

Fixed Bed Reactor Performance for Herbicide Degradation Under Solar Radiation

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ARTICLE INFO

Keywords:

Metribuzin

Photocatalysis

Titanium Dioxide

Wastewater Treatment

ABSTRACT

Photocatalysis has the best potential to replace the traditional wastewater treatment techniques such as activated carbon adsorption, chemical oxidation, and biological treatment.

Photocatalysis is a combination of a catalyst semiconductor is titanium dioxide TiO_2 with an ultraviolet light source as the sun. It has the added advantage of not introducing additives in the medium to be treated. However, when applied in slurry form, agglomeration of nanoparticle will lead to serious decrease in photocatalytic performance due to hinderance effect. Further, the present study has made an effort to use a support for the immobilization of catalyst for treating the pesticide polluted water by photocatalytic degradation. In the present paper, we present the performance of 2 kinds of Titanium dioxide (Commercial Media Ahlstrom and impregnated TiO_2 on glass) as photocatalytic support in fixed bed reactor for the degradation of Metribuzin herbicide under solar radiation. The degradation Performance was studied under various conditions such as substrate and pH solution. Solar photocatalytic degradation rate can reach 100% during 180 min of treatment with using TiO_2 immobilized on commercial support media 1048.

1. Introduction

Organic chemical products such as, dyes, endocrine disruptors, pesticides and herbicides lead to serious environmental contamination. In particular, various types of pesticide are widely employed in agricultural practice. They are one of the major causes of pollution of surface and ground waters (Oyama et al., 2004). These compounds are toxic and carcinogenic in nature even at low concentration (Ozdemir, Sahinkaya, & Onucyildiz, 2008), several of them are resistant to conventional chemical and biological treatment methods. The search for effective means of removing these compounds is of interest to regulating authorities everywhere (Kositzi et al., 2004).

Advanced oxidation processes (AOPs) have been proposed as an alternative for the treatment of this type of wastewater. Many researchers have concentrated on this goal pointing out that these processes, although making use of different reacting systems, are all characterised by the same chemical feature: production of OH radicals ($\bullet\text{OH}$) (Malato et al., 2002). Among the

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different AOPs, heterogeneous photocatalysis using UV/TiO₂ system appears as one of the most destructive technologies (Chekir, Laoufi, & Bentahar, 2014; Chen, Yang, Wang, & Lou, 2005; Gaya & Abdullah, 2008; Herrmann, 2005). The titanium dioxide photocatalyst is widely available, inexpensive, non-toxic, and shows a relatively high chemical stability (Augugliaro, Loddo, Palmisano, & Schiavello, 1995; Topalov, Molnar-Gabor, Kosanić, & Abramović, 2000; Duffy et al., 2004). However due to the difficulty of nanosized photocatalysts separating from aqueous or gaseous pollutants after reactions in suspended reactor and to avoid the filtration step, fixed-bed system appeared in which the photocatalysts were immobilized on the walls of the reactor, on the supported substrates, or around the light source (Xu et al., 2008).

The aim of the present work is to study the efficiency of two catalytic supports on the solar photocatalysis of metribuzin. In order to determine the optimal degradation conditions of this organic pollutant different parameters influencing photocatalysis were considered.

2. Material and Methods

2.1 Chemical and reagents

a) Pollutant

Selected pesticide used in this study was the metribuzin C₈H₁₄N₄OS (fig.1.) with a molecular weight of 214.32 (g/mol). Metribuzin is one of the nitrogen-containing herbicides in the family of triazine herbicides, is registered for the control of annual broadleaf weeds and grassy weeds that infest various crops, including potatoes, tomatoes ... etc.

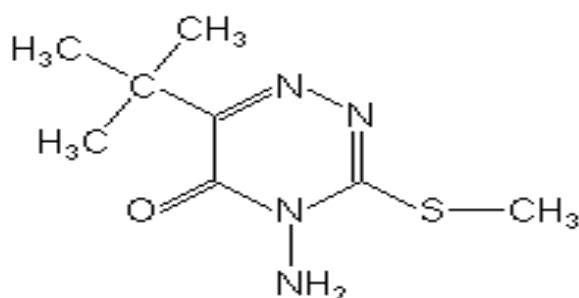


Figure 1: Chemical structure of metribuzin

Metribuzin degradation was evaluated by measuring the absorbance with spectrophotometer UV-VISIBLE, type Shimadzu UV1800. The maximum absorption band was located at 293 nm. A correlation curve between Metribuzin concentration and the absorption was pre-established.

b) photocatalysts

A commercially available titanium dioxide PC-500 was used as a photocatalyst produced by Millennium Inorganic Chemicals. This photocatalyst is in 99% anatase form with BET specific surface area of 320 m².g⁻¹ and particle diameter between 5 and 10 nm. In this study, we used titanium dioxide in two forms: TiO₂ PC-500 supported on cellulose "média 1048" and TiO₂ PC 500 Millennium impregnated and fixed on glass.

2.2. Photoreactor

All the experiments were performed under natural sun light in a step photoreactor (Fig.2) specially developed for photocatalytic application installed at the Solar Equipment Development Unit (UDES) on the north of Algeria (latitude 36°.39'; longitude 2°.42') using natural sun-light irradiation. Solar ultraviolet radiation (U.V.) was measured by global UV radiometer (KIPP&ZONEN, CMP11) mounted on a plat form tilted 36° as the reactor.

The solar photocatalytic reactor used in this experiment consists of several parts: a tank, a pump, a spillway at the top and steps. The reactor was made of three (03) regular glass steps of the same dimensions (40x20x1cm) covered with the photocatalytic media or impregnated solution (corresponding to 1.1 mg/cm²).

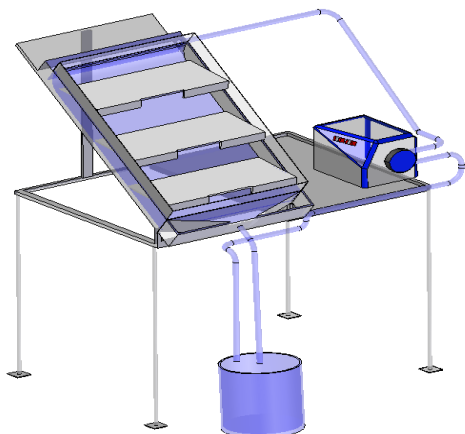


Figure.2. Experimental set-up

3. Results and discussion

3.1 Effect of pH solution

pH is an important parameter in photocatalysis, which influences the surface charge of TiO₂ and therefore adsorption of the pollutant. The pH solution was adjusted by adding NaOH or H₂SO₄.

The role of pH on the rate of photocatalytic degradation was studied in the pH range 3–9.5 at constant pesticide concentration (10 mg L⁻¹).

The obtained Results for the two kind of photocatalyst support, with varying pH from 3 to 9.5, were illustrated in Fig. 3. Table 1 summarizes the calculated k_{app} and $t_{1/2}$.

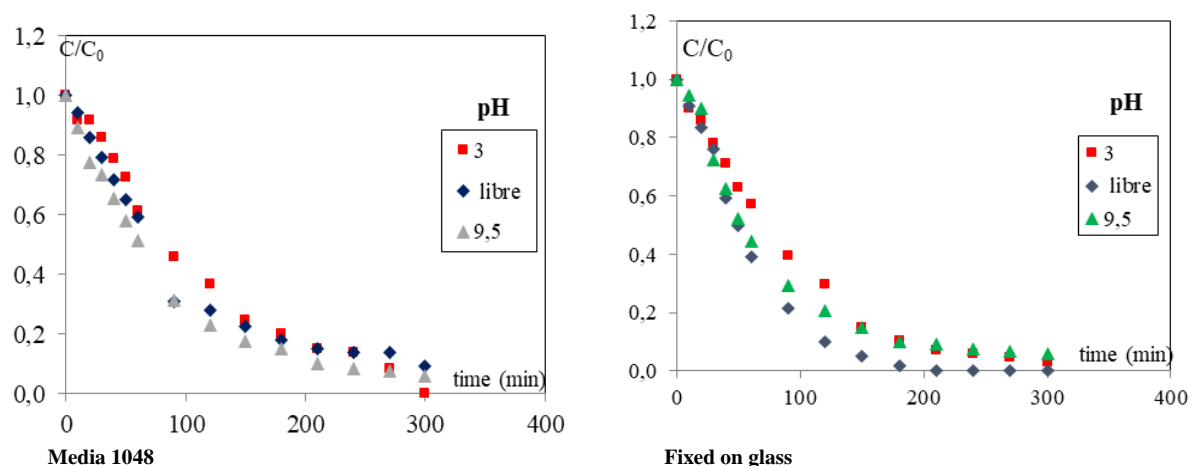


Figure 3. Temporal evolution of metribuzin elimination rate for different pH. $C_{MET}=10\text{mgL}^{-1}$

The obtained results in fig. 3 show that after 300 minutes of photocatalytic treatment, the metribuzin removal is around 97% and 94% for acidic and basic pH respectively when the TiO₂ photocatalyst is supported on tissues “media 1048”. The results are almost similar when the catalyst is supported on glass plates. While for the free pH (7.0-7.2), the degradation is complete with a yield of 100% for both types of cellulosic support.

Table 1.

Value of kinetic constants, times of half reaction for different pH solution for 2 kind of catalytic support.

	pH	k (min ⁻¹)	R ²	X %	t _{1/2} (min)	r ₀ (mg.L ⁻¹ .min ⁻¹)
Media 1048	3	0.009	0.99	97	77	0.03
	Free	0.015	0.99	100	46	0.11
	9.5	0.013	0.98	94	53	0.12
Glass	3	0.006	0.99	95	87	0.02
	Free	0.010	0.99	100	83	0.06
	9.5	0.011	0.99	94	63	0.10

3.2. Effect of Metribuzin concentration

To confirm the effectiveness photocatalysis, it is also necessary to study the photocatalytic degradation rate for different initial pollutant concentrations.

The effect of the initial metribuzin concentration on the rate of pollutant degradation was studied by varying the initial concentration from 2.5 to 20 mg/L.

All experiments were carried out with both types of photocatalytic support: TiO₂ PC-500 supported on cellulosic (media 1048) or impregnated impregnated on glass plates.

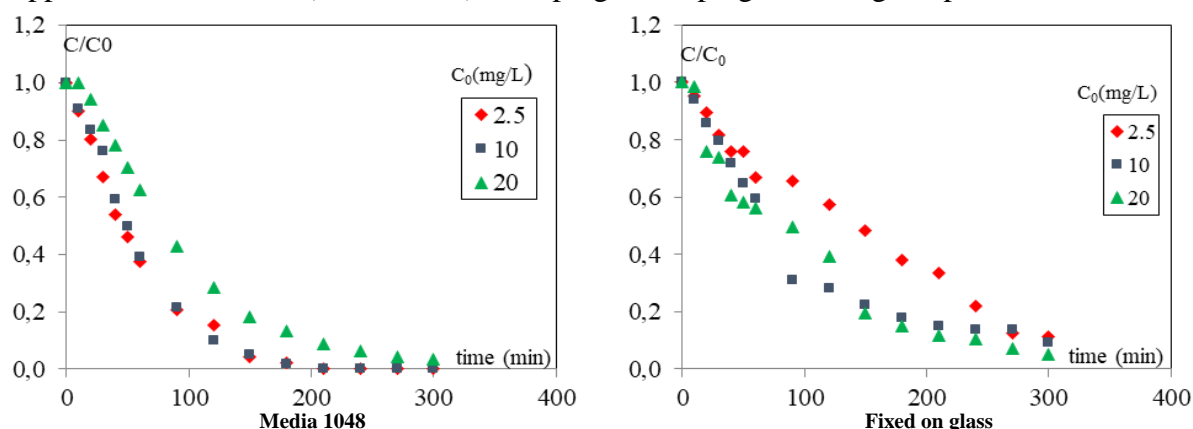


Figure 4. Temporal evolution of Metribuzin elimination rate for different concentration

The obtained results (Fig.4) show that the Metribuzin elimination rate on media 1048 photocatalytic support is greater when the pollutant concentration is lower, whereas for the second glass support the influence of the pollutant concentration is not very noticed.

Table 2.

Value of kinetic constants, times of half reaction for different pollutant concentrations

	C ₀ (mg/L)	k (min ⁻¹)	R ²	X %	t _{1/2} (min)	r ₀ (mg.L ⁻¹ .min ⁻¹)
Media 1048	2.5	0.017	0.99	100	41	0.04
	10	0.015	0.99	100	46	0.15
	20	0.007	0.97	96	96	0.14
Glasse	2.5	0.006	0.99	95	110	0.02
	10	0.008	0.99	90	82	0.08
	20	0.010	0.99	95	69	0.20

According to Table 2, metribuzin degradation follows the pseudo-first order kinetic model. The apparent rate constants for each pollutant concentration were determined by linear regression form ($\ln(C/C_0)$ versus time). We note that these values increase slightly for the glass photocatalytic support, on the other hand, for the media 1048 the apparent constant decreases by increasing the initial concentration of pollutant.

3.3. Comparative study

A comparative study of the photocatalytic degradation of Metribuzin on the two photocatalytic supports: the TiO₂ Tissue media 1048 and the TiO₂ fixed on the glass plates is presented. Figure 5 shows the kinetics of metribuzin degradation under the same optimal operating conditions, namely: $Q = 17.7 \text{ mL / s}$, $C_0 = 10 \text{ mg / L}$ and free pH.

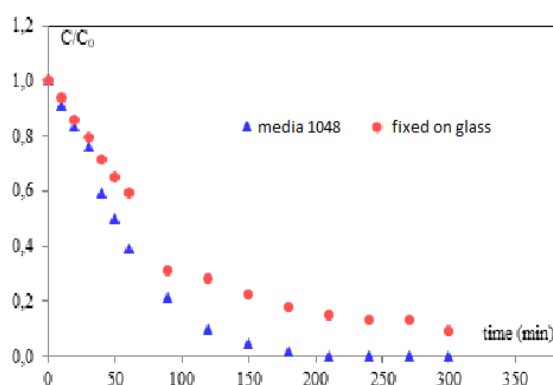


Figure 5.

Temporal evolution of Metribuzin elimination rate for both catalytic support under optimal conditions ($C_0=10 \text{ mg/L}$, free pH $Q=17.7 \text{ mL/s}$)

Figure 5 shows that the metribuzin elimination is more important with using TiO₂ media 1048 as a photocatalytic support. The degradation is complete after only 180 minutes of treatment while on the glass support, the rate of abatement does not exceed 90% after 300 minutes of treatment. Table 3 summarizes the different kinetic constants.

Table 3.

Value of kinetic constants, half-reaction times for both catalytic support

	k (min ⁻¹)	X %	R ²	t _{1/2} (min)	r ₀ (mg.L ⁻¹ .min ⁻¹)
Media 1048	0.0150	100	0.99	46	0.150
Glass	0.0084	90	0.99	83	0.084

4. Conclusion

The degradation of metribuzin on TiO₂ fixed bed was investigated under the solar irradiation. The results show that the photocatalytic process U.V./TiO₂ seems to be very efficient on the removal of herbicide resistant to conventional techniques. Solar photocatalytic degradation rate can reach 100% during 180 min of treatment with using TiO₂ immobilized on commercial support media 1048

This process was also developed using an impregnated TiO₂ on glass plates, around 90% of degradation for more time (300min).

For the similar degradation, the solar photocatalysis in fixed bed reactor can be recommended to avoid the filtration step, for its low energetic cost and a very good efficiency.

Acknowledgments

This work was supported by Solar Equipment Development Unit (UDES).

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