Comparison between TiO$_2$ and ZnO photocatalytic efficiency for the degradation of tartrazine contaminant in water

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Abstract: Wastewater containing dyes pollutants has gained more attention due to its mass discharge, high toxicity and low biodegradation. The degradation of synthetic dyes is difficult because of their complex aromatic structure. Therefore, efficient and cost-effective treatment processes of this pollutants family need to be developed. The use of a heterogeneous photocatalysis is an efficient method for water purification which includes reduction and oxidation reactions in the presence of oxygen molecules and hydroxyl anions. In photocatalysis, semiconductors are used generally in suspension. However, this method could be a more expensive when it is scaled-up because the photocatalyst particles recovery after treatment is a difficult task and leads to an amplification in process costs. An alternative method is to use the catalytic supported in different media without hampering its activity. The present study aims to develop a new photoreactor for the degradation of dyes pollutants in water. A fixed bed photocatalytic reactor incorporating ZnO or TiO$_2$ catalysts and UV from sun light radiation was used for the study of its performance in photocatalytic destruction of tartrazine contaminant. Results from this work provided essential information needed towards the construction and operation of the fixed bed photocatalytic reactor. Specifically, we have evaluated the improvement of photocatalytic activity of fixed bed catalysts for the total Tartrazine removal. It was found that the photocatalytic oxidation reaction follows the pseudo-first order model. The photodegradation ratio reach 98% after 200 min of solar radiation. Although the UV energy gives improved efficiency in degradation of dyes, solar irradiation could appear as a substitute cost effective light source because of its abundance in Algeria and the fixed bed coating of photocatalyst may resolve the problems of leaching and separation.

Key-Words: Advanced oxidation technology; heterogeneous photocatalysis; emerging contaminants, tartrazine, Titanium dioxide, Zinc oxide, fixed bed photoreactor.

1 Introduction

Dyes are extensively used in the textile industry in Algeria. They are abundant source of colored organic pollutants emanating from the textile dyeing method. Due to the high concentration of organics in the wastewater effluents and the higher stability of modern synthetic dyes, the conventional biological treatment processes are ineffective for the complete color removal from wastewater [1]. Some promising applications of homogeneous photocatalysis have been used to resolve this problem for water treatment as a nanotechnology processes [2,3].

Photocatalytic oxidation method is an effective way to deal with organic pollutants in wastewater which could be difficult to be degraded by conventional biological treatment processes. Normally the TiO$_2$ powder in nanometre size range was directly used as photocatalyst for dye photodegradation. However the titanium dioxide powder was arduous to be recovered from the solution after the treatment [4,5].

The aim of this work is to study the treatment of polluted water by persistent dyes and optimize the operating conditions of the photocatalytic reaction such as, the effect of recirculation flow-rate, solar radiation, adsorption, concentration of the pollutant in the solution and catalyst concentration. The main objective of this research is the study of the degradation of tartrazine using fixed bed reactor under solar radiation.

2. Materials and methods

2.1. Experimental system

The used photoreactor, presented in figure 1, has a rectangular inclined parallelepiped shape made in
Plexiglas having a length of 500 mm, a width of 400 mm and a height equal to 100 mm. The circulation of the solution from the reservoir to the photoreactor is assured via a peristaltic pump. The volume of water to be treated is 2 liters and the flow rate of the recirculation pump is adjustable.

The solar flux is measured at an interval of 5 minutes between 9h00 and 15h30 using a pyranometer coupled to a software (KIPP & ZONZN, CMP11) mounted on an inclination of 36° in our institution, UDES.

2.2. Pollutants

In our study, tartrazine was used as an organic pollutants model to study the parameters influencing the degradation kinetics of the heterogeneous photocatalysis in the presence of titanium dioxide and zinc oxide as catalysts under sunlight radiation. Tartrazine molecule (figure 2) is a synthetic azo dye type, widely used in industry in the manufacture of many cosmetics and pharmaceuticals in Algeria. Adsorption spectrum of this compound is situated in 427nm as shown on figure 3.

2.3. Chemical reagents

The distilled water used to prepare the aqueous solutions is obtained from a distillation system in the laboratory. The used photo-catalysts are the titanium dioxide TiO₂ and zinc oxide ZnO, titanium dioxide was obtained from Degussa. The TiO₂ powder consists of a mixture of 80% anatase and 20% rutile. It is practically insoluble in water; its specific surface area is 50m²·g⁻¹. The zinc oxide ZnO is obtained from Tianjing chemical reagent company with surface area is 9m²·g⁻¹.

2.4. Experimental procedure

This work is to provide a parametric study on the solar photocatalytic degradation of tartrazine in the presence of titanium dioxide TiO₂ or zinc oxide ZnO fixed on a glass supports. During this study and for each test, the tank is filled with 2 liters of a solution containing the pollutant. Glass plates were used to fix the TiO₂ or ZnO particles. The mixture solution is recirculated in order to homogenize the solution. Samples of 5 ml are withdrawn every 15 minutes during the time of the réaction. The samples were analyzed by UV/visible spectrophotometry to determine the evolution of the pollutant concentration.

3. Results and Discussion

The goal of this study is to optimize the operating conditions giving the best rate of degradation, the effect of many factors are tested including:

- The amount of the catalyst used;
- The concentration of the pollutant;

3.1. Tartrazine treatment by adsorption, photolysis and photocatalysis

The study of tartrazine solar photodegradation in the presence of titanium dioxide and zinc oxide
was carried out using a solar fixed bed reactor. Among the most used methods for the removal of dyes are photolysis, photocatalysis and adsorption, a comparative study was conducted to compare the efficiency of these three methods for the treatment of water polluted by tartrazine maintaining following operating conditions:

- Flow-rate of the solution: 26.37 ml/s;
- Amount of the used catalyst: 0.28 mg/cm²;
- Initial concentration of tartrazine: 10mg/L;
- Free pH: 6.7-7.1;
- Reaction volume: 2 L.

The curves presented in figures 4 and 5 represent the variation of tartrazine reduced concentration versus time for the three used processes, the adsorption process have very low efficiency, indeed, 1% and 2% yields are obtained by using TiO₂ and ZnO as adsorbents respectively. Regarding photolysis process, the degradation yield achieved does not exceed 1%. Photocatalysis has eliminated a significant amount of tartrazine with removal rates exceeding 97% for both of catalysts after 150 minutes sunlight radiation.

From these results, the photocatalytic process seems to be very efficient for the removal of organic compounds. View the important performance of this technique we were interested in the study of the degradation of the tartrazine using solar photocatalysis to optimize the operating conditions promoting this reaction.

### 3.2. Influence of the radiation type

Photocatalysis has been the subject of much research in water treatment, the aim of this study is to determine the type of radiation giving the best rate of degradation, and the protocol is to use the same experiences conditions in solar radiation by substituting an artificial irradiation source using UV light and visible light lamps.

The curves illustrated in figure 6 represent the temporal change in the reduced concentration of tartrazine for different types of radiation.
Table 1: Values of kinetic constants and reaction rate for different types of radiation.

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>( k_{app} ) (min(^{-1}))</th>
<th>( r_0 ) (mg/L.min)</th>
<th>( R^2 )</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar</td>
<td>0.023</td>
<td>0.227</td>
<td>0.99</td>
<td>775.16 W/m(^2)</td>
</tr>
<tr>
<td>UV lamp</td>
<td>0.001</td>
<td>0.005</td>
<td>0.97</td>
<td>24 W</td>
</tr>
</tbody>
</table>

The results presented in table 1 and the curves presented in the figure 6 show that the type of radiation influences the degradation of the tartrazine. Using visible lights, we recorded a negligible yield, around 3%, while the use of 24W ultraviolet light lamps eliminates 19% of tartrazine. However, when using solar radiation, the degradation yield is total. On the other hand, the apparent rate constant obtained by solar photocatalysis is 20 times greater than that obtained using UV lamps.

3.3. Influence of irradiation intensity

The intensity of solar radiation is an important parameter for the photocatalytic treatment accounting for about 5% of UV light in the global radiation. This allows the excitation of the catalyst and the generation of pairs (e\(^-\)/h\(^+\)). Two experiments were conducted under the same conditions previously used, (Q=26.37mL/s, C
\(_{TRZ}\)=10mg/L, m
\(_{TiO2}\)=0.28 mg/cm\(^2\), free pH) during two different days. Figure 7 shows the temporal evolution of the reduced tartrazine concentration during the two days: Sunny and cloudy days for the elimination of 10 mg/L of pollutants.

![Figure 7](image)

The curves in Figure 7 show that sunlight has an important effect on the degradation of dye, we recorded a degradation ratio equal to 97% during the sunny day and 88% during the cloudy day. This phenomena can be explained by the fact that UV radiation passing through the layers of the atmosphere are hindered by the presence of clouds, a decrease in light radiation can be observed, from 709 to 659 W/m\(^2\) for sunny and cloudy days respectively. The apparent constant rate (\( k_{app} \)) and degradation rate X(%) determined after 3 hours of sunlight radiation are summarized in the table 2.

Table 2: kinetic constants and degradation rate after 3 hours of irradiation.

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>( k_{app} ) (min(^{-1}))</th>
<th>( r_0 ) (mg/L.min)</th>
<th>( R^2 )</th>
<th>X (%)</th>
<th>Intensity (W/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunny</td>
<td>0.015</td>
<td>0.147</td>
<td>0.98</td>
<td>97</td>
<td>709.22</td>
</tr>
<tr>
<td>Cloudy</td>
<td>0.008</td>
<td>0.083</td>
<td>0.99</td>
<td>88</td>
<td>659.60</td>
</tr>
</tbody>
</table>

3.4. Effect of Catalyst concentration

To assess the effect of the used amount of catalyst (\( TiO_2 \) or \( ZnO \)) on the kinetics of photodegradation of tartrazine, a number of experiments was conducted with dye initial concentration equal to 10mg/L by varying the mass of used catalyst supported on glass plates between 0.28mg/cm\(^2\) to 0.84mg/cm\(^2\).

The figure 8 shows the temporal evolution of the reduced concentration of tartrazine for an initial concentration equal to 10mg/L, the tests are carried out for different amounts of catalysts supported on glass plates.

![Figure 8](image)
It appears from these results that the degradation rate of tartrazine by using different amounts of TiO$_2$ is very important and may reach the value of 100% in the case of titanium dioxide amount between 0.56 and 0.84mg/cm$^2$, however, it’s observed that the performance of degradation reach around 97% by using a concentration of 0.28mg/cm$^2$ of catalyst. On the other hand, we notice that the initial rate of the tartrazine photodegradation reaction is directly proportional to the catalyst mass. In other words, the degradation rate increases with the increase of the amount of the used catalyst to achieve an optimum value of 0.56mg/cm$^2$ corresponding to the saturation of the photon absorbance of the semiconductor. Above this value, the reaction rate constants stabilize, and several explanations can present this limit depends on the geometry and operating conditions of the used photoreactor like the saturation of the absorption by catalyst. The same result was obtained by Silva et al. in 2006 and Bizani et al. in 2006 for the degradation of DR [6,7] dye.

The influence of the concentration of ZnO on photodegradation tartrazine for the same concentrations of catalyst and for the same conditions was improved. The effect of the concentration of ZnO used on the photocatalytic degradation of tartrazine is shown in Figure 9. we note that the pollutant degradation depends on the used amount of the catalyst. The best results are obtained using an amount of 0.54mg/cm$^2$. The total elimination of tartrazine was recorded after 80 minutes of irradiation.

The kinetic constants of degradation rate ($k_{app}$) and the initial rates are summarized in Table 3. We note from the obtained results that the degradation rate constant increases with the used amount of catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$m_{cat}$(mg/cm$^2$)</th>
<th>$k_{app}$(min$^{-1}$)</th>
<th>$r_0$(mg/L.min)</th>
<th>X($%$)</th>
<th>Intensity (W/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.28</td>
<td>0.023</td>
<td>0.227</td>
<td>99</td>
<td>775.16</td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>0.030</td>
<td>0.292</td>
<td>99</td>
<td>793.01</td>
</tr>
<tr>
<td></td>
<td>0.84</td>
<td>0.029</td>
<td>0.313</td>
<td>99</td>
<td>763.61</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.28</td>
<td>0.040</td>
<td>0.388</td>
<td>98</td>
<td>863.64</td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>0.050</td>
<td>0.491</td>
<td>99</td>
<td>864.19</td>
</tr>
<tr>
<td></td>
<td>0.84</td>
<td>0.049</td>
<td>0.488</td>
<td>99</td>
<td>805.1</td>
</tr>
</tbody>
</table>

The objective of this study is to find the best conditions for the application of solar degradation...
process tartrazine minimizing the cost of this operation. It is interesting to use the smallest possible amount of catalyst that provides high degradation rates. Our choice is the catalyst amount equal to 0.28mg/cm² for further experiments.

3.5. Influence of the initial concentration of tartrazine

The purpose of these experiments was to study the influence of the initial concentration of tartrazine in the treated water, tests were performed for two types of catalyst: ZnO and TiO₂, we varied the concentration of 2, 5 and 40mg/L while maintaining the following operating conditions:

- recirculation rate 26.37 ml/s;
- Amount of catalyst used: 0.28 mg/cm²;
- Free pH;
- Reaction volume: 2 L.

The results obtained and the curves are shown below in Figure 11. These show good degradation of tartrazine for the different concentrations tested. The evolution of the reduced Tartrazine concentration demonstrates that throughout the range of concentrations studied, photodegradation is particularly rapid when the pollutant concentration decreases, the dye has been degraded by the two catalysts over 90% for TiO₂ and 87% in the case of ZnO, with a pseudo-first order kinetics. In the presence of titanium dioxide, the decomposition rate constant of this pollutant is two times greater than that obtained for ZnO.

Another study was performed under the same conditions of degradation substituting TiO₂ by ZnO. The temporal evolution of the reduced Tartrazine concentration is illustrated in Figure 12. Tartrazine has been degraded significantly with degradation kinetics of the pseudo first order. In this case, the decomposition rate constant of 2.5 mg/L of this pollutant is three times greater than that obtained for 30mg/L, and six times as much when it passes to 40mg/L.

The results given in Table 5 show that the removal efficiency of tartrazine decreases with the increase of the initial concentration of this pollutant.

Table 4. Rate constant and initial rate of degradation of tartrazine for different initial concentrations of pollutant.

<table>
<thead>
<tr>
<th>CTRZ (mg/L)</th>
<th>k_app (min⁻¹)</th>
<th>r₀ (mg/L.min)</th>
<th>X(%)</th>
<th>Intensity (W/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.021</td>
<td>0.054</td>
<td>98</td>
<td>605.88</td>
</tr>
<tr>
<td>5</td>
<td>0.020</td>
<td>0.105</td>
<td>98</td>
<td>822.81</td>
</tr>
<tr>
<td>10</td>
<td>0.023</td>
<td>0.227</td>
<td>99</td>
<td>775.16</td>
</tr>
<tr>
<td>15</td>
<td>0.013</td>
<td>0.206</td>
<td>91</td>
<td>317.98</td>
</tr>
<tr>
<td>20</td>
<td>0.011</td>
<td>0.244</td>
<td>92</td>
<td>717.85</td>
</tr>
<tr>
<td>30</td>
<td>0.010</td>
<td>0.315</td>
<td>91</td>
<td>430.85</td>
</tr>
<tr>
<td>40</td>
<td>0.016</td>
<td>0.649</td>
<td>92</td>
<td>343.33</td>
</tr>
</tbody>
</table>
Table 1: Evolution of the apparent rate constants as a function of the initial concentration of tartrazine.

<table>
<thead>
<tr>
<th>Initial Concentration (mg/L)</th>
<th>Rate Constant (10^{-4}mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.045</td>
</tr>
<tr>
<td>5</td>
<td>0.041</td>
</tr>
<tr>
<td>10</td>
<td>0.040</td>
</tr>
<tr>
<td>15</td>
<td>0.027</td>
</tr>
<tr>
<td>20</td>
<td>0.016</td>
</tr>
<tr>
<td>30</td>
<td>0.014</td>
</tr>
<tr>
<td>40</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Figur 13 represents the evolution of the apparent rate constants as a function of the initial concentration of tartrazine. It is noted that for the initial concentrations of tartrazine below 30mg/L, constant dye degradation speed is better using ZnO than in the presence of TiO2. Beyond this the constant concentration rate is two times greater for TiO2. Several explanations can be considered to justify the reduction in the rate constant by increasing the concentration of the pollutant. It is possible that the photogenerated holes h+ and/or OH radicals in the surface of the catalyst is reduced due to the overlap of the active sites by tartrazine. Thus, when the initial contaminant concentration increases, the surface of the catalyst required for the decomposition also increases [8,9].

The study allowed us to conclude that the solar photocatalysis proves to be useful as a treatment technique to reduce the toxicity of water polluted by dyes while reducing the energy treatment cost.

References:


E. Bizani, K. Fytianos, I. Poullos, V. Tsiridis, Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of...
