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Pesticide removal from water suspension by UV/TiO_2 process: a parametric study

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ABSTRACT

Linuron is a phenylurea herbicide which is generally used for eliminating various herbs. The advanced oxidation processes represent a promising alternative technology for the destruction of pesticides contained in wastewater. In this present work, the degradation of linuron is performed using a helical photochemical reactor. The UV lamp (HPA 18 W/S with a monochromatic radiation at 365 nm and a nominal power of 18 W) is set in axial position in the open space of the sheath. The experimental results showed that the photodegradation of linuron increased significantly compared with adsorption and photolysis. The parametric study of the pollutant oxidation showed that an increase in the initial concentration of catalyst (0.1–0.8 g/L) revealed the existence of an optimum for 0.3 g/L where the oxidation was complete after 4 h of radiation exposure. The best degradation of linuron was obtained at an optimum flowrate of 396 mL/min, where 98% of herbicide was oxidized after 4 h of UV illumination. Results showed also that the presence of hydrogen peroxide (an electron acceptor), acids or bases disadvantaged the photocatalytic process. Removal of linuron increased at low pH (3 and 5 adjusted along the photodegradation), where 93% was oxidized. Photodegradation of linuron process accords well with Langmuir–Hinshelwood pseudo-first-order kinetics.

Keywords: Linuron; Photocatalysis; Photolysis; Titanium dioxide; Langmuir–Hinshelwood kinetic model; Suspension

1. Introduction

The pollution of surface and ground waters by organic pollutants is caused by chemical discharges of industry, agriculture, and daily activities. Some of these pollutants are used as pesticides: substances used to fight against crop parasites or public health. Pesticides, because of their increasing use and mobility, are an environmental problem and a public health risk, some of them affect the nervous system, some may be carcinogenic and others affect the hormonal system [1]. Organic pollutants are resistant to biodegradation [2], which requires a constant improvement of water treatment processes [3]. Heterogeneous photocatalysis has recently emerged as an

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advanced oxidation process (AOP) for environmental decontamination method suitable for the treatment of water, aqueous wastes and wastewater, pollutants present at low-concentration levels [4–12]. Photocatalysis by titanium dioxide has become a very active field of research, [8,13] in particular, for the decomposition of a variety of organic contaminants present in water and aqueous wastes. Titanium dioxide Degussa P25 has proven to be the most promising semiconductor photocatalyst for widespread environmental applications because it shows a high reactivity under ultraviolet (UV) light, is nontoxic, stable, inert chemically, inexpensive and does not undergo photocorrosion [14]. Photocatalytic oxidation is an AOP utilizing a semiconducting photocatalyst such as titanium dioxide (TiO_2) and appropriate light sources such as sunlight or ultraviolet (UV) radiation ($\lambda \leqslant 380\,\text{nm}$) to generate charge carriers e^-_{cb} and h^+_{vb}, [12,15]. These charge carriers react with species that are adsorbed on their surface to generate a highly reactive hydroxyl radical $HO^{\cdot}$, which was recognized to be the most powerful oxidant [6]. These charge carriers react with species that are adsorbed on the semiconductor surface to generate a highly reactive hydroxyl radical.

Linuron ($C_9H_{10}Cl_2N_2O_2$) is a nonpolar phenylurea herbicide which is generally used for eliminating various herbs, it is an herbicide that has anti-androgenic activity in both fish and rodents and affects the estrogen-mediated process of vitellogenin production, it has also the potential to cause adverse effects on the reproductive endocrine axis of vertebrates [16]. It is stable to hydrolysis in normal pH and exists as undissociated in natural waters. Evaporation losses are negligible in the environment, and the light-induced photochemical decomposition is of relatively minor importance, that is why the photocatalytic process is required to the elimination of linuron from water [17,18].

2. Kinetic studies

The utilization of the Langmuir–Hinshelwood kinetics model to describe the mineralization process kinetics, and to associate it automatically as "proof" of the concept or notion, that reactions take place at the surface of the catalyst particle, without any corroborating independent evidence to that effect.

The Langmuir–Hinshelwood (L–H) kinetic model was initially developed to quantitatively describe gaseous–solid reactions [19]. This model was recently employed to describe solid–liquid reactions [20,21]. In this model, the rate of reaction (r) is proportional to the fraction of surface covered by the substrate (θ).

$$r = -dC/dt = k_r\theta \tag{1}$$

where C is the concentration of the substrate at time t and k_r the kinetic constant.

Under steady-state conditions, the equilibrium coverage, considering Langmuir's equation, is given as:

$$\theta = KC/(1 + KC) \tag{2}$$

So:

$$r = -dC/dt = k_r\theta = k_rKC/(1 + KC) \tag{3}$$

Eq. (3) can be simplified to a first-order reaction rate equation:

$$r = -dC/dt = k_rKC = k_{\text{app}}C \tag{4}$$

where k_{app} is the apparent reaction rate constant of a pseudo-first-order reaction, in which case one has:

$$\ln(C_0/C) = k_{\text{app}}t \tag{5}$$

The value of K, the adsorption constant, is obtained empirically through a kinetic study in the presence of light and is better than that obtained in the darkness, starting from Langmuir's isotherm [22].

By plotting $ln(C_0/C)$ vs. t, the apparent rate constant k_{app} can be determined from the slope of the curve obtained.

Estimated half life $t'_{\frac{1}{2}}$ and calculated $t_{\frac{1}{2}}$ are obtained using the following equations:

$$t'_{\frac{1}{2}} - \frac{1}{Kk_r}\ln(2) + \frac{1}{k_r}\left(\frac{C_0}{2}\right) \tag{6}$$

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k_{\text{app}}} \tag{7}$$

3. Materials and methods

In this present work, the feasibility of linuron aqueous solution photodegradation in the presence of titanium dioxide as catalyst has been investigated in laboratory-scale helical photocatalytic reactor. The double spiral photoreactor with a capacity of 0.46 L was constructed in Pyrex. The UV high-pressure mercury vapor quartz lamp radiation source, with a monochromatic radiation at 365 nm, and a nominal power of 18 W is set in axial position in the open

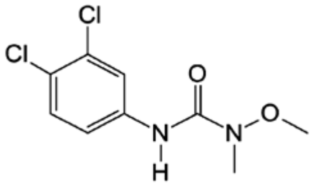

Fig. 1. Chemical structure of linuron.

space of the reactor in order to ensure maximum energy exchange between the irradiation source and the reaction mixture that flows out continuously. A pump recirculates the treated mixture between the reactor and the reservoir of 2 L capacity in closed circuit. TiO_2 photocatalyst employed was Degussa P25 with a specific surface area of 50 m^2 g^{-1}, mainly anatase (80% anatase and 20% rutile) [23]. The aqueous suspension volume was equal to 1 L. Linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea), as shown in Fig. 1, is a substituted urea herbicide used to control annual and perennial broadleaf and grassy weeds on both crop and noncrop sites. It works by inhibiting photosynthesis in target weed plants. It is labeled for field and storehouse use in such crops as soybean, cotton, potato, corn, celery, asparagus, and carrots. Linuron is a nonionic herbicide with a water solubility of 81 mg/L at 25°C, $pk_a = 12.13$ [24] and an aerobic soil half life of 49 days [25]. The concentrations of residual linuron, during different processes, were analyzed with a double ray UV/Vis spectrophotometer (Perkin Elmer Lambda 25 UV/Vis), by measuring the optical densities at 245 nm. All the chemicals that were used in the experiments were of laboratory reagent grad and used as received without further purification. The solutions were prepared with distilled water. The pH solution is adjusted by phosphoric acid (H_3PO_4) or potassium hydroxide (KOH).

4. Results and discussion

In order to determine the efficiency of the photocatalytic process, under different experimental conditions, the influence of several experimental parameters, such as the pollutant concentration, the catalyst concentration, the pH medium, and the electron acceptors.

4.1. Adsorption, photolysis, and photocatalysis

During photolysis (which is a photochemical reaction), in the absence of TiO_2, a low decrease in the concentration of linuron was observed as shown in Fig. 2. After 4 h of illumination, only 38% of linuron was removed. In the presence of hydrogen peroxide (100 mg/L), this percentage was enhanced to 54%. Adsorption of linuron, which is a physical phenomenon and not a chemical reaction, was most important than photolysis, after 4 h of adsorption, 64% of herbicide was eliminated (the herbicide was transferred from water to the TiO_2 adsorbent surface). The photocatalytic process, where radiations UV are in the presence of titanium dioxide as catalyst, leading to a total decomposition of the substrate through a radical reaction, increased the removal efficiency of linuron to 93%, [12–15]. The presence of H_2O_2 at different concentrations disadvantaged the process reducing the abatement from 93% to 60%. So it is obvious that linuron photocatalysis would be efficiency without adding hydrogen peroxide.

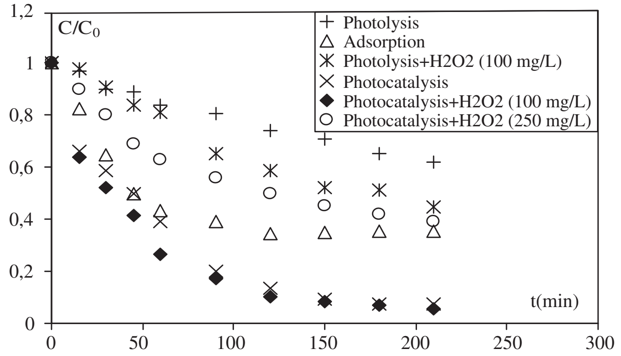

Fig. 2. Effect of different elimination processes. C_0(linuron) = 10 mg/L, $C(TiO_2) = 0.3$ g/L, $Q = 237.6$ mL/min, $C_0(H_2O_2)$ =100–250 mg/L.

This study shows that the photolytic process is slow, and there is still risk of accumulation of this herbicide in surface water. Moreover, the photocatalytic process seems to be very efficient for the removal of organic compounds resistant to conventional techniques.

4.2. Effect of flowrate recirculation on the photocatalytic process of linuron

Photodegradation of linuron was carried out with different flowrates (5.4 to 396 mL/min). As shown in Fig. 3, representing the evolution of reduced concentration of linuron vs. irradiation time, the photocatalytic degradation rates of linuron were affected by the flow recirculation.

According to Fig. 3, the photocatalytic activity of TiO_2 and the reduction of linuron concentration with reaction time were more effective with an important flowrate, as obtained by Okamoto et al. for phenol elimination [26]. Although it appeared that in the

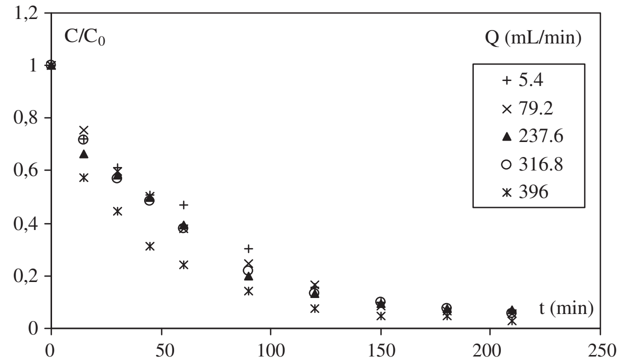

Fig. 3. Effect of flowrate on linuron. Kinetic photocatalysis at natural pH. C_0(linuron) = 10 mg/L, $C(TiO_2)$ = 0.3 g/L.

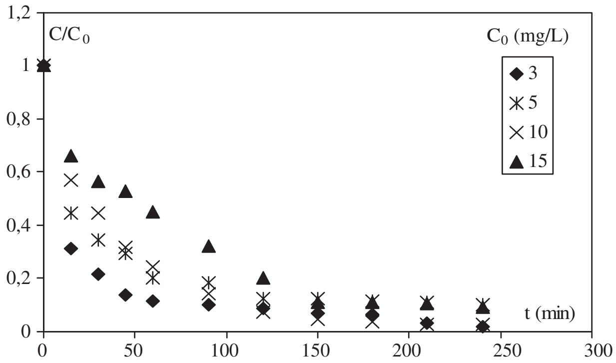

Fig. 4. Photodegradation of linuron at different initial concentrations. $C(TiO_2)$ = 0.3 g/L, Q = 396 mL/min.

Table 1
Pseudo-first-order rate constants, half-life ($t_{1/2}$), and abatement values for different flowrates

Q (mL/min)	$k_{app} \times 10^2$ (min^{-1})	R^2	$t_{1/2}$ (min)	X (t = 4 h) (%)
5.4	1.41 ± 0.02	0.976	49	94
79.2	1.58 ± 0.05	0.995	44	95
237.6	1.62 ± 0.02	0.984	43	93
316.8	1.63 ± 0.01	0.995	42	94
396	2.34 ± 0.04	0.984	30	98

Table 2
Pseudo-first-order rate constants, half-life ($t_{1/2}$), and abatement values for different flowrates

C_0 (mg/L)	$K_{app} \times 10^2$ (min^{-1})	R^2	$t_{1/2}$ (min)		X (t = 4 h) (%)
			Calculated	Estimated	
3	4.7 ± 0.01	0.988	15	17	98
5	2.7 ± 0.09	0.959	26	25	90
10	2.5 ± 0.05	0.991	28	37	97
15	1.3 ± 0.04	0.83	53	58	91

experimental conditions imposed in the present work, the difference of abatement between the flowrates studied was relatively low. Nevertheless, the optimal efficiency was obtained for a flowrate of 396 mL/min, with an abatement of 98% after 4 h exposure to UV light. For this flowrate, the residence time of the system is shorter than the number of inflow and outflow rate per minute.

As shown in Table 1, the photoreactivity experiments gave the following main indications: (i) the values of pseudo-first rate constant k_{app} (calculated on the basis of Eq. (5)) increased with the flowrate until the optimum of 396 mL/min, (ii) the values of half-life decreased by increasing the flowrate. Table 1 showed also that the abatement of linuron was growing slightly with the flowrate and the abatement reached 98% for the optimum value of flowrate. For all these reasons, we had to select Q = 396 mL/min as the optimal flowrate in our experiments.

4.3. Photocatalytic activity: effect of linuron concentration

As shown in Fig. 4, the titanium dioxide presents a very interesting activity on the degradation of linuron. The influence of linuron initial concentration shows, in Fig. 4, that the kinetic of disappearance enhanced at lower concentration [3]. This phenomenon has been observed by Para et al. [18] and Muneer et al. [27].

Because the degradation depends on the radical hydroxyl formation, the production of $HO^{\bullet}$ radicals is not sufficient in comparison with the amount of linuron adsorbed on the photocatalyst surface at higher concentrations. In view of this, it suggests that there should be equilibrium between adsorption of reactant molecules and $HO^{\cdot}$ radicals generated from the active sites. Table 2 shows that when initial concentration of linuron increased, the pseudo-first-order rate constant decreased, this decrease is due to the increased amount of linuron in solution and the interactions between molecules during adsorption and reaction.

Values of half lives calculated and estimated, reported in Table 2, increased with initial linuron concentration, for the same concentration, there was a slight difference between half lives, this could mean that the intermediates did not compete severely with linuron for adsorption, and therefore, for reaction with the reactive transient, the kinetics observed at initial time should hold during the reaction time.

4.4. TiO_2 loading

To optimize the amount of catalyst required for effective linuron degradation, different catalyst doses were studied. It is observed in Fig. 5 that 0.3 g L^{-1} was found to be the optimum, beyond this value a decrease was noted as well for apparent rate constants. This may be due to the excess TiO_2 particles that can create a light screening effect that reduces the surface area of TiO_2 being exposed to light illumination and the photocatalytic efficiency by reducing the hydroxyl radicals formation [4,11].

4.5. Effect of hydrogen peroxide on linuron photooxidation

By using TiO_2 as a photocatalyst, the undesired electron/hole recombination takes place. One strategy to inhibit this phenomenon is to add other electron acceptors such as hydrogen peroxide to the reaction. They could have several different effects such as increasing the number of trapped electrons and, consequently, avoid recombination, generating more radicals and other oxidizing species, increasing the oxidation rate of intermediate compounds, and avoiding problems caused by low oxygen concentration. To this purpose, we have studied the effect of electron acceptors, such as hydrogen peroxide, on the kinetic degradation of linuron by UV/TiO_2/H_2O_2 process, and investigated the effect of different concentrations of H_2O_2.

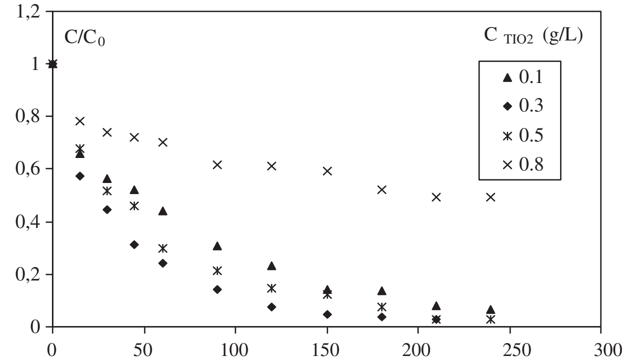

Fig. 5. Kinetic of linuron disappearance at different TiO_2 concentrations. C_0(linuron) = 10 mg/L, Q = 396 mL/min.

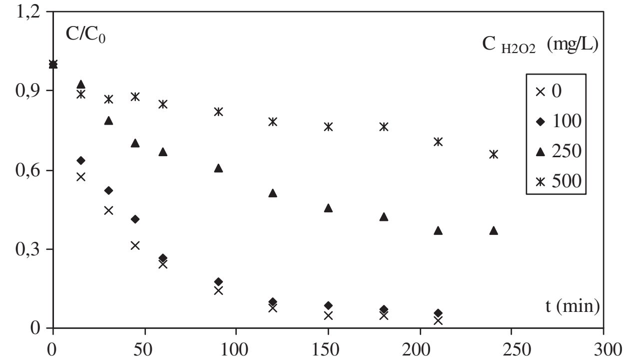

Fig. 6. Effect of H_2O_2 concentration on linuron photocatalysis. C_0(linuron) = 10 mg/L, $C(TiO_2)$ = 0.3 g/L, Q = 396 mL/min.

As shown in Fig. 6, the effectiveness of UV/TiO_2/H_2O_2 system depends on concentrations of H_2O_2. Study on the linuron elimination showed that the oxidation decreased when the hydrogen peroxide concentration increased. Besides hydrogen peroxide was found to slow down the rate markedly as shown in Fig. 6, this additive disadvantaged the degradation of linuron; nevertheless, Faisal et al. [28] found that hydrogen peroxide enhanced the rate of two dyes (Acridine Orange and Ethidium Bromide) markedly, and Rao and Chu [29] observed that in the system of P25/H_2O_2/Vis (under visible light), a pronounced enhancement of the reaction rate was observed resulting in a nearly complete decay of linuron. Several studies have shown that under UV radiations, the hydrogen peroxide played a dual role in enhancing the photocatalytic process [30,31]. The removal of linuron showed a pseudo-first-order kinetic behavior for hydrogen peroxide concentrations less than 250 mg/L and a value of 0 order at high concentration beyond 250 mg/L.

4.6. Effect of pH

The pH is a very important parameter in wastewater treatment. In systems of photocatalytic degradation, the pH is one of the factors that influence the degradation rate and abatement of micropollutants because it determines the properties of the photocatalyst surface charge and the size of the aggregates formed.

To select the acid and the base to be used for pH adjustment, some experiments were performed with different acids and bases. Fig. 7 shows the residual concentration of linuron in the presence of different acids and bases. It was found that all acids and bases enhance the decomposition of linuron markedly, although the natural pH (no acid or base were added) gave the best abatement (98%).

Because of the important abatement obtained with H_3PO_4 and KOH, where, after an irradiation time of 4 h, 95% and 90% of linuron were, respectively, oxidized, these two products were chosen for adjusting pH of the solution.

Photocatalytic degradation of linuron was studied at different pH values (in the range 3–12), adjusted and not adjusted. The nonadjusted pH means that pH

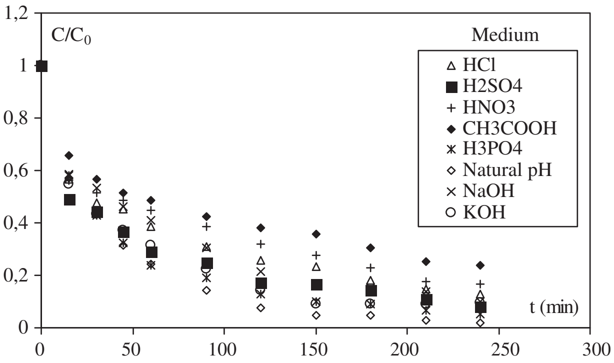

Fig. 7. Effect of acidic and basic conditions on linuron photocatalysis. C_0(linuron) = 10 mg/L, $C(TiO_2)$ = 0.3 g/L, Q = 396 mL/min.

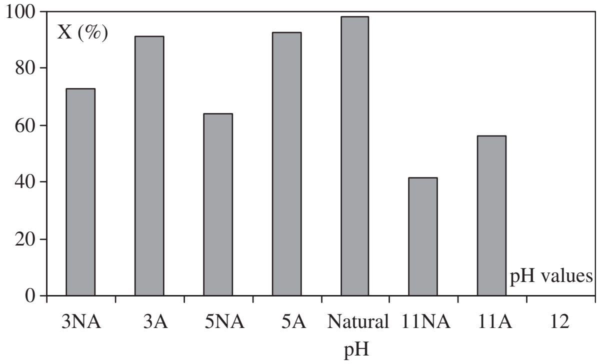

Fig. 8. Decomposition of linuron at different pH levels after 4 h of photocatalysis. C_0(linuron) = 10 mg/L, Q = 396 mL/min, $C(TiO_2)$ = 0.3 g/L.

was fixed in the aqueous suspension only at the beginning of photocatalysis, whereas the adjusted pH corresponds to the fixation of pH in the aqueous suspension at one value and maintained along the photocatalytic process. Fig. 8 shows that highest efficiency was observed at natural pH corresponding to a value of 5.23, where, as mentioned in Table 3, 98% of linuron was removed. Nevertheless, a high efficiency of degradation was observed in acidic pH (pH 3A and 5A). This may be due to nonionic nature of linuron. In natural medium, $HO^{\bullet}$ radicals attack the aromatic ring methyl groups and the hydroxylation of the aromatic ring is not favored with a decrease in pH, whereas in basic medium, the hydroxylation of aromatic ring is favored, but not the methyl group. Rao and Chu found that, for the photocatalysis of linuron on visible light, under extremely acidic (pH 2.0), and basic conditions (pH 9 and 11), linuron degradation rate was significantly retarded and an optimal pH was found at 6 [29]. It is obvious that natural pH is recommended for the degradation process under UV/TiO_2 process.

The degradation of linuron can be described by pseudo-first-order kinetics (determined by Eq. (5)) at different pH values, and the observed rate constants are summarized in Table 3.

It appeared that rate constants were more significant for the best abatements at natural pH, pH 3A, and pH 5A, the photocatalytic process was rapid at these values and consequently, values of half life decreased for these three pH.

4.7. Photodegradation of linuron in presence of a veterinary antibiotic (tylosin)

Among the various pollutants found in groundwater and rivers, pharmaceuticals are rejected by water from hospitals, domestic waste, and antibiotics given to farm animals. Antibiotics are considered as emerging environmental microcontaminants because of their potential adverse effects on ecosystems and human health. One of the best known antibiotics is tylosin, a macrolide administered to livestock and poultry. In the present work, the study focused on the evaluation of performances of UV/TiO_2 process on the degradation of aqueous solution of tylosin in the presence of

Table 3
Pseudo-first-order rate constants, half-life ($t_{1/2}$), and abatement values for different pH

pH	$K_{app} \times 10^2$ (min^{-1})	R^2	t½ (min)	X (t = 4 h) (%)
3NA	1.00 ± 0.01	0.986	69	73
3A	1.70 ± 0.02	0.994	41	91
5NA	0.60 ± 0.01	0.89	116	64
5A	2.10 ± 0.02	0.988	33	93
Natural pH	2.5 ± 0.01	0.998	30	98
11NA	0.60 ± 0.01	0.976	116	42
11A	1.00 ± 0.02	0.97	69	56

Table 4
Abatement of linuron in the presence of tylosin at different molar ratios, C_0(linuron) = 2 mg/L, Q = 396 mL/min, $C(TiO_2)$ = 0.3 g/L

Molar ratio $C_{linuron}/C_{tylosin}$	X (%)			
	Linuron in presence of tylosin	Tylosin in presence of linuron	Linuron alone	Tylosin alone
1/4	88	98	90	98
1/2	76	99	90	98
1	97	98	90	99.5
3/2	78	99.6	90	98
2	92	99	90	86.4

linuron (codegradation) at different molar ratios [linuron]/[tylosin]: 1/4; 1/2; 1/1; 3/2; and 2/1. In addition to this, this part of work was interested in studying the interactions between these pollutants. Tylosin concentration was followed by an UV–visible spectrophotometer at a wavelength of 290 nm.

Table 4 shows that for different molar ratio studied, oxidation of linuron is often hampered by tylosin; furthermore, pseudo-first-order rate constants were smaller during the codegradation, and therefore, the degradation rate of micropollutants decreased when they were together.

The results showed that for molar ratios of 1 and 2, linuron was removed better than when it was alone, as shown in Table 2, the abatement reached 97%, whereas, with ratios 1/4, 1/2, and 3/2 linuron oxidation was slowed down from an abatement of 90% to 88%, 78%, and 76%. In all cases, as shown in Figs. 9–13, when both pollutants were sets, tylosin started to be oxidized and rate constant values were more important at the beginning of photocatalysis process during codegradation.

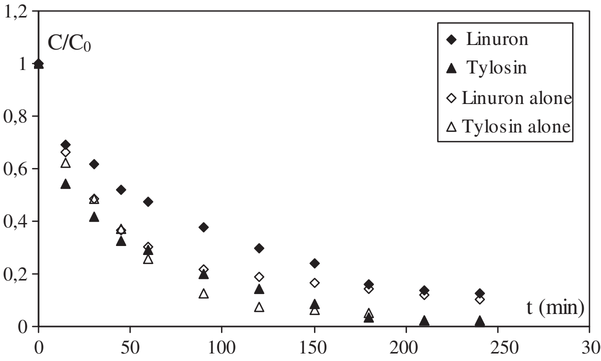

Fig. 9. Linuron photodegradation in the presence of tylosin. Molar ratio [linuron]/[tylosin] = 1/4.

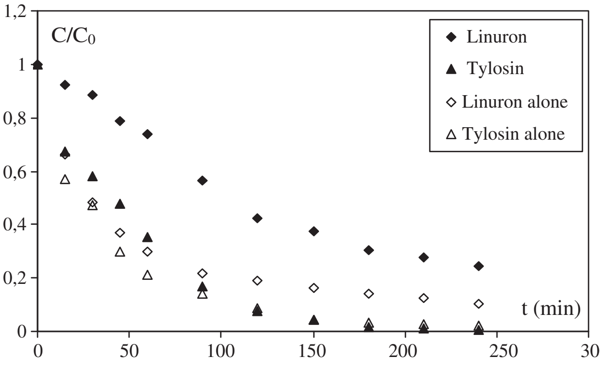

Fig. 10. Linuron photodegradation in the presence of tylosin. Molar ratio [linuron]/[tylosin] = 1/2.

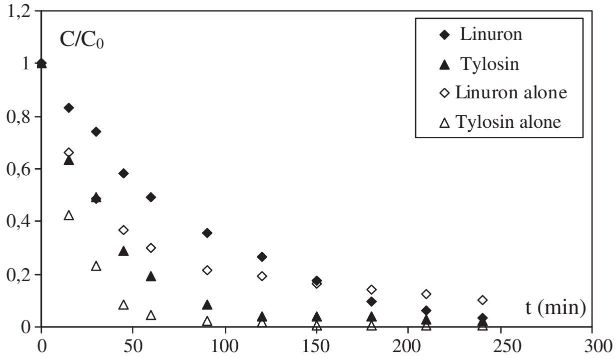

Fig. 11. Linuron photodegradation in the presence of tylosin. Molar ratio [linuron]/[tylosin] = 1/1.

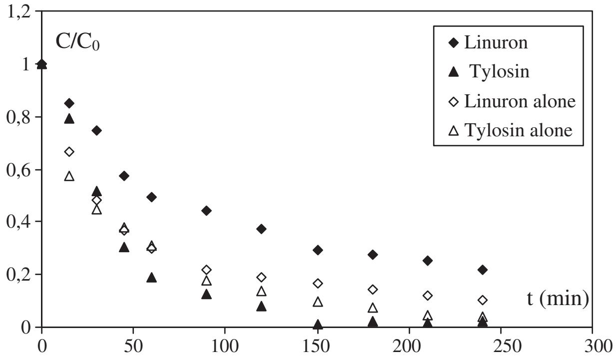

Fig. 12. Linuron photodegradation in the presence of tylosin. Molar ratio [linuron]/[tylosin] = 3/2.

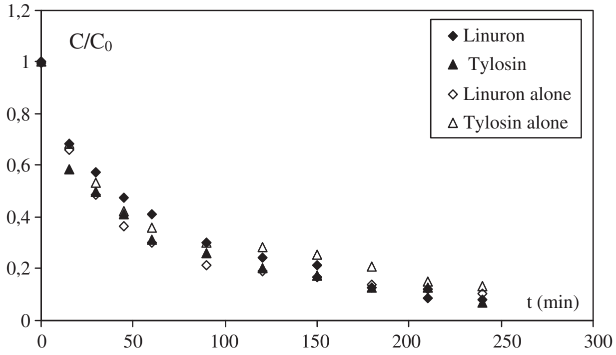

Fig. 13. Linuron photodegradation in the presence of tylosin. Molar ratio [linuron]/[tylosin] = 2/1.

5. Conclusion

The final objective of this work was to study the degradation of linuron in a double spiral reactor, conceived in our laboratory for the heterogeneous photocatalysis organic products in suspension. Experimental results showed that the disappearance rate of linuron increased significantly during photocatalysis compared with photolysis and adsorption. The influence of different parameters on the photocatalytic degradation rate is described by pseudo-first-order kinetic. Catalyst dose of $0.3\,\text{g L}^{-1}$, an important flowrate through the reactor (396 mL/min) and a low concentration of linuron was found to be optimum for easy degradation of linuron. The highest efficiency was observed at natural pH (5.23). The presence of hydrogen peroxide, acids or bases disadvantaged the process. It is found that linuron can be decomposed at room temperature and no additives required (only oxygen from the air). The Langmuir–Hinshelwood (L–H) kinetic model was verified by linearization of Eq. (3) at initial conditions r_0 and C_0 and representation of $1/k_{\text{app}}$ or $1/r_0$ vs. $1/C_0$, the adsorption equilibrium constant K and kinetic constant k_r were evaluated, respectively, to $2.48\,10^{-3}\,\text{mM}^{-1}$ and 0.393 mM/min.

Photodegradation of linuron in the presence of tylosin with different ratios showed that the oxidation of linuron was slowed down for the following molar ratios: 1/4; 1/2, and 3/2.

The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for the application of photocatalytic processes. The investigations were conducted at the laboratory scale in order to determine the optimal degradation condition and further studies are required for the practical effluent treatment.

Nomenclature

C_0 — initial linuron concentration, mg/L
C — Linuron concentration at time t, mg/L
Q — flowrate, mL/min
X — Linuron reduced percentage, %
R^2 — linear regression coefficient, –
$t_{1/2}$ — half time reaction, min
k_{app} — apparent constant kinetic, min^{-1}
K — adsorption constant, mM^{-1}
k_r — kinetic constant, mM/min
A — adjusted
NA — non adjusted

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