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Use of Packed Bed Photocatalyst and Sun Light Radiation for the Removal of Emerging Contaminant Dyes from 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 present study aims to develop a new photoreactor for the degradation of dyes pollutants in water. A fixed bed photocatalytic reactor incorporating ZnO catalyst and UV from sun light radiation was used for the study of its performance in photocatalytic destruction of tartrazin contaminant. Results from this work provided essential information needed towards the construction and operation of a fixed bed photocatalytic reactor. Specifically, we have evaluated the improvement of photocatalytic activity using Zinc oxide fixed bed for the total pollutant removal. It was found that the photocatalytic oxidation reaction follows the pseudo-first order model. The photodegradation ratio reaches 96% after 300 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 and the fixed bed coating of photocatalyst may resolve the problems of leaching and separation.

Keywords: Advanced oxidation technology; heterogeneous photocatalysis; emerging contaminants, Indigo Carmin, Zinc oxide, fixed bed photoreactor.

Introduction

The industry is a large consumer of water and generates a very important pollution of the aqueous medium with highly contaminated discharges of dyes. The treatment of this wastewater remains a major challenge, especially for developing countries that have not yet all the opportunities to integrate sustainable development concepts. Dyes are not readily biodegradable in aerobic conditions due to the complexity of their chemical structure and the presence of aromatic compounds which require a specific treatment. Conventional treatment (activated carbon adsorption, membrane processes, coagulation-flocculation, chemical oxidation etc.) have the disadvantage of transferring pollution from an aqueous phase to a new phase, and lead most to the formation of concentrated sludge, creating a problem of secondary waste or regeneration often very expensive materials[1].

Between the possible treatment techniques for contamination of aqueous effluents, advanced oxidation processes (AOPs) appear as methods of choice because they enable a total degradation of the pollutant in association with a decrease in the overall toxicity of the effluent. The AOPs are based primarily on the production of active and very specific species such as hydroxyl radicals. Photocatalysis appears as one of the least expensive methods for wastewater treatment and the mineralization of the organic compounds like pesticides and dyes[2].

Sustainable access to water resources is a major concern to all Mediterranean countries. Climate change, urban and population growth expected in the region, may aggravate the water stress already affects most countries of the South and East of the Mediterranean.

In Algeria, several factors may explain the water stress[3]:

- Delays in the 1980s and 1990s to adjust supply to water demand. In fact, water resources per inhabitant per year, which was 1 500 m^3 in 1962 was only 720 m^3 in 1990 to 630 m^3 in 1998 and 500 m^3 today, reflecting the offset relative to population growth
- The decline in rainfall for three decades, with a peak of drought in 2001-2002
- The desertification of soils that accentuates the threat of drought (and evapo-transpiration), particularly in western Algeria
- The growth of water demand (quadrupled in forty years), particularly in the north of the country and in urban areas (nine Algerians in ten live in the north of the country, 13% of the national area, and six Algerians out of ten live in more than 550 urban areas)[3].This situation could be exacerbated by the effects of climate change

The natural water potential of Algeria is currently estimated at 18 billion m^3 per year. Irrigation plays an important role in water consumption (62% of total demand in the country). The demand for drinking water, which has increased significantly since the 1970s, it is about 35% of total demand. The share of the water needs of the industrial sector amounts to only 3%.Since the early 2000s, the Algerian government has taken important steps to overcome the water shortage that affected the country.

The hydraulic issue was placed priority on the political agenda and substantial resources have been used to mobilize new conventional water resources and unconventional. The new water policy was thus structured around two strategic axes:

- The development of water infrastructure: dams, transfers, desalination seawater plants.
- Implementation of several wastewater treatment plants and development of new processes for water treatment.

The increasing pressure on water resources by 2050 will have to consider the need to extend the irrigated surfaces, to supply water for the growing population and respond to potential water needs of the energy sector (possibility of shale gas with hydraulic fracturing, used for the operation and maintenance of solar power plants, etc.). Water potential is estimated at 18 billion m^3/year distributed as follows[4].

- 12.5 billion m^3 / year in the northern regions of which 10 billion in surface runoff and groundwater resources 2.5 billion (renewable).
- 5.5 billion m^3/year in the Sahara region whose 0.5 billion in surface runoff and 5 billion.

In addition to these natural resources, the use of desalination plants can also take more important part of dam water to agriculture. Algeria has in 2013 nine large desalination plants capable to produce up to 1.4 million m3 of desalinated water per day.

The reuse of treated wastewater to meet the growing water needs of the agricultural sector has long been hampered because of the dilapidated state of the treatment plants. In the new water policy, it has become a priority and investments have been made in the rehabilitation of old plants and building new ones.

The stated aim of the authorities is to account for 239 treatment plants for wastewater (WWTP) in 2014, corresponding to a capacity of 1.2 billion m^3 per year of treated wastewater. The increasing use of this non-conventional water resource provides an additional incentive to improve the treatment capacity of wastewater and increase the connection rate specific to the sewerage system.

Results and Discussion

Comparison of different methods of indigo carmine degradation

To compare the efficiency of three processes adsorption, photolysis and photocatalysis on the elimination of Indigo Carmine in a solar reactor. Experimentations were carried out by maintaining the following conditions:

- The recirculation flow-rate of the solution: 26.37 mL/s
- The initial concentration of indigo: 10 mg/L
- Free pH
- Reaction volume: 2L

The curves of the Figure 1 show the evolution of reduced concentration of Indigo versus time for the three used processes.

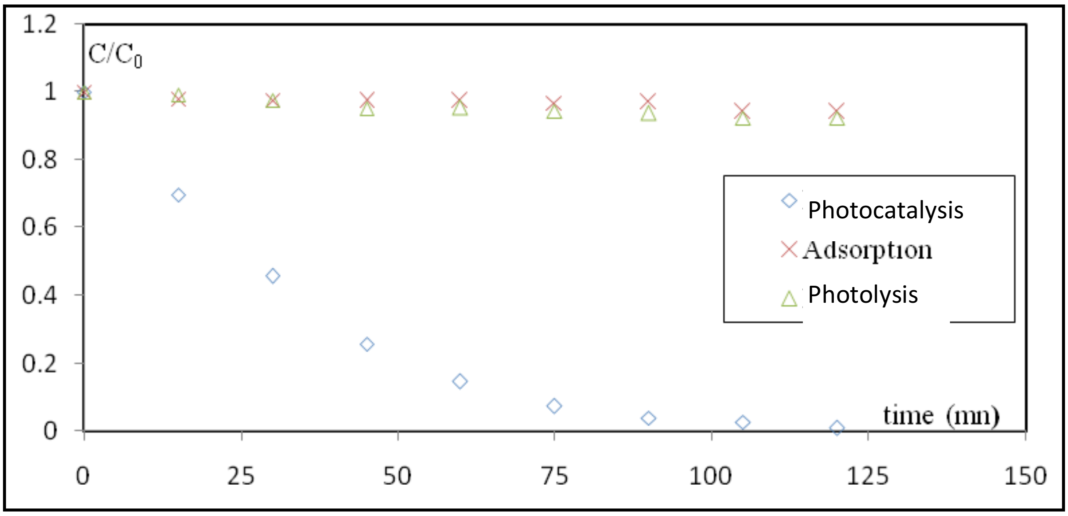

Figure 1.Temporal evolution of the reduced concentration of Indigo Carmin (C_{indi}=10 mg/L, V=2 L, free pH, C_{TiO2}= 0,28 mg/cm^2).

The curves in the Figure 1 present the temporal evolution of the reduced concentration of indigo carmin using various processes;it is concluded that the Indigo Carmin adsorption is insignificant(6%), the same amount was obtained by the photolysis process. A yield approaching 100% was obtained for the TiO_2 catalyst, thus signifying that the photocatalysis is the most appropriate method for the removal of this dye.

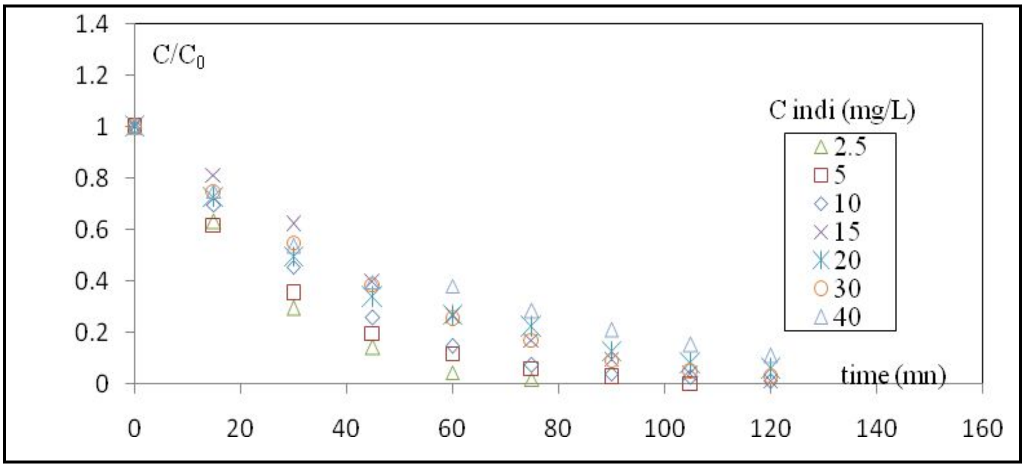

Figure 2. Temporal evolution of the reduced concentration of Indigo Carmin for Different initial concentrations of this pollutant.(Cindi = 10 mg / L, V L = 2, free pH CTiO2 = 0.28 mg / cm2).

Influence of the initial concentration of indigo carmin

Since the amount of the material to be degraded is a factor that determines the efficiency of the industrial waste treatment process. In this part, we studied the effect of the initial concentration of indigo carmin (2.5, 5, 10, 15,30 and 40 mg/L) on the efficiency of solar photocatalysis method using TiO_2 and ZnO as semiconductors. The reactions were performed at free pH after a 2 h reaction time. The results of this study are presented below in the Figures 2 and 3.

As shown in Figures 2 and 3, it's noted that theinitial concentrations used influences the removal of indigo carmin (DG), the degradation rate after about 2 hours of exposure to solar radiation is between 89-99% for TiO_2 and 92% -99% for ZnO. When the initial concentration of the dye increases, the amount adsorbed on the surface of TiO_2 (P25) increases (outside the DG dye); the same result was obtained by other authors[5]on colorants such as Acid Red 14, Acid Blue 193 and the blue Live 71. However, the opposite effectwasfound to gray (4GL).

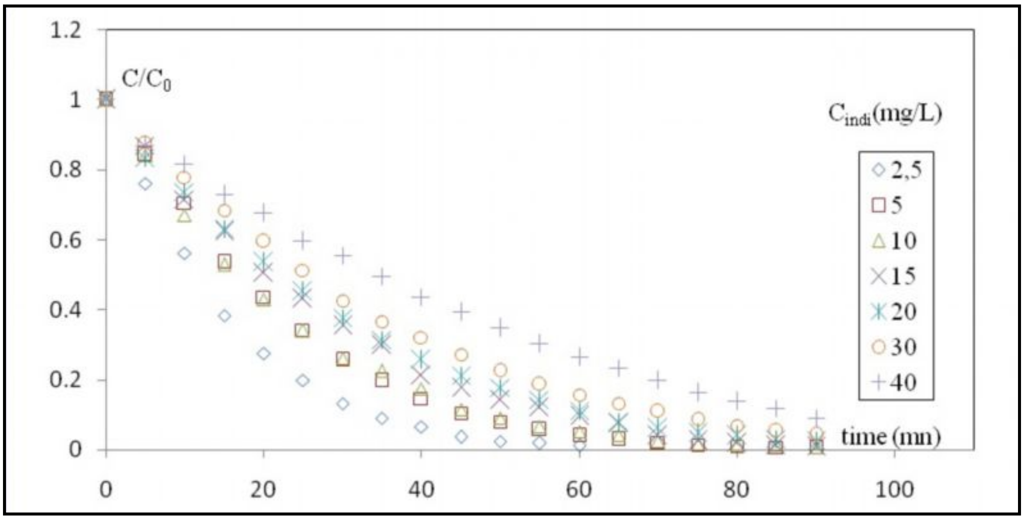

Figure 3. Temporal evolution of the reduced concentration of Indigo Carmin for different initial concentrations of this pollutant.(C_{indi}=10 mg/L, V=2 L, free pH, C_{ZnO} = 0.28 mg/cm^2)

The curves illustrate the temporal evolution of the reduced concentration of indigo carmin. These results improve that when pollutant concentration increases the rate constant decreases. The solar degradation of dye is favored when using ZnO. From a concentration high than 40 mg/L, the rate constants are quite similar for both catalysts. The degradation of this pollutant is strongly influenced by the initial concentration. Similar results have been reported for the photocatalytic oxidation of Methyl Orange and the Rhodamin[6], the blue Live 53[7], the black 5 reagent[8] and reactive Red 198[9].

The apparent speed constant, initial rates, degradation rates determined after two hours of irradiation and the half-reaction time for different initial concentrations of Indigo carmin are summarized in Table 1.

Table 1. Values of kinetic constants, initial rates, degradation rates after 2 hours of irradiation and a half-reaction time for the different initial concentrations of indigo carmin for different semiconductor

	Concentration of indigo carmin (mg/L)	k_{app} (min^{-1})	r_0 (mmol. $L^{-1}min^{-1}$)	$t_{1/2}$ (mn)	R^2	X%
TiO_2	2.5	0.041	0.1077	16.90	0.984	98.29
	5	0.037	0.1844	18.73	0.991	99.70
	10	0.03	0.3004	23.10	0,985	99.10
	15	0.022	0.3237	31.50	0,971	99.08
	20	0.022	0.42161	31.50	0,987	94.15
	30	0.021	0.5927	33	0,99	97.46
	40	0.018	0.7167	38.5	0,988	89.00
ZnO	2.5	0.071	0.176	9.762	0,992	98.80
	5	0.047	0.296	14.747	0.986	99.52
	10	0.043	0.345	16.11	0.998	99.41
	15	0.038	0.589	18.24	0.991	98.35
	20	0.03	0.656	23.104	0.995	97.68
	30	0.028	0.784	24.755	0.998	97.00
	40	0.021	0.841	33	0.993	92.84

To assess the effectiveness of treatment and to value the results of the discoloration, we determined the kinetic constants k. Figure 4 expresses the variation of k versus indigo processing time for both catalysts.

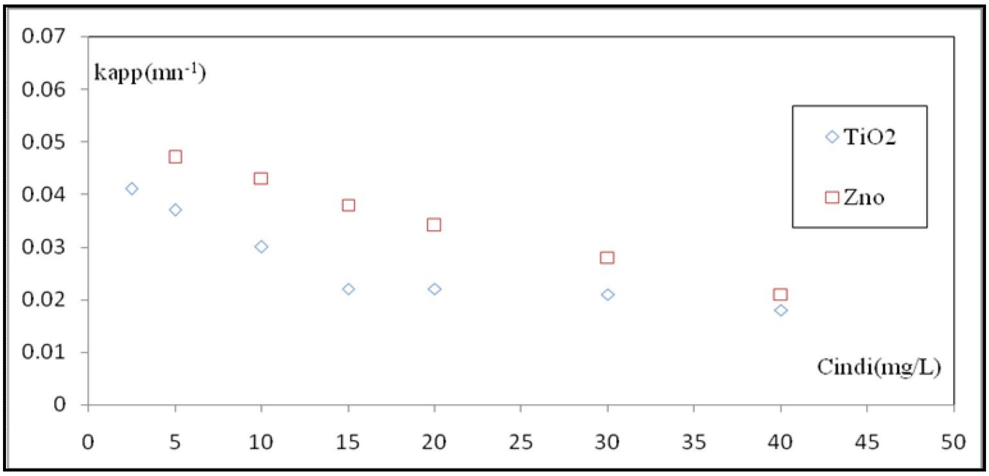

Figure.4. Evolution of apparent constant rate depending on the initial concentration of Indigo Carmin for TiO_2 and ZnO. (C_{indi} =10 mg/L, V=2L, free pH, Ccat = 0.28 mg/cm^2)

Langmuir-Hinshelwood model application

To verify the model of Langmuir-Hinshelwood,1/Kapp was represented versus C_0 in the curve of the Figure 4. Expression of the initial speed for the Langmuir-Hinshelwood model is given by the following equation.

$$r_0 = K_{app}.C_0=(Kr.K.C)/(1+K.C_0) \qquad (1)$$

r_0 :initial degradation rate (mg/L.min).

K :Constant rateof adsorption (L/mg).

k_r :Apparent constant rateofphotodegradation (mg/L.min).

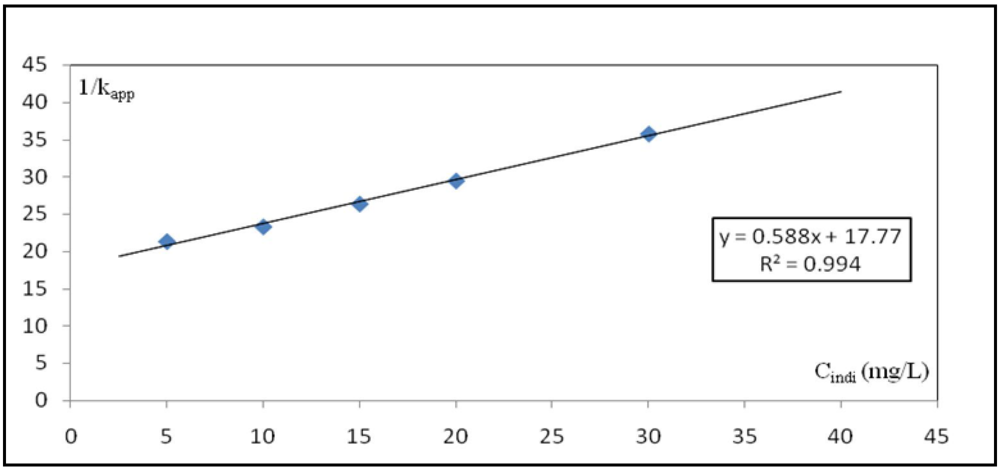

Figure 5. Evolution of 1/kappversus C_0

As shown in the Figure 5, the plot of 1/kr depending on the initial pollutant concentration C_0, is represented by a straight line. The slope of this line is equal to 1/kapp, the x-intercept present 1/(kr.K) .The study shows that the kinetic model of Langmuir-Hinshelwood described satisfactorily photocatalytic degradation of Indigo Carmin in the presence of sunlight. The essential characteristics of the isotherm of Langmuir-Hinshelwood can be expressed by a dimensionless constant kr.

Effect of pH of the solution

To better understand the effect of pH on the kinetics of photodegradation of indigo carmin, 10 mg/L as initial concentration was used and the pH was adjusted at values of 3, 5, 8 and 10 by measuring the absorbance at its characteristic wavelength to 610nm. These experiments were conducted to show the effect of pH on the discoloration of the solution using two semiconductors. The curves of the results obtained are shown in Figure 6.

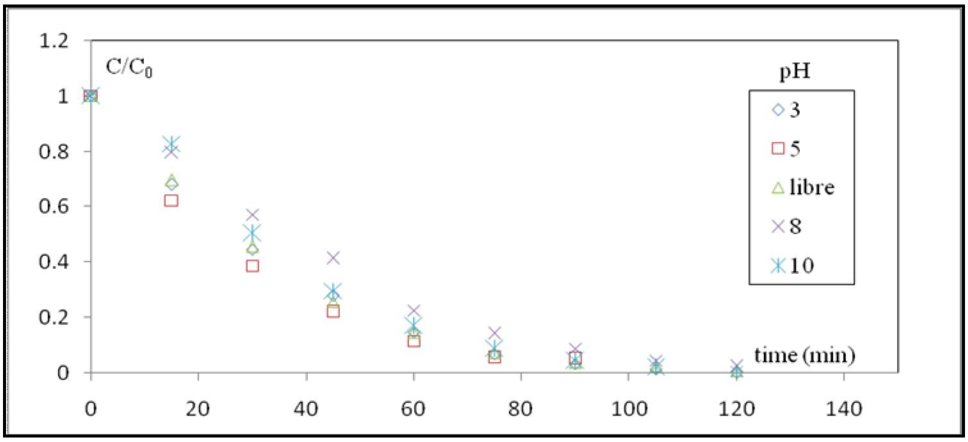

Figure6. Temporal evolution of indigo carminusing $TiO_2$for diferent pH (C_{indi} =10 mg/L, V=2 L, free pH, C_{TiO2}=0.28 mg/cm^2)

The effect of pH was developed in order to see the behavior of the solution for various unadjusted pH values of indigo carmin solution using ZnO. The evolution of the reduced concentration of the pollutant over time is illustrated in Figure7.

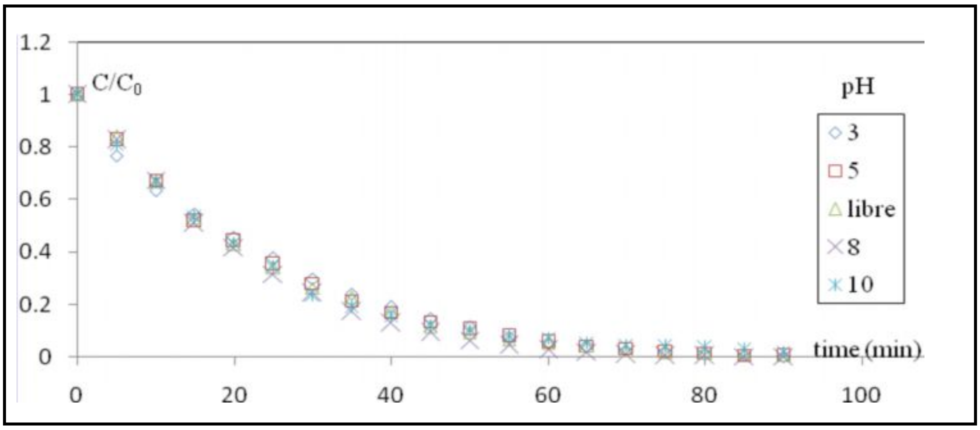

Figure7. Evolution of pH indigo carminover time using ZnO as catalyst (C_{indi}=10 mg/L, V=2 L, free pH,C_{ZnO}=0.28 mg/cm₂)

According to the results in Figure 7, we note that the rate of degradation for both catalysts exceed the 99% , the total loss for different values of pH studied is obtained after 120 minutes of reaction which is consistent with good adsorption on the surface of two catalysts. The rate constants are more important in the case of ZnO, there was minimal variation for both catalysts.

Table 2. Values of the kinetic constants for the different pH values for the titanium dioxide and zinc oxide

	pH	k_{app}(min^{-1})	R^2	X%
TiO_2	3	0.03	0.986	99.83
	5	0.032	0.997	99.84
	Libre	0.03	0.985	99.1
	8	0.027	0.965	97.53
	10	0.029	0.963	99.43
ZnO	3	0.042	0.9957	99.84
	5	0.044	0.996	99.69
	Libre	0.043	0.998	99.41
	8	0.045	0.994	99.85
	10	0.045	0.995	98.01

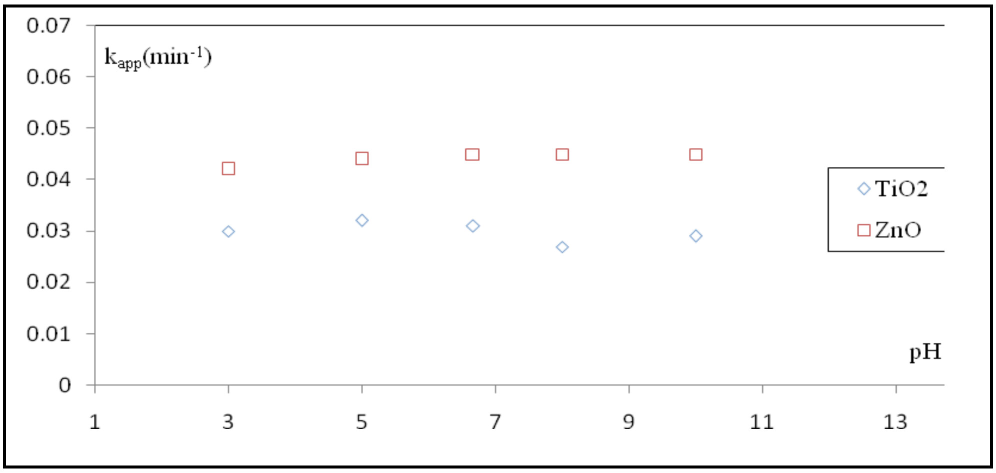

Figure8. Values of the rate constants of indigo Carmin over pH of the solution. (Cindi = 10 mg /L, V = 2 L, free pH, C_{ZnO} = 0.28 mg/cm^2)

Conclusion

This work aims to study the removal of dyes in industrial effluents by advanced oxidation process especially heterogeneous photocatalysis. The application of this method has demonstrated its effectiveness in the field of clearance of contaminated water, up to very significant mineralization rate. Our goal is photo-degradation of dye under sunlight. The experimental device is a solar fixed bed reactor; the degradation of indigo carmin is effected by the oxidizing action of the OH° radicals produced in the medium to be treated.

A parametric study was performed under solar radiation to determine the optimal conditions for the degradation of tartrazine and indigo carmin in the presence of titanium dioxide (TiO_2) and zinc oxide (ZnO) as catalysts. This study showed:

- Recirculation flow rate of the solution of 26.37mL/s promotes better degradation;
- The pollutant degradation kinetics is described by the model of Langmuir Hinshelwood and the order of the reaction is pseudo first order;
- Increasing the amount of catalyst (TiO_2 and ZnO) accelerates the degradation photocatalytic tartrazine until a plateau of 0.56 mg/cm^2;
- The initial rate of degradation of dye increase with increasing initial concentration while apparent rate constant decreases;
- Changing the pH has a minimal influence on the degradation of both pollutants.

References

1. Amalric, L., Guillard, C., Blanc-Brude, E., Pichat, P. Correlation between the photocatalytic degradability over TiO2 in water of meta and para substituted methoxybenzenes and their electron density, hydrophobicity and polarizability properties. *Water Research*, 1996, 30, 1137- 1142.
2. Guillard, C., Lachheb, H., Houas, A., Ksibi, M., Elaloui, E., Herrmann, J.M. Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO2 comparison of the efficiency of powder and supported TiO2.; *Journal of Photochemistry and Photobiology A-Chemistry*, 2003,158, 27-36.
3. Mozas, M.and Ghosn, A. État des lieux du secteur de l'eau en Algérie, Institut de prospective économique du monde méditerranéen, Vol. 25, 2013.
4. Hannachi, A., Gharzouli ,R., Djellouli, T. Gestion Et Valorisation Des Eaux Usées En Algérie. *Larhyss Journal*, 2014, 19, 51-62.
5. Bulut, Y., Gozubenli, N. and Aydin, H. Equilibrium and kinetics studies for adsorption of direct blue 71 from aqueous solution by wheat shells. *Journal of Hazardous Materials*, 2006, 144, 300-306.
6. Kansal, S.K., Singh, M., D. Sud. Studies on photodegradation of two commercial dyes in aqueousphase using different photocatalysts. *Journal of Hazardous Materials*, 2006, 141 (3), 581-590.
7. Sobana, N. and Swaminathan, M. Combination effect of ZnO and activated carbon for solar assisted photocatalytic degradation of Direct Blue 53. *Solar Energy Materials and Solar Cells*, 2007, 91 (8), 727-734.
8. Tang, C., Chen, V. The photocatalytic degradation of reactive black 5 using TiO2/UV in an annular photoreactor. *Journal of Water Research*, 38, 2775–2781, 2004.
9. Mahmoodi, N.M., Arami, M., Yousefi-Limaee, N. Photocatalytic degradation of triazinicring containing azo dye (Reactive Red 198) by using immobilized TiO2 photoreactor: Bench scale study. *Journal of Hazardous Materials*,133, 113–118, 2006.

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