

Photocatalytic decontamination of pharmaceutical effluent in a double tube reactor by ZnO catalyst physico chemical characterization and optimization.

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Abstract

This work focused on the study of the elimination of a non-steroidal anti-inflammatory drug (diclofenac) using heterogeneous photo catalysis as a treatment. The study investigated the effect of parameters (catalyst concentration, initial diclofenac concentration, ratio $r = ([H_2O_2])/([ZnO])$, and volume flow) on the photocatalytic degradation of diclofenac. The analyses performed are pH, electrical conductivity, turbidity, surface tension, chemical oxygen demand, nitrite and diclofenac concentration. The study showed that: The heterogeneous photo catalytic degradation is influenced by: The concentration of the ZnO catalyst; The concentration of 1.5 g/L gives a better degradation in diclofenac with a percentage of elimination of 52%; The initial concentration of diclofenac; The concentration of 100 mg/L of diclofenac gives a better degradation with a percentage of elimination of 52%; The ratio $r = ([H_2O_2])/([ZnO])$; The three ratios (1;5; and 10%) give a total degradation after one hour of treatment; The volume flow rate of 25 mL/s gives a total degradation after one hour of treatment. Optimal conditions for heterogeneous photo-catalysis are: $[ZnO]=1.5$ g/L, $[diclofenac]=100$ mg/L, Volume flow rate= 25 mL/s For a volume flow rate of 20 mL/s, optimal conditions are met by adding H_2O_2 .

Keywords: Photo degradation, Drugs, Double-tube reactor, Volume flow, ZnO, H_2O_2

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Introduction

Water pollution is caused by different categories of chemical and biological toxic substances. Heavy metals, organic dyes, pesticides, drugs such as anti-inflammatory drugs are known to be frequent pollutants that threaten human health and the environment, Diclofenac is an NSAID.

It is fairly poorly eliminated, with variable rates of 17 to 70% in treatment plants, which explains its fairly frequent presence in surface waters [1,2]. The catastrophic decline of Pakistani white-collar vultures due to kidney failure is believed to be the result of feeding on improperly treated animal carcasses containing diclofenac residues [3]. Based on EC50s, anti-inflammatory drugs such as diclofenac, ibuprofen, naproxen or ketoprofen are considered highly toxic to bacteria and toxic to invertebrates and algae [4].

Aquatic systems play a major role in the transport and dissemination of drug residues through the water cycle. Thus, it is recognized that Waste Water Treatment Plants (WWTPs) are the main source of dispersion of pharmaceutical compounds for human use in the environment. Photocatalysis appears to be one of the cheapest POAs to be set up to lead to the degradation of organic compounds, it is a process that is rapidly developing in environmental engineering [5,6]. This decontamination by photo catalytic process used in research laboratories has found applications in several industrial sectors [7-9].

The objective of this study is the optimization of operating conditions for the removal of an anti-inflammatory drug in dynamic mode in a double tube reactor. The study focused on the effect of parameters (catalyst concentration, initial diclofenac concentration, ratio $r = [H_2O_2]/[ZnO]$ and volume flow) on the photo catalytic degradation of diclofenac.

The analyses performed are pH, electrical conductivity, turbidity, surface tension, chemical oxygen demand, nitrite and diclofenac concentration.

Materials and Methods

Diclofenac, raw formula $C_{14}H_{10}Cl_2NNaO_2$, is a member of the non-steroidal anti-inflammatory drug (NSAID) family (Figure 1).

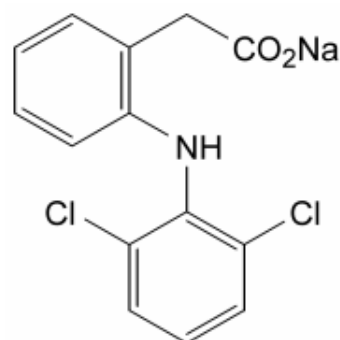


Figure 1. Chemical formula of diclofenac.

The nomenclature of diclofenac according to IUPAC is:

1. Sodium [2-[(2, Dichlorophenyl) amino]phenyl] acetate, molar mass equal to 318.1 g/mol. Its melting temperature is about 280°C.
2. Appearance: White or slightly yellowish crystalline powder, slightly hygroscopic.
3. Solubility: fairly soluble in water, easily soluble in methanol, soluble in 96% ethanol, sparingly soluble in acetone (Pharmacopée Européenne 2008).
4. Diclofenac is a Non-steroidal Anti-inflammatory Drug (NSAID).

The reactor used is tubular in shape with an outer diameter of 12 mm, an inner diameter of 10 mm, a length of 175 mm, a width of 195 mm and a volume of 70 mL. The experimental set-up used is shown in Figure 2.

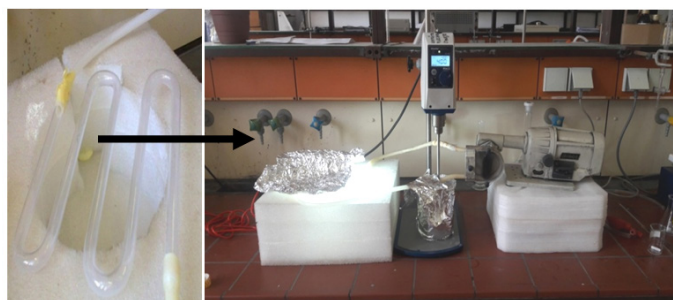


Figure 2. Experimental set-up used.

The catalyst used during the photo catalytic treatment is Zinc Oxide (ZnO) [10-12]. Zinc oxide is an abundant material on earth and is non-toxic. It is also inexpensive unlike other materials.

Zinc oxide is a compound insoluble in water but soluble in acids and alcohols. The molar mass of ZnO is 81.38 ± 0.02 g/mol and its melting temperature is 1975°C . In its natural state, it is ruby red in color and occurs abundantly in ores, while artificially prepared ZnO is colourless or white. For each test, the solution of the pollutant to be treated is put into a beaker with a volume of 1 liter and stirred with a speed of 400 rpm using a mechanical stirrer type WiseStir HS-30D. This solution passes through the reactor with the help of a Heidolph peristaltic pump. A sample is taken every hour during a period of 5 hours to perform a series of physico-chemical analyses. For this, the samples are centrifuged at 2000 rpm for 8 minutes to remove the catalyst.

In order to achieve the best NSAID degradation conditions, we have proceeded to the variations of the following parameters:

ZnO catalyst concentration: 0.5;1 and 1.5 g/L.

Concentration of diclofenac: 50;75 and 100 mg/L.

Ratio $r = ([\text{H}_2\text{O}_2])/([\text{ZnO}])$: 1;5 and 10%.

Volume flow rate: 20.5;22 and 25 mL/s.

The physico-chemical parameters monitored are: pH, electrical conductivity, turbidity, surface tension, COD, Nitrites and the concentration of diclofenac.

Results and Discussion

The study focused on the effect of parameters (catalyst concentration, initial diclofenac concentration, ratio $r = [\text{H}_2\text{O}_2]/[\text{ZnO}]$ and volume flow) on the photo catalytic degradation of diclofenac.

The analyses performed are pH, electrical conductivity, turbidity, surface tension, chemical oxygen demand, nitrite and diclofenac concentration.

Influence of the ZnO catalyst concentration

The study of heterogeneous photo catalytic degradation was carried out using the ZnO catalyst whose concentrations are (0.5;1 and 1.5 g/L). The concentration of diclofenac is 100

mg/L. The volume flow rate is 20.5 mL/s.

Hydrogen potential (pH): The pH variation during heterogeneous photo catalytic treatment as a function of the three ZnO concentrations is shown in Figure 3.

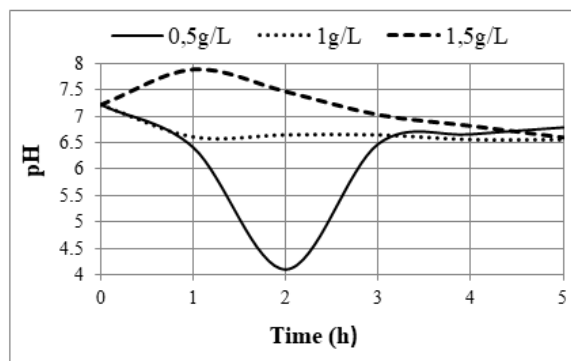


Figure 3. pH variation during heterogeneous photo-catalysis as a function of ZnO concentrations.

For the 0.5 g/L ZnO concentration; the pH decreases from 7.22 to 4.1 after 2h of treatment and then increases to 6.79 at t=5h.

For the two concentrations of (1 and 1.5 g/L) ZnO; the pH varies very little during treatment (it is between 6.61 and 7.89).

The pH influences the charge on the ZnO particles, the size of the aggregates and the positions of the conductance and valence bands. Thus, the ionization state of ZnO varies with pH.

At pH values more acidic than PZC, the ZnO particle will be positively charged and attraction will be enhanced for anionic molecules [13].

Electrical Conductivity (EC): The variation of EC during heterogeneous photo catalytic treatment as a function of the three ZnO concentrations is shown in Figure 4.

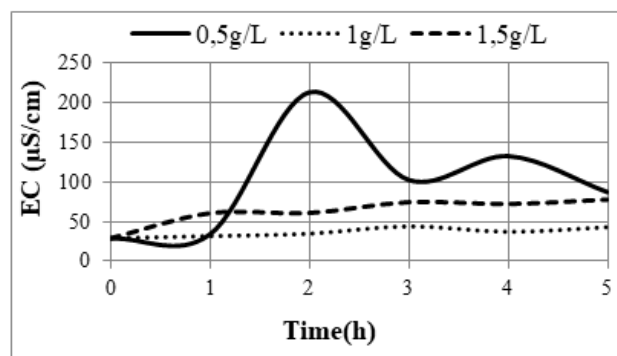


Figure 4. EC variation during heterogeneous photo-catalysis as a function of ZnO concentrations

For the 0.5 g/L ZnO concentration; the EC increases from 28.9 to 213 $\mu\text{S}/\text{cm}$ after 2h of treatment, then decreases to 87.1 $\mu\text{S}/\text{cm}$ at t=5h.

For both concentrations of (1 and 1.5 g/L) ZnO; EC increases from 28.9 to (42.9 and 77.8 $\mu\text{S}/\text{cm}$) respectively at t=5h.

The EC of the aqueous solution is mainly related to the presence of ions in the medium.

The higher the conductivity, the greater the degradation of diclofenac.

Turbidity (Tu): The variation of Tu during the heterogeneous photo-catalytic treatment as a function of the three ZnO concentrations is shown in Figure 5.

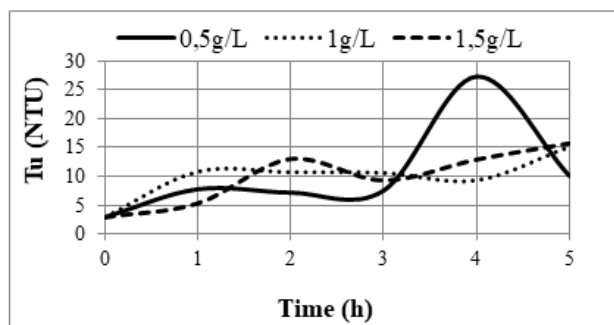


Figure 5. Variation of Tu during heterogeneous photo-catalysis as a function of ZnO concentrations.

For a ZnO concentration of 0.5 g/L; turbidity increases from 2.9 to 27.3 NTU at $t=4$ h and then decreases to 10.1 NTU at $t=5$ h.

For both concentrations of (1 and 1.5 g/L) ZnO; turbidity increases from 2.9 to (15.1 and 15.7 NTU) respectively at $t=5$ h.

Turbidity is an important parameter and is likely to affect the photocatalytic efficiency. Indeed, high turbidity can affect optical properties and hinder light penetration [14].

Some authors have shown that a turbidity lower than 5 NTU would not affect light penetration.

Above this value, turbidity would interfere with the optimal use of light [15,16]. This explains the decrease in the efficiency of photo catalytic treatment when turbidity increases.

Surface tension (Ts): The variation of Ts during heterogeneous photo catalytic treatment as a function of the three ZnO concentrations is shown in Figure 6.

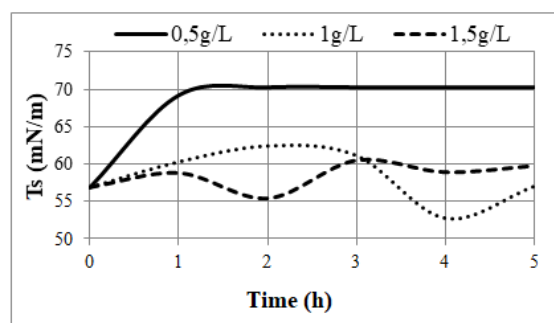


Figure 6. Variation of Ts during heterogeneous photo-catalysis as a function of ZnO concentrations.

For a ZnO concentration of 0.5 g/L; the Ts increases from 56.9 to 70.26 mN/m after 2 hours of treatment. Beyond 2 hours the Ts is constant until the end of the treatment.

For ZnO concentrations (1 and 1.5 g/L); Ts increases from 56.9 to (57 and 59.76 mN/m) respectively during treatment.

The variations in Ts are explained by the degradation of diclofenac, which leads to the appearance of other molecules, leading to physico-chemical modifications of the solution and the catalyst.

This reflects different types of interactions between the solid

(ZnO) and the liquid:

1. Interactions due to London forces, also called dispersive forces. They always take place regardless of the molecules present.
2. Interactions due to all other types of forces (polar, acid/base, hydrogen bonds).

Chemical Oxygen Demand (COD): The variation of COD during heterogeneous photo catalytic treatment as a function of the three ZnO concentrations is shown in Figure 7.

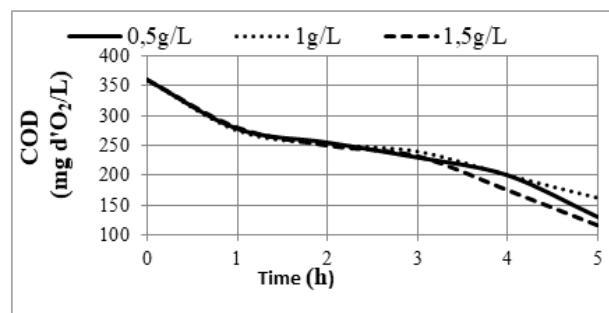


Figure 7. Variation of COD during heterogeneous photo-catalysis as a function of ZnO concentrations.

For the three concentrations (0.5; 1 and 1.5 g/L) of ZnO; the COD decreases from 360 to (130, 162 and 116 mg O₂/L) respectively.

The chemical oxygen demand represents the amount of oxygen consumed by oxidizable materials in the water. The decrease in COD in the presence of the ZnO catalyst is explained by the absorption of light by the catalyst and the production of hydroxyl radicals responsible for the degradation of organic matter.

Nitrites: The variation of nitrites during heterogeneous photo catalytic treatment as a function of the three ZnO concentrations is shown in Figure 8.

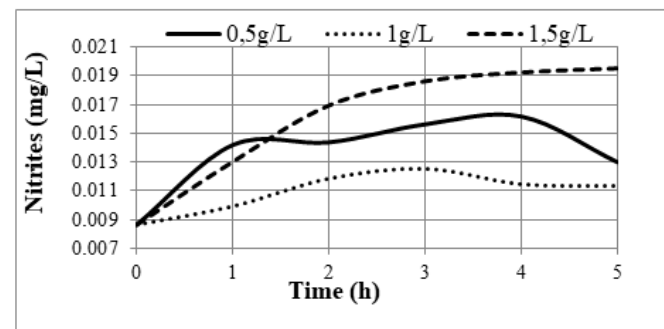


Figure 8. Variation of nitrites during heterogeneous photo-catalysis as a function of ZnO concentrations.

For the ZnO concentration of 0.5 g/L; the nitrite concentration increases from 0.0086 up to 0.0162 mg/L after 4 h of treatment and then decreases to 0.0130 mg/L at $t=5$ h.

For the concentration of 1 g/L of ZnO; the nitrite concentration increases from 0.0086 to 0.0125 mg/L after 3 h of treatment and then decreases to 0.0113 mg/L at $t=5$ h.

For 1.5 g/L ZnO concentration; nitrite concentration increases during treatment from 0.0086 up to 0.0195 mg/L.

Nitrites can affect the photo catalytic process in several ways:

1. Radical and hole scavengers which influence the quantum efficiency and thus the oxidation efficiency of the pollutant,
2. Compete with the drug during adsorption to ZnO.
3. Capture photons. - Corrosion or alteration of the photocatalyst.
4. React directly with the photo catalyst
5. However, it is interesting to recall that the relative effects of these ions on the photo catalytic process can be variable depending on the pH which influences the zwitterionic nature of ZnO [17-20].

Concentration of diclofenac: The variation in concentration during heterogeneous photo catalytic treatment as a function of the three ZnO concentrations is shown in Figure 9.

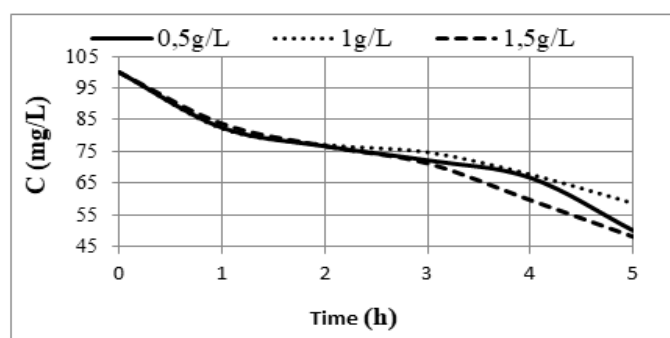


Figure 9. Variation of diclofenac concentration during heterogeneous photo-catalysis as a function of ZnO concentrations.

For the three studied ZnO concentrations (0.5;1 and 1.5 g/L), the diclofenac concentration decreases to (50.06;58.65 and 48.11 mg/L) respectively.

The performance of the heterogeneous photo-catalytic degradation of diclofenac as a function of the three ZnO concentrations is shown in Figure 10.

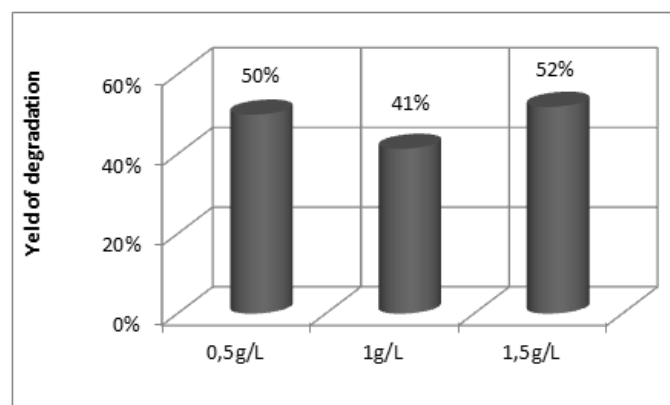


Figure 10. Performance of heterogeneous photo-catalytic degradation of diclofenac concentration.

The concentration of 1.5 g/L of ZnO gives a high percentage removal in diclofenac concentration which is 52%.

The presence of more ZnO can lead to the formation of zinc oxide aggregates which finally do not develop a larger ZnO-diclofenac contact surface than in the case of the 1 g/L concentration, thus decreasing the percentage of degradation.

Increasing the ZnO concentration to 1.5 g/L also leads to the formation of zinc oxide aggregates, but the catalytic surface

area increases, leading to an increase in the percentage of degradation.

The decrease in efficiency of one ZnO concentration compared to another can be explained by many characteristics.

However, characteristics such as specific surface area, charge recombination, interfacial charge transfer dynamics, particle size, crystallinity, pH etc. can have an influence.

On the other hand, the activity of a photocatalyst is also influenced by the type of degradation intermediates generated. A study carried out by has shown that the photo catalytic activity varies according to the pollutant tested [14]. Indeed, by applying a high concentration of ZnO, more photons can be absorbed and therefore more radicals can be formed. In addition, more diclofenac can be adsorbed on the surface of the photo-catalyst. This promotes the degradation of diclofenac.

Influence of diclofenac concentration

The study of heterogeneous photo catalytic degradation was carried out with three concentrations of diclofenac (50;75 and 100 mg/L). The concentration of the ZnO catalyst is 1.5 g/L. The volume flow rate is 20.5 mL/s.

Hydrogen potential (pH): The pH variation during heterogeneous photo catalytic treatment as a function of the three concentrations of diclofenac is shown in Figure 11.

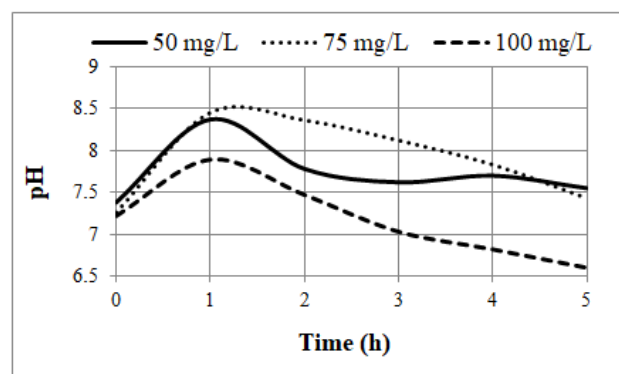


Figure 11. pH variation during heterogeneous photo-catalysis as a function of diclofenac concentrations.

The pH increases from (7.38;7.26 and 7.22) to (8.37;8.45 and 7.89) respectively for the three concentrations studied and after 1 hour of treatment and then decreases until the end of treatment. These results can be explained by the competition reactions for the active sites on the surface of ZnO which involves the displacement of OH⁻ ions, thus decreasing the trapping of holes by these hydroxyl ions and reducing the charge separation.

Moreover, the occupation of these active sites can lead to the exclusion of organic compounds from the active sites on the surface of the photo-catalyst [15].

Electrical Conductivity (EC): The EC variation during heterogeneous photo catalytic treatment as a function of the three concentrations of diclofenac is shown in Figure 12.

For both concentrations (50 and 100 mg/L) of diclofenac;conductivity increases from (22.6 and 28.9 μS/cm) to (99 and 77.8 μS/cm) respectively during treatment.

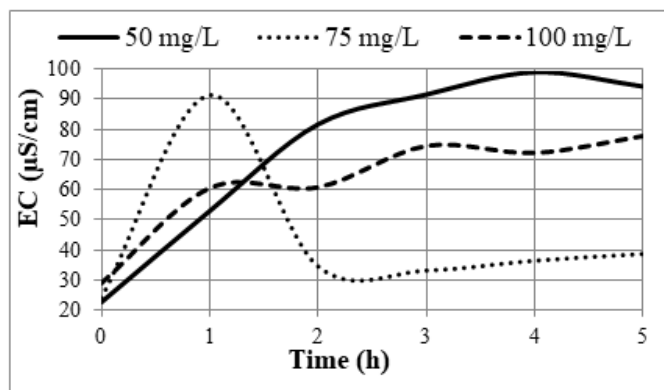


Figure 12. Variation of EC during heterogeneous photo-catalysis as a function of concentrations of diclofenac .

For the concentration of 75 mg/L diclofenac; conductivity increases from 24 to 91.4 $\mu\text{S}/\text{cm}$ after 1 h of treatment and then decreases to 34.5 $\mu\text{S}/\text{cm}$ at $t=2$ h and remains constant.

The EC of the aqueous solution is mainly related to the presence of ions in the medium. The results show that the EC value obviously takes a significant part in the degradation of the organic compound. Indeed, the higher the conductivity, the greater the degradation of diclofenac.

Turbidity (Tu): The variation of Tu during the heterogeneous photo catalytic treatment as a function of the three concentrations of diclofenac is shown in Figure 13.

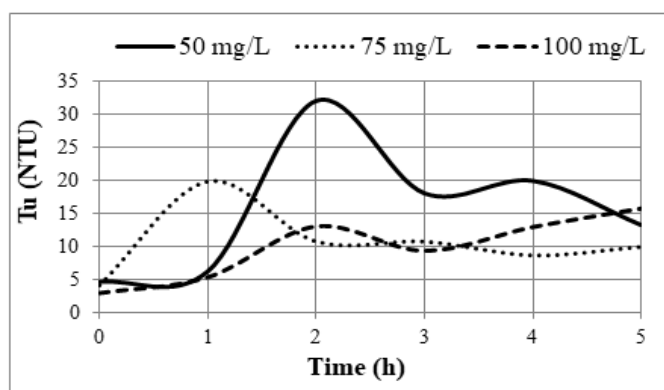


Figure 13. Variation of Tu during heterogeneous photo-catalysis as a function of concentrations of diclofenac.

For the concentration of 50 mg/L diclofenac; turbidity increases from 4.6 up to 32 NTU after 2 h above $t=2$ h the Tu is unstable (values are between 13.2 and 18 NTU).

For the concentration of 75 mg/L of diclofenac; turbidity increases from 4.1 to 19.8 NTU after 1 hour of treatment and then it varies little (between 8.6 and 10.7 NTU).

For 100 mg/L diclofenac concentration; turbidity increases from 2.9 to 15.7 NTU at $t=5$ h.

The variation in turbidity during treatment may be due to light-deflecting degradation products. Thus, photo-dismutation of the catalyst may be possible.

Surface tension (Ts): The variation of Ts during heterogeneous photo catalytic treatment as a function of the three concentrations of diclofenac is shown in Figure 14.

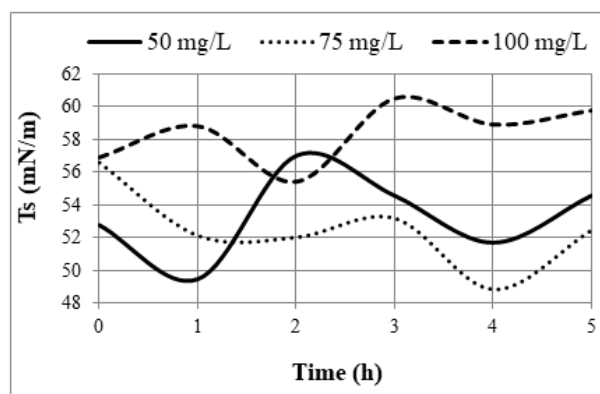


Figure 14. Variation of Ts during heterogeneous photo-catalysis as a function of concentrations of diclofenac.

For the concentrations studied (50;75 and 100 mg/L) of diclofenac; fluctuations are observed during treatment.

The observed fluctuations in surface tension are explained by the fact that during treatment, the diclofenac molecule is degraded leading to degradation by-products that compete with the parent molecule. This calls for a concentration gradient in the liquid which influences the Solid/Liquid contact surface.

One can distinguish the angle at the advance θ_a which is at the front of the drop or liquid front and the angle at the retreat θ_r which is at the back and generally, $\theta_a > \theta_r$ [16,17].

The difference between these different angles comes in particular from the roughness and heterogeneity (chemical, morphological) of the surface, or the degradation by-products.

Chemical Oxygen Demand (COD): The variation in COD during heterogeneous photo catalytic treatment as a function of the three concentrations of diclofenac is shown in Figure 15.

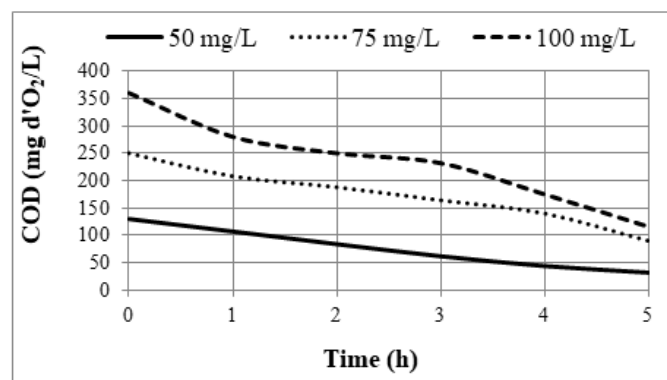


Figure 15. Variation of COD during heterogeneous photo-catalysis as a function of concentrations of diclofenac.

For all three concentrations (50;75 and 100 mg/L) of diclofenac; COD decreases from (130;250 and 360 mg O₂/L) to (32;90 and 116 mg O₂/L) respectively.

Chemical Oxygen Demand (COD) represents the amount of oxygen consumed by oxidizable materials in the water.

The decrease in COD in the presence of the ZnO catalyst is explained by the absorption of light by the catalyst and the production of the hydroxyl radicals responsible for degradation.

Degradation products can also induce different interactions between ZnO and diclofenac, especially in the case of negatively

charged compounds at basic pH such as carboxylic acids, which appear in the mechanisms of photo-catalytic degradation.

Different diclofenac/ZnO surface interactions could lead to a modified degradation mechanism and thus to different kinetics.

Nitrites: The variation of nitrites during heterogeneous photo catalytic treatment as a function of the three concentrations of diclofenac is shown in Figure 16.

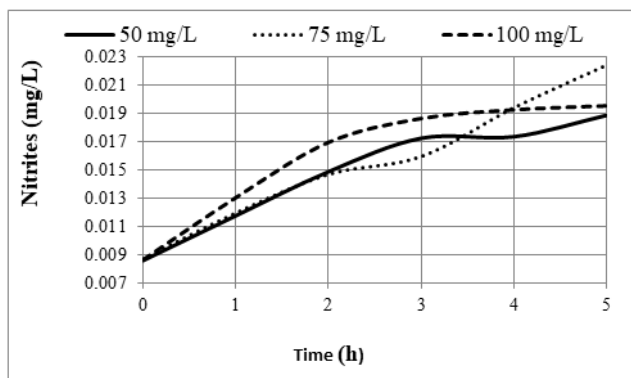


Figure 16. Variation of nitrites during heterogeneous photo-catalysis as a function of concentrations of diclofenac.

For all three concentrations (50;75 and 100 mg/L) of diclofenac;the nitrite concentration increases during treatment from (0.0086;0.0087 and 0.0086 mg/L) to (0.0188;0.0224 and 0.0195 mg/L) respectively.

The increase in nitrite concentration indicates that degradation begins with the breakdown of the nitrogen bond and the cyclic nucleus of diclofenac.

Concentration of diclofenac: The variation in concentration during heterogeneous photo catalytic treatment is shown in Figure 17.

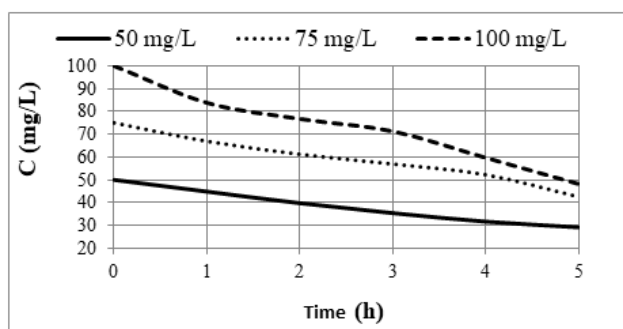


Figure 17. Variation in diclofenac concentration during heterogeneous photo-catalysis.

For all three concentrations (50;75 and 100 mg/L) the concentration of diclofenac decreases during treatment to (29.15;42.47 and 48.11 mg/L) respectively.

The yield of heterogeneous photo-catalytic degradation to diclofenac is shown in Figure 18.

The 100 mg/L concentration of diclofenac gives a high percentage of elimination which is 52%.

The higher the initial concentration of diclofenac, the greater the efficiency of the photo-catalytic degradation of diclofenac.

Influence of the hydrogen peroxide (H₂O₂) concentration

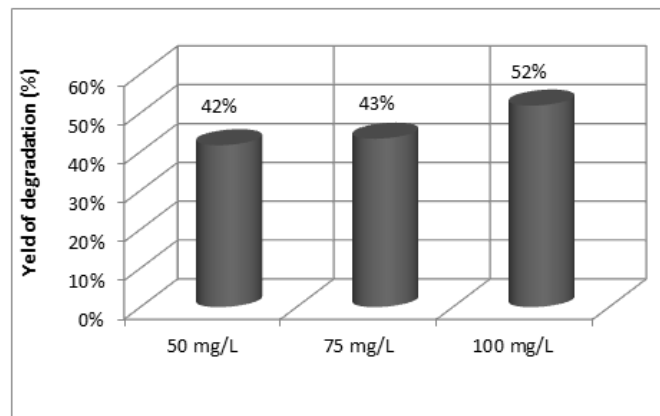


Figure 18. Heterogeneous photo-catalytic degradation efficiency of the concentration of diclofenac.

The study of heterogeneous photo catalytic degradation was carried out using hydrogen peroxide H₂O₂ whose ratio $r=[H_2O_2]/[ZnO]$ is (1;5 and 10%).

The concentration of diclofenac is 100 mg/L. The catalyst concentration is 1.5 g/L. The volume flow rate is 20.5 mL/s.

The results showed that degradation is complete after 1 h of treatment for all three r-ratios. These results are confirmed by the absence of the diclofenac absorption peak (274 nm). The absorption spectrum of diclofenac is shown in Figure 19.

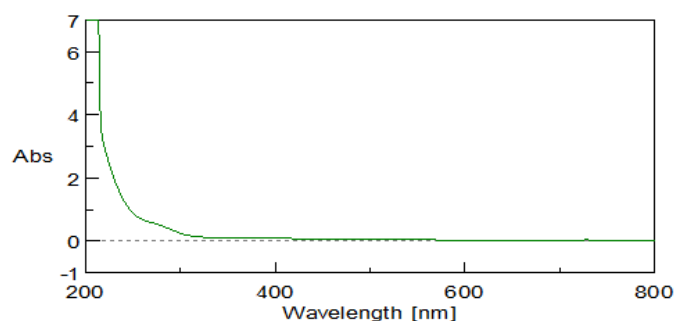


Figure 19. Absorption spectrum of diclofenac in hydrogen peroxide concentration.

These results are explained by the effect of hydrogen peroxide on the optical properties of ZnO. A study has shown that in the presence of H₂O₂, ZnO has an emission band with a maximum of 3.24 eV and a wide composite band composed of three sub-bands at 2.2 eV;2.06 eV and 1.8 eV. This promotes the formation of a large amount of OH.

Thus, the concentration of hydrogen peroxide causes an increase in the amount of OH. Radicals in the medium and therefore the degradation yield increases.

It should also be noted that the quantity of the organic pollutant drops abruptly after one hour of treatment. This high efficiency is mainly due to the rapid formation, in large quantities, of OH radicals which facilitates the attack between a large quantity of the oxidizing agent and diclofenac.

Hydrogen potential (pH): The variation of pH during heterogeneous photo catalytic treatment as a function of the three ratios r is shown in Figure 20.

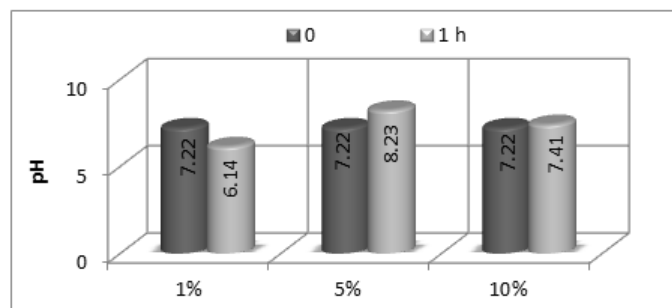


Figure 20. Variation of pH during heterogeneous photo-catalysis as a function of report r.

For the 1% ratio; the pH decreases from 7.22 to 6.14 after 1 hour of treatment.

For both ratios (5 and 10%); the pH increases from 7.22 to (8.23 and 7.41) respectively after 1 hour of treatment.

For pH values more acidic than PZC, the ZnO particle will be positively charged and attraction will be favoured for anionic molecules.

Electrical Conductivity (EC): The variation of EC during heterogeneous photo catalytic processing as a function of the three ratios r is shown in Figure 21.

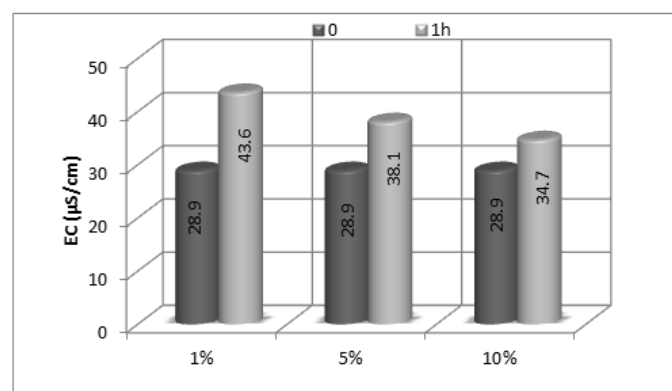


Figure 21. Variation of EC during heterogeneous photo-catalysis as a function of report r.

For all three ratios (1;5 and 10%); EC increases from 28.9 to (43.6;38.1 and 34.7 $\mu\text{S}/\text{cm}$) respectively after 1 hour of treatment.

The EC of the aqueous solution is mainly related to the presence of ions in the medium. The results show that the EC value obviously takes a significant part in the degradation of the organic compound. The increase in electrical conductivity is due to the presence of the degradation compounds of diclofenac. Indeed, the higher the conductivity, the greater the degradation of diclofenac.

Turbidity (Tu): The variation of Tu during photo-catalytic treatment as a function of the three ratios r is shown in Figure 22.

For all three ratios (1%;5% and 10%); Tu increases from 2.9 to (9.6;7.4 and 8.3 NTU) respectively after 1 hour of treatment.

Turbidity is an important parameter and is likely to affect the photocatalytic efficiency. Indeed, high turbidity can affect the optical properties and hinder light penetration. This will decrease the absorption of photons by the photocatalyst.

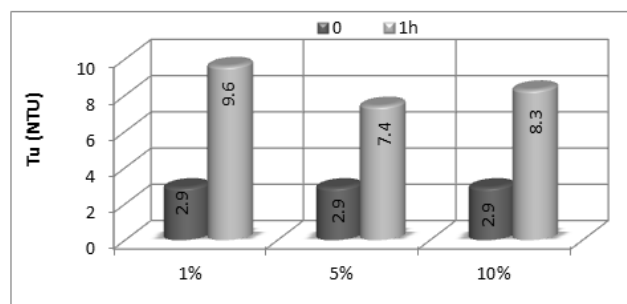


Figure 22. Variation of Tu during heterogeneous photo-catalysis as a function of report r.

Surface tension (Ts): The variation of Ts during heterogeneous photo-catalytic treatment as a function of the three ratios r is shown in Figure 23.

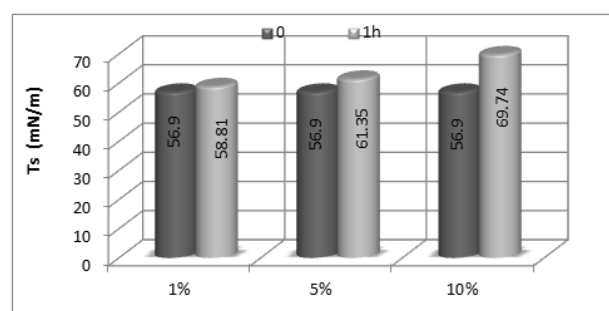


Figure 23. Variation of Ts during heterogeneous photo-catalysis as a function of report r.

For all three ratios (1;5 and 10%); Ts increases from 56.9 to (58.81;61.35 and 69.74 mN/m) respectively after 1 hour of treatment.

As the surface tension increases, the catalyst is well wetted, which may increase the transfer of liquid/solid material. This increases the photocatalytic efficiency.

Nitrites: The variation of nitrites during heterogeneous photocatalytic treatment as a function of the three ratios r is shown in Figure 24.

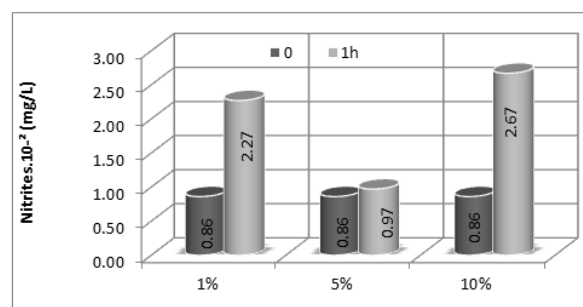


Figure 24. Variation of nitrites during heterogeneous photo catalysis as a function of report r.

For all three ratios (1;5 and 10%); nitrite increases from 0.0086 to (0.0227;0.0097 and 0.0267 mg/L) respectively after 1 hour of treatment.

The increase in nitrite concentration indicates that degradation begins with the breakdown of the nitrogen bond and the cyclic nucleus of diclofenac.

Influence of volume flow rate

The study of heterogeneous photo catalytic degradation was

performed at three volume flow rates (20.5;22 and 25 mL/s). The concentration of diclofenac is 100 mg/L. The catalyst concentration is 1.5 g/L.

The results showed that the degradation is complete for the volume flow rate 25 mL/s after 1 h of treatment.

This result is confirmed by the absence of the diclofenac absorption peak (274 nm).

The absorption spectrum of diclofenac for the 25 mL/s volume flow rate is shown in Figure 25.

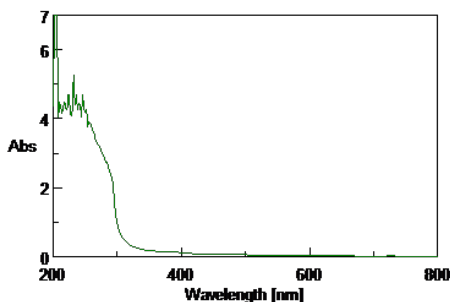


Figure 25. Absorption spectrum of diclofenac in volume flow rate. Hydrogen potential (pH): The variation of pH during heterogeneous photo catalytic treatment as a function of the three volume flows is shown in Figure 26.

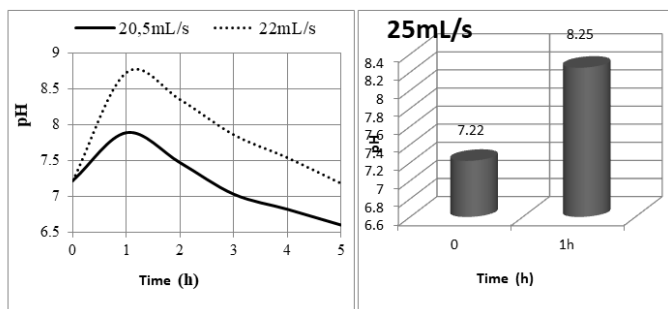


Figure 26. Variation of pH during heterogeneous photo-catalysis as a function of volume flow.

For both volume flows (20.5 and 22 mL/s);the pH increases from 7.22 to (7.89 and 8.73) respectively at t=1 h and then varies little.

For the volume flow rate of 25 mL/s, the pH increases from 7.22 to 8.25 after 1 h of treatment.

The increase in pH is due to competition reactions for the active sites on the surface, which involves the displacement of OH-ions, thus reducing the trapping of holes by these hydroxyl ions and reducing charge separation.

Moreover, the occupation of these active sites can lead to the exclusion of organic compounds from the active sites on the surface of the photo-catalyst [18].

Electrical conductivity (EC): The variation of EC during heterogeneous photocatalytic treatment as a function of the three volume flows is shown in Figure 27.

For the volume flow rate of 20.5 mL/s;the EC increases from 28.9 to 74.5 $\mu\text{S}/\text{cm}$ after 3 hours of treatment;beyond 1 hour the EC varies little.

For a volume flow rate of 22 mL/s;EC increases from 28.9 to

51.6 $\mu\text{S}/\text{cm}$ after 1 h of treatment, then decreases to 38.2 at t=2 h, after 2 h it varies little.

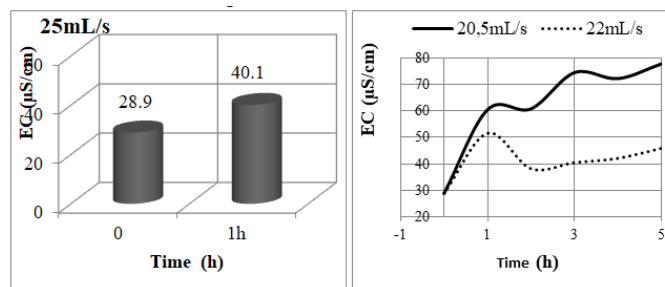


Figure 27. EC variation during heterogeneous photo-catalysis as a function of volume flow.

For a volume flow rate of 25 mL/s;EC increases from 28.9 to 40.1 $\mu\text{S}/\text{cm}$ after 1 hour of treatment.

The electrical conductivity of the aqueous solution is mainly related to the presence of ions in the medium. The results show that the EC value obviously takes a significant part in the degradation of the organic compound. Indeed, the higher the conductivity, the greater the degradation of diclofenac.

Turbidity (Tu): The variation of Tu during the heterogeneous photo catalytic treatment as a function of the three volume flows is shown in Figure 28.

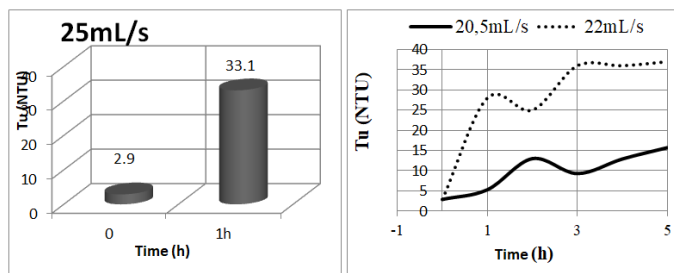


Figure 28. Variation of Tu during heterogeneous photo-catalysis as a function of volume flow rate.

For volume flow rate of 20.5 mL/s;Tu increases from 2.9 to 15.7 NTU at t=5 h.

For volume flow rate of 22 mL/s;Tu increases from 2.9 to 37 NTU at t=5 h.

For volume flow rate of 25 mL/s;Tu increases by 2.9 NTU to 33.1 NTU after 1 h of treatment.

High turbidity can affect the optical properties and hinder light penetration. This will decrease the absorption of photons by the photocatalyst.

Some authors have shown that a turbidity lower than 5 NTU would not affect light penetration.

Above this value, turbidity would interfere with optimal use of light [18-20].

This explains the decrease in the efficiency of photo catalytic treatment when turbidity increases.

Surface tension (Ts): The variation of Ts during heterogeneous photo catalytic treatment as a function of the three volume flows is shown in Figure 29.

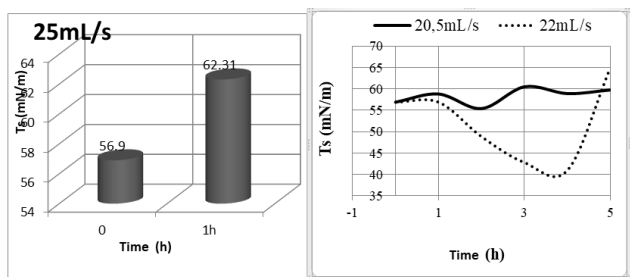


Figure 29. Variation of T_s during heterogeneous photo-catalysis as a function of volume flow rate.

For a volume flow rate of 20.5 mL/s; T_s varies little (between 56.9 and 59.76 mN/m).

For a volume flow rate of 22 mL/s; T_s decreases from 56.9 mN/m to 40.97 mN/m at $t=4$ h and then increases to 64.96 mN/m at $t=5$ h.

For the volume flow rate of 25 mL/s; T_s increases from 56.9 to 62.31 mN/m after 1h of treatment.

The surface tension of the solutions is lower than that of pure water (72 mN/m). The interaction between the phases in a reactor depends on the velocity and physico-chemical properties of the fluid phases, as well as the geometric and physico-chemical properties of the solid particles. It is important to note that the contact surface between phases, which itself depends on the surface tension, varies according to the flow regime.

Chemical Oxygen Demand (COD): The variation of COD during heterogeneous photo catalytic treatment as a function of the three volume flows is shown in Figure 30.

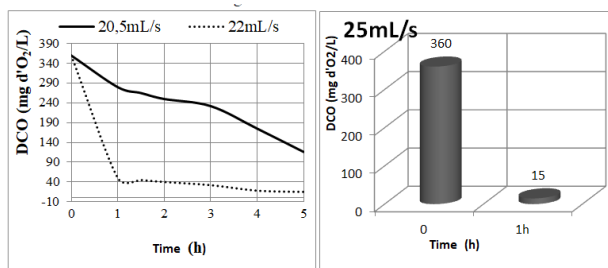


Figure 30. Variation of COD during heterogeneous photo-catalysis as a function of volume flow rate.

For both volume flow rates (20.5;22 mL/s); COD decreases from 360 to (116 and 15 mg O₂/L) respectively during treatment.

For the 25 mL/s volume flow rate, COD decreases from 360 to 15 mg O₂/L after 1 hour of treatment.

Chemical Oxygen Demand (COD) represents the amount of oxygen consumed by oxidizable materials in the water. The decrease in COD in the presence of the ZnO catalyst is explained by the absorption of light by the catalyst and the production of hydroxyl radicals responsible for degradation. It can be seen that the rate of mineralization is rapid at the beginning of the treatment and then it decreases. Indeed, at the beginning of the treatment, the mother molecule and its degradation products are more easily oxidized by hydroxyl radicals leading to the formation of aliphatic compounds like carboxylic acids that resist well to mineralization by these same radicals [21-24].

Nitrites: The variation of nitrites during heterogeneous photo catalytic treatment as a function of the three volume flows is shown in Figure 31.

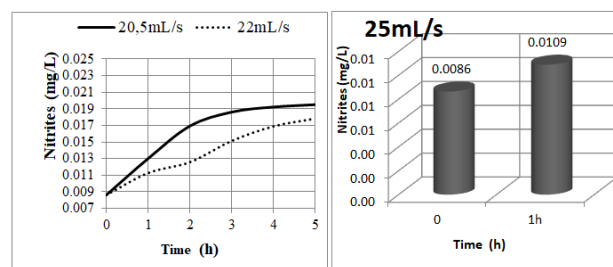


Figure 31. Variation of nitrites during heterogeneous photolysis as a function of volume flow rate.

For both volume flow rates (20.5;22 mL/s); the nitrites increase from 0.0086 to (0.0195;0.0178 mg/L) respectively after 5 h of treatment.

For the volume flow rate 25 mL/s, nitrite increases from 0.0086 to 0.0109 mg/L at $t=1$ h.

The increase in nitrite concentration indicates that degradation begins with the breakdown of the nitrogen bond and the cyclic nucleus of diclofenac.

Nitrites can affect the photocatalytic process in several ways:

1. Radical and hole traps which influence the quantum efficiency and thus the oxidation efficiency of the pollutant,
2. Compete with the drug during adsorption to ZnO,
3. Capturing photons - Corrosion or alteration of the photocatalyst
4. React directly with the photo catalyst [25].

However, it is interesting to recall that the relative effects of these ions on the photo catalytic process can be variable as a function of the pH, which influences the zwitterionic nature of ZnO.

Concentration of diclofenac: The variation in concentration during the heterogeneous photo catalytic treatment as a function of the three volume flows is shown in Figure 32.

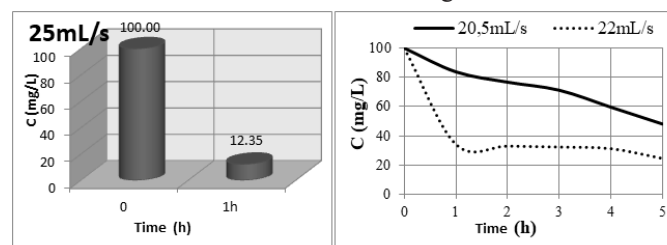


Figure 32. Variation in volume flow rate during heterogeneous photo-catalysis.

For both volume flow rates (20.5;22 mL/s) the diclofenac concentration decreases to (48.11;24.56 mg/L) respectively during treatment.

For the volume flow rate 25 mL/s, the diclofenac concentration decreases from 100 to 12.35 mg/L after 1 hour of treatment.

The photo-catalytic degradation performance of diclofenac as a function of the three flow rates is shown in Figure 33.

Concentration as a function of volume flow rate. The volume flow rate of 25 mL/s gives the highest removal percentage (100%). The increase in degradation yield with increasing flow rate is explained by:

The thickness of the absorbent layer of the treated fluid varies along the reactor. Indeed, at the reactor inlet, the conversion is null $x=0$, and the absorbent layer consists only of ZnO. In this case, the majority of the photons are absorbed by the ZnO.

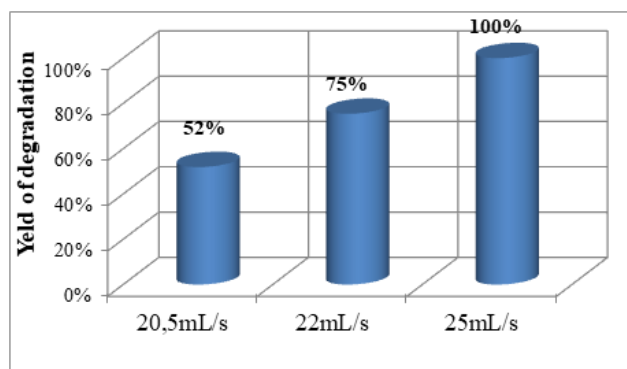


Figure 33. Heterogeneous photo-catalytic degradation efficiency of diclofenac concentration as a function of volume flow rate.

Then along the reactor, the conversion progresses and the layer becomes depleted in diclofenac and, conversely, it becomes enriched in degradation compounds. The photons are then absorbed by both ZnO and degradation compounds.

The distribution of the absorbed photons between ZnO and the degradation compounds will depend on the hydrodynamic conditions of the reactor.

The hydrodynamic regime is defined by the Reynolds number.

Table 1 regroups the Reynolds number for the three volume flows studied.

Table 1. The Reynolds number for the different volume flow.

Value	Volume		
ρ (Kg/m ³)	10 ³		
μ (Pa.s)	10 ⁻³		
V (mL/s)	20.5	22	25
Re	2611	2802	3184

For both volume flows (20.5 and 22 mL/s) the regime is transient.

For the volume flow rate of 25 mL/s the regime is turbulent.

For a given Reynolds number, the efficiency of photo-catalysis is influenced by:

1. The amount of material passing through the reactor.
2. The residence time τ_s of the molecules in the reactor.
3. The light power.

The flux density of incident photons will play on the local speed of the photochemical reaction, which can impact the local and average characteristic times in the zone of illuminated fluid.

Conclusions

This work focused on the study of the elimination of a

non-steroidal anti-inflammatory drug (diclofenac) using heterogeneous photo catalysis as a treatment.

The study investigated the effect of parameters (catalyst concentration, initial diclofenac concentration, ratio $r=[H_2O_2]/[ZnO]$ and volume flow) on the photocatalytic degradation of diclofenac.

The analyses performed are pH, electrical conductivity, turbidity, surface tension, chemical oxygen demand, nitrite and diclofenac concentration. The heterogeneous photo catalytic degradation is influenced by:

1. The concentration of the ZnO catalyst.
2. The concentration of 1.5 g/L gives a better degradation in diclofenac with a 52% removal percentage.
3. The initial concentration of diclofenac.
4. The concentration of 100 mg/L of diclofenac gives a better degradation with a percentage of elimination of 52%.
5. The ratio $r = ([H_2O_2])/([ZnO])$.
6. The three ratios (1;5 and 10%) give a total degradation after one hour of treatment.
7. The volume flow rate.
8. The volume flow rate of 25 mL/s gives a total degradation after one hour of treatment.

Optimal conditions for heterogeneous photo-catalysis are:

$[ZnO]=1.5$ g/L, $[diclofenac]=100$ mg/L, volume flow rate= 25 mL/s.

For a volume flow rate of 20 mL/s, optimal conditions are achieved by adding H₂O₂.

Author Contributions

Author Fateh Naitali was a major contributor in working and writing the manuscript. Author Hafida Ghoualem was a major contributor in working and writing the manuscript.

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Ethics Approval and Consent to Participate

Not applicable

Consent for Publication

Not applicable

Availability of Data and Materials

The results and materials presented in this article are realized in the laboratory of Laboratory of Electrochemistry-Corrosion, Metallurgy and Inorganic Chemistry. Faculty of Chemistry. University of Sciences and Technology. Houari Boumediene. Box N°32 El-Alia. Bab-Ezzouar. Algiers. Algeria.

The data tables are presented in different forms in the manuscript and are available from the authors.

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Competing Interests

The authors Fateh Naitali and Hafida Ghoualem declare that they have no competing interests

Conflicts of Interest

The authors Fateh Naitali and Hafida Ghoualem declare that they have no competing financial interests

There are no competing interests related to this work

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