Congo Red Photocatalytic Decolourization using Modified Titanium

A. López–Vásquez, D. Santamaría, M. Tibatá, and C. Gómez

Abstract—A study concerning the photocatalytic decolourization of Congo red (CR) dye, over artificial UV irradiation is presented. Photocatalysts based on a commercial titanium dioxide (TiO_2) modified with transition metals (Ni, Cu and Zn) were used. The dopage method used was wet impregnation. A TiO_2 sample without salt was subjected to the same hydrothermal treatment to be used as reference. Congo red solutions to several pH conditions (natural and basic) were used to evaluate photocatalytic performance of each doped catalysts. Photodecolourization percentage was measured spectrofotrometically after 3 h of treatment to 499 nm as response variable. Kinetics investigations of photodegradation indicated that reactions obey to Langmuir-Hinshelwood model and pseudo–first order law. The rate constant studies of photocatalytic decolourization reactions for $Zn–TiO_2$ and $Cu–TiO_2$ photocatalysts indicated that in all cases the rate constant of the reaction was higher than that of TiO_2 undoped. These results show that nature of the metal modifying the TiO_2 influence on the efficiency of the photocatalyst evaluated in process. Ni does not present an additional effect compared with TiO_2, while Zn enhances the photoactivity due to its electronic properties.

Keywords—Congo red, Dopage, Photodecolourization, Titanium dioxide.

I. INTRODUCTION

PHOTOCATALYTIC degradation by semiconductors is a new, effective and rapid technique for the removal of pollutants from water [1–2]. Heterogeneous photocatalysis that uses semiconductors as photocatalyst (TiO_2/UV) uses photons from UV range of solar spectrum as energy source to generate free radicals that conduced to oxidation compounds. However, due to wide band gap (3.2eV), TiO_2 just can use UV region, that conforms less than 5% of solar spectrum, while visible region represents about 45% of solar energy. If the used semiconductor has an adequate band gap between valence and conduction band, can be overcome it by energy content on a solar photon ($\lambda < 300nm$).

Recently, the interest to improve the optical response of TiO_2 has growed from UV spectrum to visible to increase photocatalysis efficiency for TiO_2. Since the treatment costs can be further reduced by efficiently utilizing solar light as the source of excitation, extensive efforts are currently underway to develop TiO_2 based photocatalysts that are not only capable of supporting visible light activated photodegradation, but also possess improved photocatalytic reactivity as compared to that of the pure material.

The band gap of titanium dioxide would be decreased and visible light absorption would be increased owing to the incorporation of metals into dioxide structure [5–7]. Various studies reported that doped TiO_2 with transition metal ions such as V, Cr, Mn, Fe, Ni or Au extends light absorption into the visible region. The role of loaded metal is trapping and subsequently transfering of photoexcited electron onto photocatalyst surface and decreasing the recombination of hole-electron pairs [8]. But little literature related to the effect of metals such as Ni, Cu and Zn depositing on the surface of TiO_2 by means of photoreduction on optical absorption capability [9]. The loaded metals on TiO_2 should be chemically stable during the photocatalytic oxidation reaction or storage in atmospheric condition.

Dopage with metals is one of the most efficient strategies to change the intrinsic structure of the gap of TiO_2, which can promote the photocatalytic activity increasing solar light sensibility. Doping TiO_2 structure modified its crystalline size and/or surface due the presence of metallic nanocompounds deposited over surface. Several methods such as sol–gel, impregnation (organometallic complex, commercial materials, etc.), co–precipitation, implantation, photodeposition, etc. are used to catalyst dopage.

The aim of the present study is evaluated the effects of doping of TiO_2 with salts such as Ni, Cu and Zn *via* wet impregnation during CR photocatalytic decolourization at natural (pH=5.7) and alkaline (pH=9.0) conditions.

II. EXPERIMENTAL

A. Materials

Congo red (C.I. Direct Red 28, M.W. = 696.67 g mol/l, $C_{32}H_{22}N_6O_6Na_2S_2$), sodium hydroxide, hydrochloric acid, copper sulphate, zinc sulphate and nickel sulphate were obtained from Merck. The semiconductor employed was commercial TiO_2 (Degussa P25), in powder form, and was used as support. According to the manufacturer, P25 has a primary particle size of 40 μm, a specific surface area of 50 m^2/g and its crystalline mode is 20% rutile and 80% anatase. Solutions were prepared by dissolving appropriate amount of

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the dye in deionized and distilled water before each experiment.

B. Preparation of doped TiO₂ photocatalysts

The influence of cation doping of TiO_2 on its photocatalytic performance for the decolourization of CR was investigated by incorporating cations such as Ni, Cu, and Zn into the crystalline structure of TiO_2. A series of TiO_2 photocatalysts doped at 5% w/w has been prepared. From now on, these samples will be denoted as M–TiO_2, where M indicates the doping cation. Precursors salts used for the preparation were $NiSO_4$, $Cu SO_4$ and $ZnSO_4$, respectively, purchased to Merck. The doped catalysts were prepared via wet impregnation.

For the preparation of doped M–TiO_2, an appropriate amount of respective sulphate of each salt, was calculated to give the desired concentration in the final material. A suitable amount of TiO_2, dispersed in deionized water, was then added to the solution and the mixture was stirred during 4 h to achieve complete dissolution of the salt. The slurry was maintained at 120ºC until nearly all the water evaporated for 2 h. and the solid residue was subsequently calcined in air at 400ºC for 12 h. A reference (undoped) TiO_2 photocatalyst was also prepared following this method.

C. Experimental procedure

Photocatalytic experiments were performed in the open 100-ml Pyrex vessel. The radiation source, five black lamps (20 W, manufactured by Opalux®), was irradiated perpendicularly to the surface of solution, and the distance between the UV source and the vessel containing reaction mixture was fixed at 15 cm. The experiments were performed at ambient temperature at 18 °C. The suspension pH values were adjusted at desired level using 0.01 N NaOH or 0.01 N HCl solutions and, then, the pH values were measured via pH meter (Schott Lab 850). For all the experiments, doped photocatalyst amount was 0.5 g/l. Before irradiation, dye solution was stirred in the dark for 30 min after the addition of the catalyst. Next, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous. The suspension was sampled at regular intervals and immediately filtrated by syringe filter (Minisart 0.45 µm, Sartorius) to remove completely any catalyst particles. The concentration of the solution samples was measured by UV–Vis spectrophotometer (Merck, Spectroquat Pharo 300). Making use of the latter method, conversion percentage of Congo red was obtained at different intervals. Absorption peaks corresponding to Congo red appeared at 499 and 347 nm. The degree of photodecolourization (X), as a function of time, was calculated by $X = (C_0 – C)/C_0$ where C_0 is the initial concentration of dye, and C the concentration of dye at time t.

III. RESULTS

Fig. 1 represents obtained data for CR photocatalytic decolourization after 3 h of treatment. One set was done by exposing Congo red solution to UV with only TiO_2 undoped (blank condition).

The pH of electrolyte can vary the surface charge of the photocatalyst and also shifts the potential of some redox reaction. Thus, it affects the adsorption of organic solutes, and consequently its reactivity and some reaction rate.
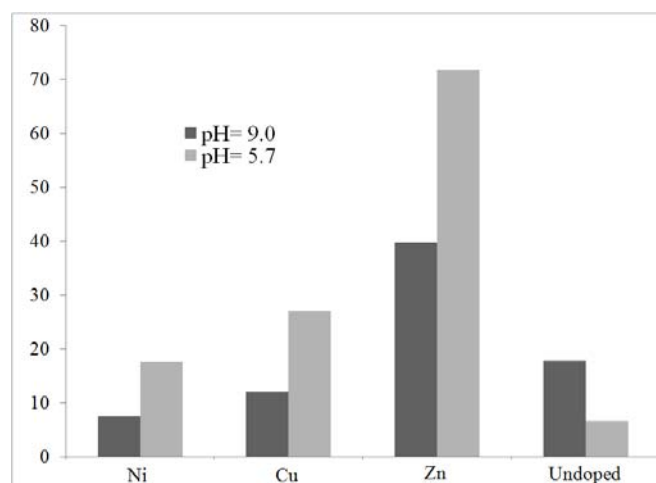

Fig. 1 CR photocatalytic decolourization using TiO_2 modified

The amphoteric behavior of most semiconductor oxides influences the surface charge of the photocatalyst [10]. Photocatalyst surface is positively charged in acidic media, whereas it is negatively charged under alkaline condition. The effect of pH on the photodegradation efficiency, which include type metal of doped photocatalyst (M–TiO_2) and fixed concentration of dyes (25 mg/dm³), were examined in a natural and alkaline condition.

The results shown that removal efficiency of dyes was carried out effectively at natural pH = 5.7 (in acidic solutions). Thus, for the azo dyes with sulfonic group in their structures, at low pH range, electrostatic interactions between the positive catalyst surface and dye anions lead to strong adsorption of the latter on the metal oxide support [11]. It seems that at acid characteristics of metal doping, surface adsorption is more effective than photocatalytic degradation for removal of Congo red. However, surface adsorption merely transfers dye from solution to solid and mineralization does not occur. For example, in the photodecolourization with photocatalyst Zn–TiO_2 confirmed this behavior. There was also the photodecolourization of RC dye in acidic solution, which is probably due to the formation of hydroxyl radicals. In the alkaline solution, dye may not be adsorbed onto negative surface of photocatalyst effectively, thus the photodegradation efficiency decreases.

The photodecolourization process is highly pH–dependent and the process exhibits different behavior with the chemical character of the metal. Therefore, the process was done at pH 5.79 and 9.0. As a result of its chemical structure, the dye undergoes massive decolourization at acid pH. According to these results, the photocatalytic behavior was Zn > Cu > Ni at natural pH (5.7). Decolourization values (%) for M–TiO_2/UV system (after 3 h. illumination) were found 71.78, 26.94, 17.71 and 39.8, 12.07, 7.56, to alkaline and acid conditions respectively.

A series of kinetical experiments involving the decolourization of Congo red was carried out in the presence

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of M–TiO₂ with UV illumination at different pHs. The findings are given in Fig. 2 and each datum shown in graph represents the concentration at different time.
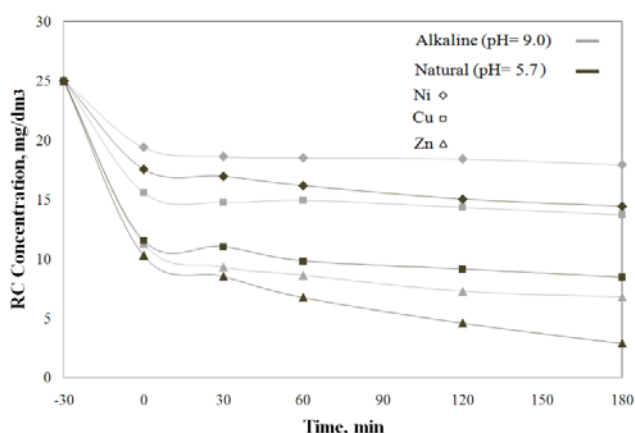

Fig. 2 Kinetics for RC photocatalytic decolourization during experiment.

The initial concentration influenced by compounds in the photocatalytic degradation rate of most organic compounds is also described by pseudo–first order kinetics. Photodecolourization rates of chemical compounds on semiconductor surfaces follow the Langmuir–Hinshelwood model according to Eq. 1 [12].

$$r = \frac{dC}{dt} = k_r\theta = \frac{k_r KC}{1+KC} \qquad (1)$$

where k_r is the reaction rate constant, K is the adsorption coefficient of the reaction, and C is the reactant concentration.

The values of k_r and K are used to explain the coefficients defining the rate determining reaction events, and pre–equilibrium adsorption within an adsorbed monolayer at the oxide surface and the aqueous solution interface, respectively. The effect of light intensity is also incorporated in k_r, and K especially expresses the equilibrium constant for fast adsorption–desorption processes between surface monolayer and bulk solution [13]. Integration of Eq. 1 yields the following (Eq. 2):

$$ln\left(\frac{C_0}{C}\right) + K'(C_0 - C) = k_r Kt \qquad (2)$$

When the initial concentration C_0 is small, (Eq. 2) changes into Eq. 3, which expresses a pseudo–first order reaction kinetic regime.

$$ln\left(\frac{C_0}{C}\right) = k_r Kt = kt \qquad (3)$$

where k is the pseudo–first-order reaction rate constant, $k = k_r K$ in min⁻¹. A plot of $ln(C_0/C)$ versus t for different concentrations of dye is shown in Fig. 3
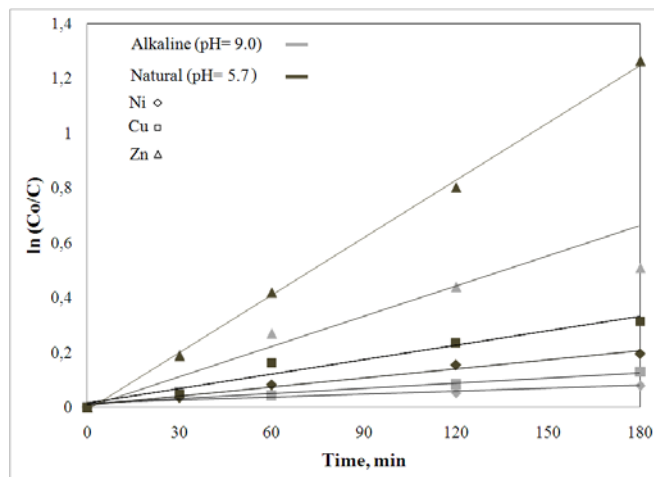

Fig. 3 Plot of photodecolourization rate of Congo red on M–TiO₂ aqueous solution *vs.* irradiation time at different conditions: (a) pH= 5.7, (b) pH= 9.0.

In order to study the nature of the photochemical reaction with several kinds of doped TiO₂ catalyst, apparent rate constant (k) is calculated from the slopes of the plots for Congo red (see Table I). The k values depend on the pH, which decreases gradually along with the increase the initial pH of the solutions.

TABLE I
RATE CONSTANTS FOR RC PHOTOCATALYTIC DECOLOURIZATION
IN THE PRESENCE OF M – TiO₂

Metal	$k \times 10^3$, (min⁻¹)	
	pH= 5.7	pH= 9.0
Zn	7.0	2.7
Cu	1.8	0.6
Ni	1.1	0.4

Adsorption of Congo red on M–loaded TiO₂ was also significantly increased in the presence of electronegative species. Adsorption behavior of catalysts in an anion containing media is given in Fig. 4.
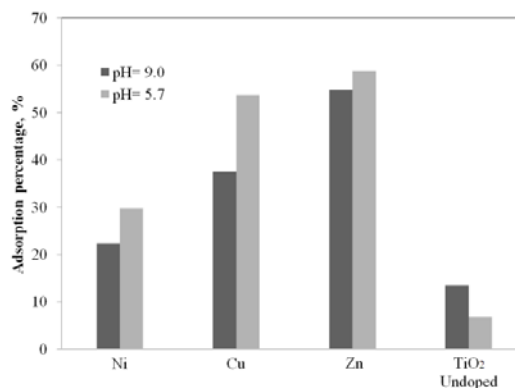

Fig. 4 Initial adsorption percentage of Congo red on M–TiO₂ at pH 5.7 and 9.0

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IV. CONCLUSIONS

The following conclusions could be drawn from the present investigation:

1. According to UV–Vis absorption spectra, no aggregation occurred in Congo red dye solutions in pH's whether natural or basic.

2. The photocatalytic efficiency of metal Zn on TiO_2 support was shown to be remarkably greater than that of TiO_2 in decolourization of Congo red azo dye.

3. Control experiments demonstrated that both Zn as Cu shows better performance than Ni (poor photoactivity compared with TiO_2 undoped) for decolourization of dye.

4. The photodecolourization degree of dye was obviously affected by the metal presence.

5. Efficiency of photocatalytic decolourization processes strongly depend upon the pH of the solution, nature of dye and doping metal characteristics.

6. Finally, it can be concluded that Zn–TiO_2 is an efficient photocatalyst in Congo red decolourization.

7. Initial adsorption is strongly influenced by medium pH. Such behavior is due to amphoteric behavior of dye and its relationship with doping metal.

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