

Photodegradation of salicylic acid in aqueous phase by TiO_2 / UV System

Radia Djouder ^{1,2*}, Aïcha Nadia Laoufi ^{2†} and Fatiha Bentahar ²

¹ Division Bio Energie et Environnement

Centre de Développement des Energies Renouvelables

B.P. 62, Route de l'Observatoire, Bouzaréah, Alger, Algérie

² Laboratoire des Phénomènes de Transfert, Département de Génie

Chimique et de Cryogénie, Faculté de Génie Mécanique et de Génie des Procédés

Université des Sciences et de la Technologie Houari Boumediene, USTHB

B.P. 32, El Alia, Bab Ezzouar, Alger, Algérie

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Abstract – Man uses the background where he lives and transforms it; he becomes the factor controlling the ecosystem conditions and the main reason of degradation of environment especially by industrialization and rejecting wastewaters. Water pollution can be soluble or not. The main categories of the water soluble pollution are represented by: inorganic pollutants, biological pollutants and organic pollutants. There are numerous methods to treat wastewaters; they depend on the characteristics of pollution. This study aims to examine the application of the advanced oxidation process, particularly heterogeneous photocatalysis. This process has been applied for degradation of salicylic acid dissolved in water; its degradation occurs in a photocatalytic reactor made up of a titanium dioxide (TiO_2) as a semiconductor supported on a glass plate placed at the middle of the reactor and subjected to the U.V irradiation. The assessment of the parameters influence related to the reactor such as recirculation flow and initial concentration of pollutant has shown that at low recirculation flow, the photodegradation of pollutant was accelerated about 98 % of salicylic acid was degraded after 3 hours of irradiation, in addition the heterogeneous photocatalysis process is applied even at low concentration. Kinetic analyses indicated that the photodegradation of pollutant can be described by a pseudo-first-order reaction. The Langmuir Hinshelwood model was used to assess the kinetics of the heterogeneous photocatalytic process, the rate constant, k_{app} for the photocatalytic degradation was determined at different concentrations.

Résumé – L'homme utilise l'environnement et le transforme, il est devenu le facteur déterminant dans l'écosystème et il est la principale cause de la dégradation de l'environnement, particulièrement par l'industrialisation en rejetant des eaux usées. La pollution de l'eau peut être soluble ou non. Les principales catégories de pollution soluble de l'eau sont représentées par des polluants inorganiques, des polluants biologiques et des polluants organiques. Il existe divers procédés de dépollution des eaux usées, elles dépendent des caractéristiques de la pollution. L'objet de cette étude est d'examiner l'application des procédés d'oxydation avancée, en particulier la photocatalyse hétérogène. Ce procédé a été appliqué pour la dégradation de l'acide salicylique dissous dans l'eau, sa dégradation a été réalisée dans un réacteur photocatalytique en utilisant le dioxyde de titane (TiO_2) comme semi conducteur supporté sur une plaque en verre placée au centre du réacteur et soumis à une irradiation UV. L'évaluation de l'influence des paramètres liés au fonctionnement du réacteur, tels que le débit de recirculation et la concentration initiale en polluant, a montré qu'à faible débit de recirculation, la photodégradation du polluant a été accélérée, environ 98 % de

* radia_djouder@yahoo.fr

† nlaoufi@usthb.dz - fbentahar@usthb.dz

l'acide salicylique ont été dégradés après 3 heures d'irradiation. De plus, le processus de la photocatalyse hétérogène y a été appliqué même à faible concentration. L'étude cinétique a indiqué que la photodégradation du polluant peut être décrite par une réaction de pseudo premier ordre, le modèle de Langmuir - Hinshelwood a été utilisé pour évaluer la cinétique du procédé de la photocatalyse hétérogène, la constante de vitesse (k_{app}) a été déterminée à différentes concentrations initiales.

Keywords: Heterogeneous photo catalysis - TiO_2 - Advanced oxidation process Water treatment.

1. INTRODUCTION

In recent years, the application of advanced oxidation processes in water and wastewater treatment is the subject of several studies and research topics. In majority of the existing process, the parameter responsible of an efficient degradation is the existence of highly reactive hydroxyl radicals [1].

These free radicals are molecules capable of oxidizing numerous organic complex, no chemically oxidizable or compounds difficult to oxidize. Heterogeneous photocatalysis is an alternative method for removing organic pollutants in water, this process can be carried out under ambient conditions of temperature and pressure and may lead a total mineralization of organic carbon to CO_2 [2].

Heterogeneous photocatalysis is based on the irradiation of a semiconductor material, when semiconductor absorb ultraviolet radiations from sun light or another light source (fluorescent lamps), it will produce reactive group (electron/positive hole pairs) [3, 4].

In the presence of oxygen, the electron may induce reduction and leads to formation of hydroxyl radicals. These radicals are well known to be strong oxidant agents and react efficiently without any selectivity with most organic substrates [5-7].

Titanium dioxide (TiO_2) is widely used as semiconductor photocatalyst, because it is chemically stable, non toxic and low cost material [3, 8, 9].

In addition, it has been proposed to solve various environmental problems because of its ability to eliminate microorganisms such as bacteria and viruses, controlling odor and degrading organic pollutants such as pesticides and phenol [10, 11].

The photocatalytic degradation rate of different organic compounds depends on various parameters. In this paper, we report our investigation of photodegradation of salicylic acid in aqueous solution, using TiO_2 immobilized on a glass plate under U.V irradiations, and assess the influence of various parameters such as recirculation flow and initial pollutant concentration.

2. MATERIAL AND METHODS

2.1 Photocatalytic reactor

Photocatalytic reactor was constructed with parallelepiped geometry in which was placed ordinary glass plate supporting the catalyst. The U.V irradiations were assembled on a support so as to be parallel to the plan of reactor and to the catalytic bed and positioned 19 cm above reactor. The aqueous solution is continuously circulated with a peristaltic pump, (Fig. 1).

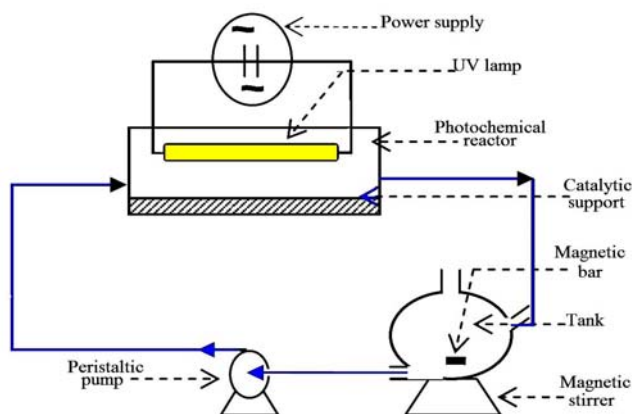


Fig. 1: Experimental installation

2.2 Procedure and analysis

Aqueous solution of salicylic acid is running on the reactor in continuous system before irradiation for a period of one hour to achieve adsorption equilibrium. In all experiments, the total solution volume was 300 ml. Salicylic acid concentrations during irradiation at selected time intervals were followed by UV visible spectrometry Lambda 25 from Perkin-Elmer.

3. RESULTS AND DISCUSSION

3.1 Effect of recirculation flow

The photocatalytic degradation rate of salicylic acid is affected by the recirculation flow. Figure 2 shows the evolution of reduced concentration of salicylic acid according to irradiation duration.

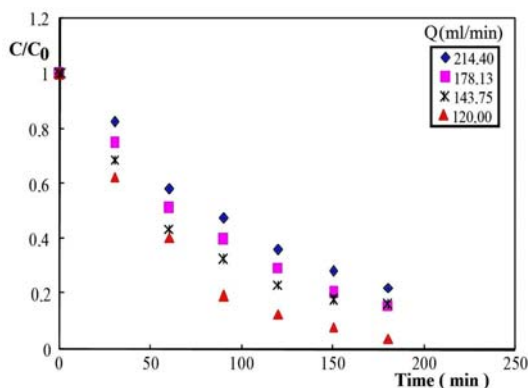


Fig. 2: Evolution of the reduced concentration of salicylic acid versus time for different flow rates.

Conditions: $C_0 = 7.24 \times 10^{-2}$ mM , Lamp power 400 W

Results obtained shows that the pollutant was highly eliminated with a low recirculation flow, we note about 98 % of salicylic acid disappear after 3 hours exposure to ultraviolet light with a recirculation flow of 120 ml/min.

3.2 Effect of initial concentration

A. Parametric study

The effect of salicylic acid concentration was studied in a range between 3.62×10^{-2} to 7.24×10^{-2} mM; Irradiation of solution containing effluent with natural pH; recirculation flow value 120 ml/min and UV lamp power 18 Watts resulted that the photo catalysis process is applied even at low concentration. (Fig. 3)

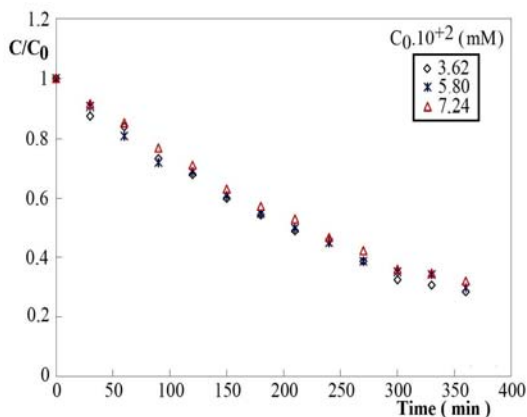


Fig. 3: Evolution of the reduced concentration of salicylic acid versus time for different initial concentrations

Conditions: $C_0 = 7.24 \times 10^{-2}$ mM , Lamp power 18 W

B. Kinetic study

The kinetics of photocatalytic degradation of salicylic acid follows the Langmuir - Hinshelwood scheme.

$$r = \frac{-dc}{dt} = \frac{k_r \times K \times C}{1 + (K \times C)} \quad (1)$$

where r , represents the rate of photo oxidation, C , the concentration of the reactant, t , the irradiation time, k_r , the rate constant of the reaction and K , is the adsorption coefficient of the reactant. At mM concentrations $C \ll 1$, the equation can be simplified to the apparent rate order equation [12, 13].

$$\ln \frac{C_0}{C} = k_r \times K \times t = k_{app} \times t \quad (2)$$

Figure 4 shows the kinetic of photodegradation of salicylic acid. The degradation rate of salicylic acid is of first-order.

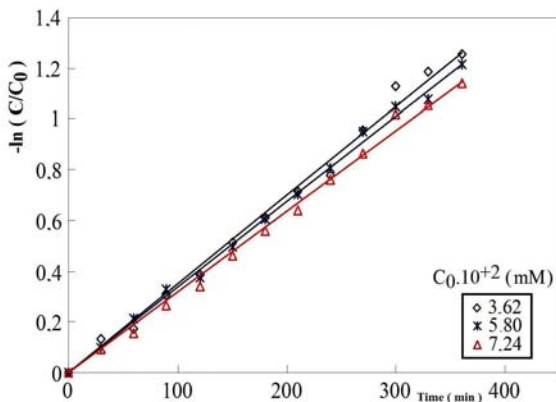


Fig. 4: Kinetic of photocatalytic degradation of the salicylic acid.

First linear transform, $\ln(C_0 / C) = f(t)$

Conditions: $C_0 = 7.24 \times 10^{-2} \text{ mM}$, Lamp power 18 W

k_{app} is the apparent first order rate constant given by the slope of the graph of $-\ln(C / C_0)$ versus t and C_0 is the initial concentration of the salicylic acid. Consequently under the same condition, the initial degradation rate could be written in a form

$$r_0 = k_{\text{app}} \times C_0 \tag{3}$$

The different values of k_{app} and r_0 for different initial concentrations are combined in the following **Table**.

Table 1: Different values of k_{app} and r_0

$C_0 \ 10^{+2} \text{ (mM)}$	$k_{\text{app}} \text{ (min}^{-1}\text{)}$	$r_0 \ 10^{+4} \text{ (mMmin}^{-1}\text{)}$
3.62	0.0036 ± 0.0002	1.30 ± 0.07
5.80	0.0034 ± 0.0001	1.96 ± 0.06
7.24	0.0033 ± 0.0002	2.39 ± 0.14

The photocatalytic degradation kinetic of salicylic acid has been studied by several researchers. Regazzoni *et al.* [14] observed zero order kinetics in the field of high initial concentrations of pollutant.

Ould Mame [15] reported that the rate of reaction of salicylic acid photodegradation conforms with the first order kinetic in low concentrations and becomes zero order in the field of high concentrations.

4. CONCLUSION

The photocatalytic degradation of salicylic acid is affected in various manners, by recirculation flow and initial concentration.

The recirculation flow of solution is an important variable to consider in photodegradation of salicylic acid; it was found that the degradation of this pollutant was obtained at low flow.

We noted that about 98 % of salicylic acid disappears after 3 hours of irradiation with the lowest flow (120 ml/min).

The photocatalysis process is applied even at low concentration. Kinetic photocatalytic degradation of salicylic acid corresponds to the first order reaction, Langmuir - Hinshelwood model serves as a basis for the photodegradation of salicylic acid.

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