CHEMICAL ENGINEERING

Enhancement of the potential biodegradability and the mineralization of a pesticides mixture after being treated by a coupled process of TiO_2-based solar photocatalysis with constructed wetlands

INGENIERÍA QUÍMICA

Mejora de la biodegradabilidad potencial y la mineralización de una mezcla de pesticidas después de ser tratada con un sistema acoplado de fotocatálisis solar con TiO_2 y humedales artificiales

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Abstract

Solar heterogeneous photocatalysis is an advanced oxidation technology, which allows a successful treatment of many recalcitrant and emergent pollutants, such as: pesticides, industrial dyes and pharmaceutical compounds. Nonetheless, despite its effectiveness, the costs of applying this process are high when it is necessary to achieve a complete mineralization or to obtain an environment-friendly effluent. Photocatalytic–biological coupled systems have become in a feasible alternative able to treat efficiently these pollutants. In this work, a coupled system consistent of two compound parabolic collectors (CPC) solar photoreactors and a subsurface flow constructed wetland (SFCW) at pilot-scale was tested for degrading a mixture of commercial pesticides used in sugar cane crops. For measuring the process performance, regarding to the pollutant removal, the increase of the BOD_5/COD ratio and the total organic carbon (TOC) removal were estimated for each separated system and the coupled system. Three different levels of solar UV accumulated energy and feed flow-rates to the SFCW were considered for the experimental design. The pilot-scale coupled system increased the BOD_5/COD ratio from 0.15 to 0.90, and the TOC removal (total mineralization) was around 80%.

Keywords*: Diuron, 2,4-D, Ametryne, Heliconia psittacorum, biodegradability.*

Resumen

La fotocatálisis solar homogénea es un proceso de oxidación avanzada que permite tratar de forma exitosa un gran número de contaminantes recalcitrantes, como: pesticidas, tintas industriales y compuestos farmacéuticos. No obstante, a pesar de su efectividad, los costos de aplicación de este proceso son altos cuando se trata de alcanzar la mineralización completa o de obtener un efluente amigable con el medio ambiente. Los sistemas acoplados fotocatalítico-biológicos se han convertido en una alternativa factible para tratar de forma eficiente estos contaminantes. En este trabajo, un sistema acoplado de dos reactores solares de colectores parabólicos compuestos (CPC) y humedales artificiales de flujos sub-superficial (HFSS) a escala piloto se evaluó para degradar un mezcla de pesticidas comerciales usados en el cultivo de la caña de azúcar. Para medir el desempeño del proceso para eliminar el contaminante, se estimaron el aumento de la relación DBO_5/DQO y la reducción del carbono orgánico total (COT) para cada sistema por separado y para el acople. Se consideraron tres diferentes niveles de radiación solar UV acumulada y de flujos de alimentación al HFSS en el diseño experimental. La relación DBO5/DQO aumentó de 0.15 a 0.90 y la reducción de COT (mineralización total) estuvo alrededor del 80%.

Palabras clave: *Diurón, 2,4-D, Ametrina, Heliconia psittacorum, biodegradabilidad.*

1. Introduction

Pesticides have become in emergent pollutants of an increasing concern. Due their persistence in aquatic environment and their recalcitrance to conventional treatments (majorly biological), they can reach all the stages of the trophic chain in water ecosystems. One of the most frequent sources of pollution by pesticides is the rinsing of used containers. The wastewater produced by this way is usually spilled, with no prior treatment, on surface water bodies (Malato et al., 1999). Just for sugar cane crops in Colombia, they are used around 63000 MT of pesticides for plagues control (Asocaña, 2008). Considering that only a small part of the pesticide ends up in the crops, it is evident that it is necessary to look for a suitable wastewater treatment for mitigating the adverse effect of pollution by these compounds.

Advanced oxidation technologies (AOTs), like solar photocatalysis, emerge as alternatives of treatment; nonetheless, these technologies can be more expensive than the conventional systems which are not so effective (Blanco et al., 2001). By coupling a photocatalytic treatment with a biological system, the operating costs can be reduced and the operating conditions can be optimized (Ballesteros et al., 2009, Hincapié et al., 2005, Malato et al., 2009, Parra et al., 2002, Pulgarín et al., 1999). Sarria et al. (Sarria et al., 2003, Sarria et al., 2002) have studied the coupled systems using homogeneous photocatalysis and fixed-bed biological reactors for removal of recalcitrant pollutants as pesticides and dyes. The use of constructed wetlands has also been reported as a biological alternative of the coupled system to remove pesticides (Araña et al., 2008). The target of the photocatalytic-biological coupled systems is to achieve a complete detoxification of a polluted effluent by optimizing the used area by the process and reducing the installation and maintenance costs of the photocatalytic system, which is the more expensive technology. Previous works have shown that a suitable strategy for accomplishing a satisfactory mineralization degree of a polluted effluent, with these coupled systems, is to improve its biodegradability by pre-treating the effluent with heterogeneous photocatalysis. Some pollutants, such as: benzalkonium chloride (López Loveira et al., 2012), phenol derivatives (Li et al., 2012, Botía et al., 2012), antibiotics (cyproconazole, tetracycline and tylosin) (Yahiat et al., 2011a, Yahiat et al., 2011b), methadone (Postigo et al., 2011), pesticides (Zapata et al., 2010) and industrial dyes (Chong et al., 2010), were successfully treated by coupled systems at laboratory and pilot scales.

In this work, a combined system consisting of a solar photocatalytic TiO2-based reactors and a system of subsurface constructed wetlands (SSCW) was studied. The CPC-type solar photoreactors and the SSFCW were tested at pilot-scale for treating a typical mixture of pesticides used for the sugar cane crops, consisting of 2,4-D, diuron and ametryne. The potential biodegradability (measured as the BOD5/COD ratio) increased when the pesticide mixture was treated with the coupled process and also the total organic carbon (TOC) content was reduced. The Heliconia psittacorum specie was planted in one of the SSCW in order to observe if its presence improved the performance of the biological degradation of the effluent treated by the photocatalytic system.

2. Materials and methods

2.2 Preparation of synthetic mixture of pesticides and simulated domestic wastewater

An herbicides mixture used in the Colombian sugar cane crops was synthetically prepared, from a stock solution, using commercial formulations of 2,4-D (2,4-dichlorophenoxyacetic acid), diuron, and ametryne. This mixture was prepared and diluted with tap water to simulate the concentration of wastewater produced in the rinsing of empty herbicides containers. The following commercial products were diluted in 1 L of tap water: 10 mL of Profiamina® (720 g/L of 2,4-D as dimethylamine salt), 2 g of Karmex® (70% w/w of diuron), 20 mL of Igram® (99%

w/w of ametryne) 1 mL of Inex-A® (Cosmoagro) and 0.67 g of Cosmo-Aguas® (Cosmoagro). The last two components are common proprietary surfactants and pH regulator additives used in the formulation of the herbicides mixture for sugar cane crops. The pH was adjusted at 9.0 with NaOH (Merck).

For the SSCW could get adapted to the photocatalytic-treated effluent and the biofilm could grow on the filtrating medium, a simulated wastewater was prepared. This domestic wastewater was made from the components listed in Table 1. The chemical characterization of this synthetic wastewater was as follows: TOC = 64.44 ppm; COD = 198 mg/L; and BOD_5 = 150 mg/L.

2.2 Coupled system (Solar CPC photoreactor – SSCWs)

The pilot-scale CPC photoreactors used in this study consisted of two sets of ten Duran® glass tubes (1200 mm in length, 32 mm O.D., 1.4 mm wall thickness), supported by two metal structures.

Table 1. *Composition and concentrations of the synthetic wastewater*

Components	Concentration mg/L
Magnesium sulfate ($MgSO_4$)	32.40
Iron chloride ($FeCl_3$)	0.77
Bi-hydrogen potassium phosphate (KH_2PO_4)	17.00
Hydrogen potassium phosphate (K_2HPO_4)	43.50
Ammonia chloride (NH_4Cl)	3.40
Hydrogen sodium phosphate (Na_2HPO_4)	35.40
Urea	108.60
Potassium chloride (KCl)	43.50
Sugar ($C_{12}H_{22}O_{11}$)	50.00
Powder milk	50.00

The high reflectance (0.85) involute aluminum CPC surfaces were located underneath the glass tubes. The reactors were operated in a recirculation mode using a 40 L recycle feed tank and a recycling centrifugal pump (0.5 HP of nominal power) that delivered 30.2 L/min. The flow rate was measured by a calibrated flowmeter. The pipeline and accessories used in the pilot plant were made of PVC, 1 in. diameter. These two serial CPC modules had an exposed area of 2.5 m^2 and an irradiated volume of 29 L (Figure 1). The accumulated radiation was measured with an Acadus S85 radiometer.

Two SSCWs were used for this study: one without plants as a control unit and the other one with *Heliconia psittacorum* planted. The dimensions of the SSCWs were as follows: 0.57 m of length, 0.37 m of width and 0.37 m of depth. The material of the containers was polypropilene and the deepest layer of the filtrating medium consisted of Bentocol® bentonite, as seen in Figure 2.

A medium size grave layer was put over the bentonite, and the surface was covered with a fine coal of 4 cm. The total estimated volume was 40 L and the porosity of 0.44. At the first, three *Heliconia psittacorum* rhizomes were planted in one of the SSCWs for observing how the characteristic microorganisms of the Heliconia's rhizosphere affect the studied parameters.

Figure 1. *Solar CPC reactors (Universidad del Valle, Cali-Colombia)*

***Figure 2**. Pilot-scale subsurface constructed wetlands*

Both SSCWs were stabilized after a month of a continuous feed of the synthetic wastewater.

The BOD_5 and COD analyses were carried out according the Standard Methods protocols, whereas the TOC analyses were made in a Shimadzu TOC 5050 analyzer.

2.3 Experimental design

For the photocatalytic treatment, a single factor experimental design was used. The controllable factor selected was the UV energy accumulated by the reactors. Three levels of UV accumulated energy were considered: 9.0, 11.3 and 13.5 kJ per liter of treated volume.

For the coupled treatment, a split-plot experimental design was considered. This kind of experimental design is suitable for analyzing the effect of the type of constructed wetland by using blocks. After treating the effluent with solar photocatalysis, the pretreated wastewater was fed to the SSCWs and three levels of affluent flow rate were considered: 5, 10 y 15 L/d. The type of SSCW was also considered, with two levels representing to the types: one without plants (or control unit) and one with *Heliconia psittacorum* plants.

The decrease of biodegradability was analyzed by using the BOD_5/COD ratio, with an analysis of variance (ANOVA) of this response variable. This statistical tool allows estimating the effect of the controllable variables on the surface variable based on the sample variance of each effect. For the photocatalytic process, the increase of the BOD_5/COD ratio was studied separately, considering the effect of the accumulated UV energy in the reactors.

3. Results and discussion

3.1 Potential biodegradability of the wastewater treated by solar photocatalysis and by the coupled process

The BOD_5/COD ratio increased for all the UV accumulated energy levels tested, as seen in Figure 3.

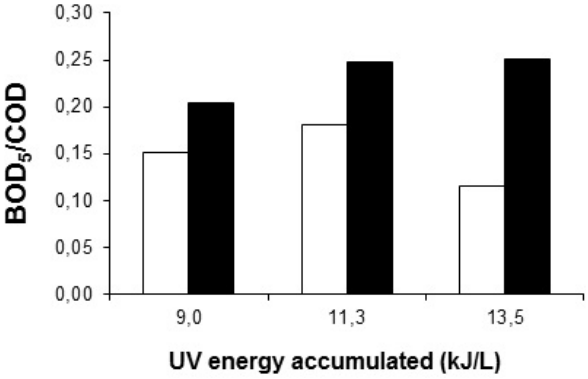

***Figure 3.** BOD_5/COD ratio increase for the photocatalytic treatment. (White: initial and black: final)*

The final BOD_5/COD ratios were within the range from 0.20 to 0.25, which is considered moderately biodegradable (Pulgarín et al., 1999). For the case of 13.5 kJ/L of accumulated UV energy in the photocatalytic treatment, the increase of the BOD_5/COD ratio was more significant. This was because of the oxidation reactions yielded simpler byproducts. Pesticides such as: diuron, 2,4-D and ametryne, can be degraded in smaller molecules. The s-triazine herbicides (ametryn) are more stable due to the presence of the triazine ring nucleus, whereas the phenoxy-acids (2,4-D) and phenylureas (diuron) can achieve complete

mineralization more easily (Konstantinou and Albanis, 2003). For the s-triazine herbicides, the reported degradation mechanisms consist of the oxidation of the side alkyl chain and possible reductive paths leading to dehalogenated s-triazines. In the case of the phenylureas, the photocatalytic degradation is given by the attack of the hydroxyl radicals to the aromatic ring and the side alkyl chains; nonetheless, this attack depends strongly on the pH of the medium. With neutral or alkaline pH, the attack of the aromatic ring is favored and the degradation is faster. And for the 2,4-D, the expected byproducts of the photocatalytic degradation are: hydroxy-phenoxy acids, chlorophenols and some quinonidal, or semiquinonidal derivatives. Due to its simpler chemical structure, the degradation of the phenoxy acids is faster than the other mentioned pesticides (Konstantinou and Albanis, 2003).

The mineralization level of the pesticides mixture depended on the amount of UV radiation that the solar CPC reactor received. With more available photons, the probability of generating more hydroxyl free radicals also increases and thus, these oxidant species can break more chemical bonds and yield byproducts that can be degraded by biological systems. These oxidation byproducts, specially the obtained when the aromatic rings are broken, are more susceptible to be metabolized by the microorganisms present in biological systems, such as: stabilization ponds, active sludges and constructed wetlands. From the treated pesticides used for this study, the aniline derivatives, chlorophenols and carboxylic acids are reported to be more biodegradable than the parent compounds (Lapertot et al., 2006).

Figure 4 shows the increase of the BOD_5/COD ratio for the combined system. In all the cases, the BOD_5/COD ratios of the SCCWs inlet streams were over 0.20, whereas for the outlet streams, they were between 0.45 and 0.90. The SSCW with plants had a better performance when the wastewater was pretreated by solar photocatalysis with the lowest level of accumulated UV energy, whereas the tendency was the opposite when the UV accumulated energy was increased. This was because of the kind of intermediates produced when the organic matter oxidized by photocatalysis could be more susceptible to be degraded by the microorganisms that inhabit the plants rhizosphere than the ones found in the biofilm on the filtrating medium. It has been reported that the substrate (filtrating medium) and the vegetation can influence the performance of the SSCW for removing organic matter (Li et al., 2008). In this case, the filtrating medium was kept unchanged for both SSCWs, but the presence of the plants (*Heliconia psittacorum*) improved slightly the BOD5/COD ratio when the affluent was pretreated with the low level of accumulated

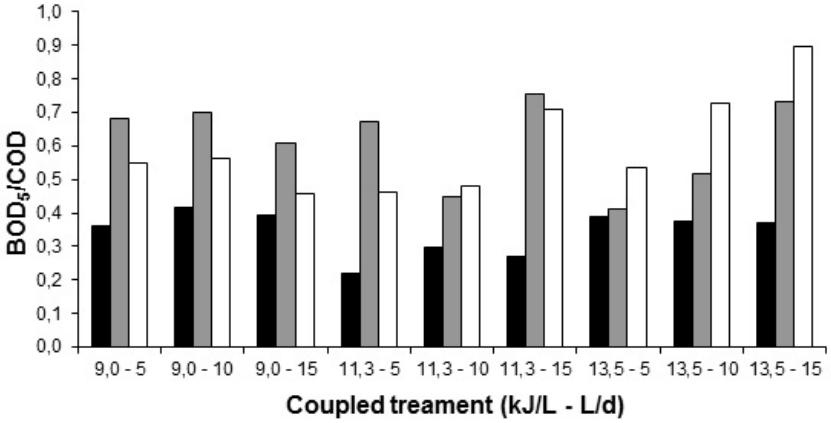

Figure 4. *BOD_5/COD increase for the coupled process (Black: wetland inlet, gray: planted wetland outlet and white: control wetland outlet)*

UV energy (9 kJ/L). The bacteria associated (mostly gram-positive cocobaciles and baciles) to the rhizosphere of the *Heliconia psittacorum* (Salgado-Bernal et al., 2012) could help to degrade the pollutants and their photo-oxidation byproducts since it has been reported that they are capable to remove organic matter represented as COD content. Nonetheless, their contribution showed to be more significant in the first stages of the pollutants degradation. For supporting this observation, it is necessary a further analysis for identifying the photocatalysis byproducts by more precise analytic techniques, such as HPLC-MS, and to study the different metabolic pathways of the specific bacterial strains responsible for the biodegradation.

Table 2 shows the results of the ANOVA for the BOD_5/COD ratio increase due to the coupled treatment. The most incident effect was the UV accumulated energy by the photocatalytic process, followed by the flow rate of the feed to the SSCWs. This means that the chemical transformation of the pollutants was more influenced by the photocatalytic treatment than the biological one. By other hand, the variance due to the type of SSCW is smaller than the residual error variance; so, the effect of this variable is considered not significant. However, as it was discussed above, the contribution of the bacteria belonging to the plants rhizosphere was more evident with low levels of UV energy in the pretreated wastewaters (Figure 4). This contribution was not so evident with high levels of accumulated UV energy because the photocatalysis byproducts could have simpler chemical structures easier to be biodegraded by the filtrating medium and without help from the microbial species of the plants rhizosphere.

Although the mechanisms of COD and BOD removals are very complex, previous studies have shown an empirical relationship between these two parameters (Akratos et al., 2008, Liolios et al., 2012). The increase of the ratio BOD_5/COD, after being treated by the wetland, is product of the organic matter contributed by this biological process. Whereas the BOD_5 practically remained constant after the biological treatment, the COD decreased in all the cases considered in the experimental design (results not shown in this paper).

The flow rate of the pretreated wastewater fed to the SCCWs had a very significant effect on the BOD_5/COD ratio increase. This was due to hydraulic retention time (HRT) derived from the flow rate of the affluent. The smaller flow rates, the larger HRTs and this represent more biological transformations of the organic matter (Haber et al., 2003). Nonetheless, the opposite trend, observed for the high level of accumulated

Table 2. *ANOVA of the BOD_5/COD ratio increase*

Source	SS	DF	SSA	F_0	p-Value
A: Flow rate	16610.90	2	8305.46	11.87	0.0208
B: UV accumulated	25487.20	2	12743.60	18.21	0.0098
C: Type of SSCW	1.54	1	1.54	0.00	0.9649
AB	15464.4	4	3866.09	5.52	0.0633
AC	4066.09	2	2033.04	2.91	0.1662
BC	3947.49	2	1973.75	2.82	0.1721
Residual error	2799.15	4	699.79		
TOTAL	68376.70	17			

UV energy, could be related more to the nature of the photocatalysis byproducts obtained at this condition. Table 2 shows a smaller p-value for the UV accumulated energy, which means that this variable was more relevant that the flow rate of the wastewater fed to the SCCWs.

3.2 TOC removal achieved by solar photocatalysis and by the coupled process

The TOC removal of the pollutant mixture was slightly improved with the coupled process respect to the level achieved by the photocatalytic one (Figure 5).

These values increased when the UV accumulated energy by the photocatalytic reactor increased. This can be explained by the same reason of the observed behavior in Figure 4. The more hydroxyl free radicals, the simpler byproducts of the oxidation can be obtained.

The type of SSCW did not influence on the mineralization achieved by the coupled process. The presence of the plants did not contribute to improve the system ability for reducing the TOC load. The highest mineralization obtained by the coupled system was 80%, due majorly to the photocatalytic treatment.

This result can be explained because the biological transformation of the intermediates produced by photocatalysis did not lead the production of CO_2 from the organic matter (proper of the aerobic microorganisms) but the production of alcohols, aldehydes and other organic compounds proper of the anaerobic microorganisms (Faulwetter et al., 2009). Another reason could be the contribution of organic matter by the constructed wetlands, as it was explained before. This contribution of organic matter could represent an increase of TOC content; therefore, the overall TOC removal by the SSCW was marginal compared to the achieved by solar photocatalysis.

4. Conclusions

The coupled system of CPC-type photoreactor and SSCWs treated satisfactorily a mixture of commercial pesticides, with a considerable increase of the BOD_5/COD ratio as the most important benefit. The increase of this parameter was more influenced by the UV energy received by the photocatalytic reactor than the other ones studied effects. This was due to the chemical transformation of the pollutants by photocatalysis was not selective and it could generate simpler compounds, whereas the biological process (mainly anaerobic) is more strict regarding

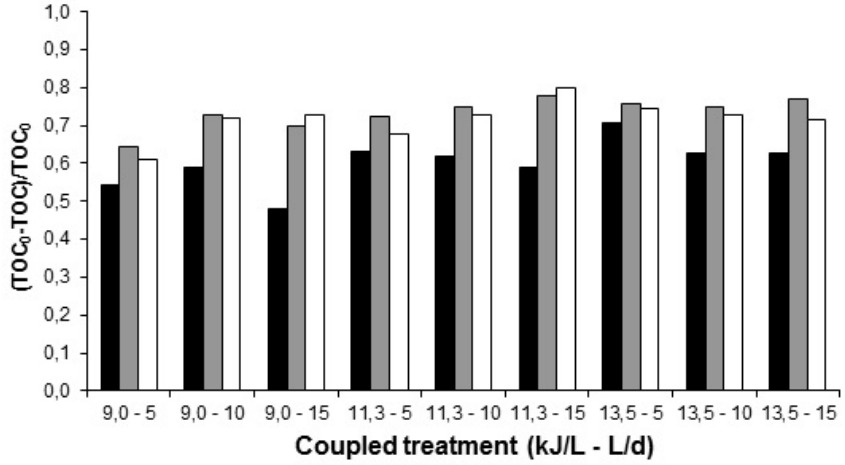

Figure 5. *TOC removal observed in the coupled process (Black: wetland inlet, gray: planted wetland outlet and white: control wetland outlet)*

to the substrate nature. This observation was more evident with the TOC removal since the anaerobic metabolic pathways of degradation could be the dominant ones in the wetlands and the byproducts of this biodegradation could be organic compounds of significant TOC contents. For obtaining more conclusive remarks, it is necessary to carry out further chemical analyses of the wastewaters like HPLC-MS, in order to identify clearly the byproducts obtained by solar photocatalysis and the coupled system.

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