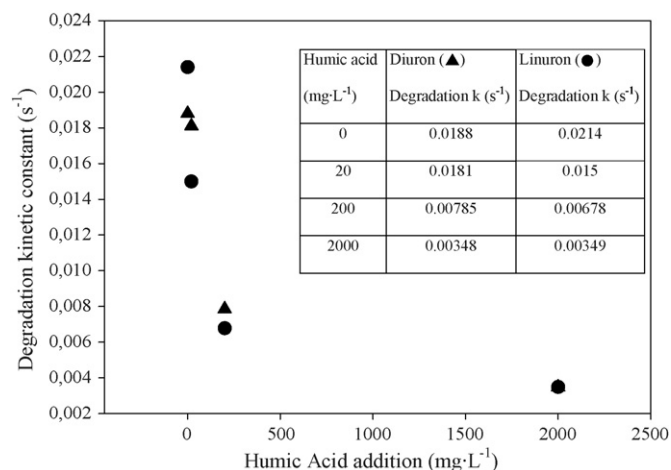


Fig. 4. Diuron and Linuron pseudo-first order degradation kinetic constants in presence of different concentrations of humic acid during photo-Fenton treatment. Fe(II) = 15.9 mg L⁻¹, [H₂O₂] = 202 mg L⁻¹, $T = 25^\circ\text{C}$.

all photo-Fenton components (i.e., reactants and UVA light) there was no herbicides degradation. On the other hand, TOC corresponding to HA did not decreased after the photo-Fenton treatment, probably due to the low intensity of the light source used in this experimental work (i.e., 0.21 mW cm⁻²).

As shown in Fig. 4, the Diuron and Linuron degradation kinetics by photo-Fenton are significantly affected by the presence of HA. The more HA is present in the solution, the slower the degradation of pesticides results. For HA concentration above 200 mg L⁻¹ only minor differences in herbicide removal were found. This effect was also observed in a similar work when O₃/UV process was used [40].

Therefore, a concentration of 200 mg L⁻¹ of HA was selected for subsequent experiments. The TOC corresponding to this HA concentration is 73 ± 7 mg L⁻¹. This high concentration ensures the applicability of the present proposed degradation strategy in a real water sample since TOC corresponding to humic substances in surface waters generally ranges from 3 to 20 mg L⁻¹ [42].

Fig. 5 shows the relative TOC evolution of solution A (Diuron and Linuron), B (Diuron, Linuron and 200 mg L⁻¹ of HA) and C (200 mg L⁻¹ HA) during the photo-Fenton treatment. The TOC concentration of photo-treated solution B was 110 ± 5 mg L⁻¹. The subtraction of 73 ± 7 mg L⁻¹ of TOC, corresponding to HA, was required at the end of photo-Fenton process of solution B in order to compare the mineralization results in the presence of HA with the results in absence of the interference (i.e., TOC_{B-C} = 37 ± 9 mg L⁻¹, TOC_A = 32 ± 4 mg L⁻¹). It has been reported that HA can compete with target compounds for hydroxyl radicals, thus slowing down the degradation of those compounds [41]. Moreover, a UVA light screening can be also a possible explanation of the slower degradation of Diuron and Linuron with increasing HA concentration.

3.4. Assessment of photo-treated effluent biodegradability

After photo-Fenton process, A and B solutions were proposed for a posterior biological treatment. The analysis of BOD₅

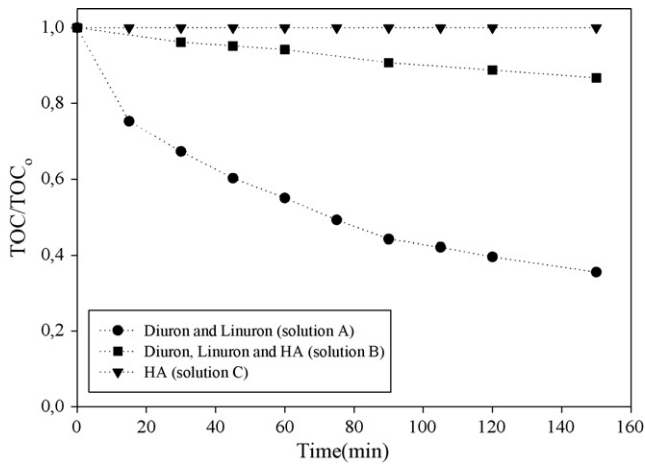


Fig. 5. Relative TOC evolution versus irradiation time of solutions A (Diuron and Linuron) and B (Diuron, Linuron and HA) and C (HA) during photo-Fenton treatment. $[\text{Fe(II)}] = 15.9 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2] = 202 \text{ mg L}^{-1}$, $T = 25^\circ \text{C}$.

and toxicity were required in order to assess the compatibility with the biological system. To assess the biodegradability of the photo-treated solutions that contained Diuron, Linuron and HA, it was necessary to evaluate the biodegradability of solution C (i.e., HA alone). Results indicate that the biomass was not able to assimilate HA after the photo-Fenton treatment (i.e., $[\text{BOD}_5]_{\text{C}} < 5 \text{ mg L}^{-1}$, $\text{COD}_{\text{C}} = 203 \pm 10 \text{ mg L}^{-1}$, $[\text{BOD}_5/\text{COD}]_{\text{C}} < 0.02$). A BOD_5/COD ratio higher than 0.40 ensures the biocompatibility of photo-treated solution A ($[\text{BOD}_5/\text{COD}]_{\text{A}} = 0.51 \pm 0.1$) [43].

COD value of photo-treated solution B (i.e., $\text{COD}_{\text{B}} = 264 \pm 10 \text{ mg L}^{-1}$) was corrected with COD value of solution C as HA was recalcitrant to OH^\bullet attack in the chemical process. On the other hand, the BOD_5 value of solution C was used to correct the corresponding values of photo-treated solution B (i.e., $[\text{BOD}_5]_{\text{B}} = 28 \pm 1 \text{ mg L}^{-1}$). In this way, $[\text{BOD}_5]_{\text{B-C}} = 26 \pm 3 \text{ mg L}^{-1}$ and $\text{COD}_{\text{B-C}} = 61 \pm 14 \text{ mg L}^{-1}$.

These corrected results of photo-treated solution B were compared with the results obtained with photo-treated solution A (i.e., $[\text{BOD}_5/\text{COD}]_{\text{B-C}} = 0.41 \pm 0.1$, $[\text{BOD}_5/\text{COD}]_{\text{A}} = 0.51 \pm 0.1$). Both can be considered biodegradable since the BOD_5/COD threshold for a wastewater to be considered easily biodegradable is 0.4 [43]. Nevertheless, a difference in COD measurements was observed ($\text{COD}_{\text{B-C}} = 61 \pm 14 \text{ mg L}^{-1}$, $\text{COD}_{\text{A}} = 33 \pm 4 \text{ mg L}^{-1}$), thus indicating a different oxidation state in the by-products formed during the mineralization process. This different oxidation state of the generated by-products is due to the reduction of photo-Fenton efficiency as explained above.

Toxicity of photo-treated effluents was analyzed by means of BioTox equipment. EC_{50}^{15} values for all the solutions after photo-Fenton process were higher than TOC effluent concentration. This means that none of the solutions (A, B or C) were toxic [14]. According to BOD_5 , COD and EC_{50}^{15} data, it can be suggested that intermediates coming from Diuron and Linuron herbicide oxidation with or without the presence of HA are good candidates for a SBR treatment.

3.5. Biological treatment of photo-treated solutions

In an attempt to gain more insight into the biodegradability of the pre-treated solutions, a SBR was used to simulate a real biological treatment. Three SBR were studied in parallel. The SBR 1 was fed with photo-treated solution A (Diuron and Linuron). SBR 2 was fed with photo-treated solution B (Diuron, Linuron and HA). Finally, SBR 3 was fed with solution C (HA). A start-up period (one 10-day hydraulic retention time (HRT) cycle for each SBR) was initially required. The influent was a completely biodegradable municipal wastewater obtained from the WWTP. The purpose of this preliminary step was to ensure the biomass viability and to establish, as a reference, the residual TOC that the SBR system is not able to handle. The steady TOC obtained, attributed to the metabolites released by the biomass, remained stable at 6.5 mg L^{-1} . The operation with the herbicides samples was performed once the blank cycle was completed.

When SBR 1 was fed with photo-treated solution A, around 80% of TOC removal was daily achieved without any required acclimation process. The residual TOC present in SBR 1 matched the TOC concentration attributed to the metabolites released by the stabilized biomass ($\text{VSS} = 0.60 \pm 0.03 \text{ g L}^{-1}$). Fig. 6 shows data obtained along this experiment for a total of 16 cycles. From the data it was concluded that Diuron and Linuron herbicides could be completely removed from water with the coupled chemical–biological process. More details about those experimental results are reported elsewhere [22].

SBR 2 and SBR 3 were used to investigate the biodegradability of Diuron and Linuron photo-treated effluents in the presence of HA. The initial TOC of the photo-treated solution B was $110 \pm 10 \text{ mg L}^{-1}$ while the initial TOC of recalcitrant solution C was $73 \pm 7 \text{ mg L}^{-1}$. Removal of TOC in the SBR 3 was not expected since $(\text{BOD}_5/\text{COD})_{\text{C}}$ ratio was 0.02. Nevertheless, due to the previous detected HA biosorption, TOC measurements at the end of the biological treatment in the SBR 3 ($65 \pm 3 \text{ mg L}^{-1}$) did not match the TOC measurements of the initial solution ($73 \pm 7 \text{ mg L}^{-1}$). Non-adsorbed HA was replaced according to the HRT, and TOC accumulation was not observed. Stabilization

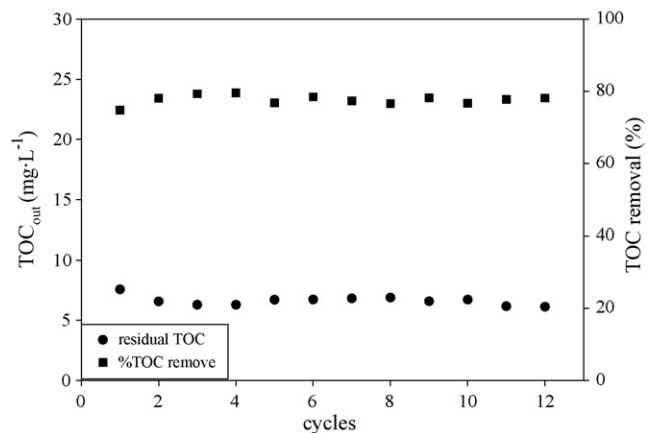


Fig. 6. Final TOC and percentage of TOC removal after aerobic biological treatment (SBR 1) of photo-treated solution A (Diuron and Linuron). ($[\text{Fe(II)}] = 15.9 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2] = 202 \text{ mg L}^{-1}$) during 12 cycles. HRT = 2 days, $T = 20^\circ \text{C}$. Stabilized $\text{VSS} = 0.60 \pm 0.03 \text{ g L}^{-1}$.

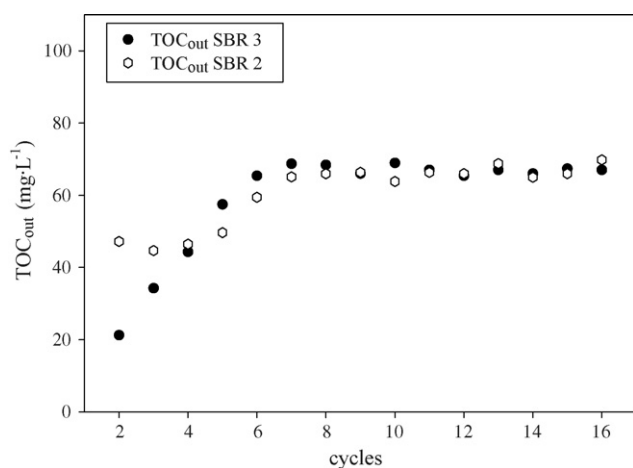


Fig. 7. TOC concentration at the end of the biological treatment for photo-treated B (SBR 2) and C (SBR 3) solutions. $T = 20^{\circ}\text{C}$, $\text{HRT} = 2$ days. Stabilized $\text{VSS}_{\text{SBR 2}} = 0.56 \pm 0.03 \text{ g L}^{-1}$, $\text{VSS}_{\text{SBR 3}} = \text{not stable}$.

of VSS in the SBR 3 was not possible, giving more evidence of the biorecalcitrant nature of HA. On the other hand, when the SBR 2 was fed with photo-treated solution B, 42% of TOC reduction was observed. The final TOC in the SBR 2 matched the final TOC in the SBR 3. This value corresponds to the HA that could not be assimilated by the biomass (i.e., $65 \pm 3 \text{ mg L}^{-1}$). Fig. 7 shows the TOC evolution at the end of the biological treatment for both, SBR 2 and SBR 3 during 16 cycles. VSS stabilization was reached in SBR 2 (i.e., $\text{VSS} = 0.56 \pm 0.03 \text{ g L}^{-1}$).

From the data it can be concluded that by-products generated during the chemical treatment could be completely assimilated by the biomass in a secondary biological process. Therefore, the elimination of herbicides by means of a chemical and biological coupled system, in the presence of HA, was possible.

4. Conclusions

The coupled photo-Fenton (chemical) and biological treatment is an effective method for the elimination of Diuron and Linuron herbicides from water when HA is also present in solution.

Pesticides degradation via photo-Fenton process becomes slower with increasing HA concentration. A UVA light screening as well as OH^{\bullet} radicals quenching process can be the explanation of this negative effect on the degradation rates.

$[\text{Fe(II)}] = 15.9 \text{ mg L}^{-1}$ and $[\text{H}_2\text{O}_2] = 202 \text{ mg L}^{-1}$ are required in the chemical step to convert initial toxic and non-biodegradable herbicides into intermediates suitable for a posterior biological treatment. The complete removal of the TOC that has been generated during the chemical herbicide oxidation is achieved in a SBR using 2 days of HRT. The residual TOC, observed at the end of the biological treatment, corresponds to the biorecalcitrant HA that cannot be assimilated by the biomass.

Adsorption of HA onto the aerobic alive biomass has been observed and characterized. The adsorption process follows

a pseudo-second-order adsorption kinetic model. Moreover, biosorption equilibrium has been described by the Freundlich isotherm model.

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