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Photocatalytic Discoloration of Methyl Orange and Indigo Carmine on TiO$_2$ (P25) Deposited on Conducting Substrates: Effect of H$_2$O$_2$ and S$_2$O$_8$$^{2-}$

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ABSTRACT

The photocatalytic degradation of Methyl Orange (Mo) has been investigated in aqueous solutions using thin layers of TiO$_2$ deposited on stainless steel by electrophoresis. The effects of photocatalyst support, pH, the addition of hydrogen peroxide and the addition of peroxodisulfate ions have been investigated. The results suggest that conducting glass was the best photocatalyst support but due to its cost, we privilege the use of the system TiO$_2$/stainless steel. Hydrogen peroxide and peroxodisulfate ions have a positive effect on reaction rate. S$_2$O$_8$$^{2-}$ was the best oxidant which allows in a few minutes (~30 min) the total disappearance of MO. Using the best condition for MO degradation; we studied the photocatalytic degradation of Indigo Carmine, an indigoid dye.

Key words: Photocatalysis, methyl orange, hydrogen peroxide, peroxodisulfate, indigo carmine

INTRODUCTION

Dyes are a large group of organic compounds used in different fields such as food, textile, cosmetic and chemical processes. Much waste water is produced during these processes. A sizable fraction of synthetic or natural organic dyes is lost during the dying process and is released in the effluent water streams from the above industries or laboratories (Rajeshwar *et al.*, 2008). Of the synthetic dyes manufactured today, azo compounds are dominant (50-70). Methyl orange belongs to one of the most important classes of commercial dyes and it has a very short excited-state life and is stable in visible and near UV light (Nam *et al.*, 2002). Methyl orange is an anionic azo dye with good stability and special color characteristics. It is widely used in the printing, textile and photographic industries (Guo *et al.*, 2011). Methyl orange is also much used in chemical laboratories as a color indicator. Azo dyes are known to be carcinogens because of their decomposition to aromatic amines (Guivarch, 2004). Therefore, discoloration and detoxification of azo dye effluents have an increasingly important environmental significance in recent years.

Indigo carmine is considered a highly toxic indigoid dye. Contact with it can cause skin and eye irritation. It can also cause permanent injury to the cornea and conjunctiva (Barka *et al.*, 2008). Many common methods such as adsorption on activated carbon, ultrafiltration, reverse osmosis, etc., are used for the removal of dye pollutants. However, they are non-destructive and merely transfer pollutants from one phase (for example, aqueous) to another (for example, adsorbent)

(Maleki *et al.*, 2006). For some azo dyes removal in water, biodegradation method is slow and inefficient (for example, acid orange 7). Chlorination and ozonation are also relatively inefficient and have high operating cost (Rajeshwar *et al.*, 2008). Due to their synthetic origin and the presence of complex aromatic structure, many textile dyes are difficult to degraded by these methods (Atmani *et al.*, 2009; Pasukphun *et al.*, 2010). New methods for water treatment, as well as improvements in the existing processes, are required to protect our environment. Advanced Oxidation Processes (AOPs) such as heterogeneous photocatalysis using titanium dioxide have gained much attention today. In this process, when TiO_2 is illuminated by photons of energy equal to or greater than its band gap energy, the promotion of electrons from the valence band to the conduction band occurs. While electrons are attracted by their acceptors such as oxygen, metal cations and photoproduced holes react with electron donors (here organic compounds). The mechanism can be represented by the following steps (Ahmed *et al.*, 2010):

$$TiO_2 + hv \rightarrow TiO_2\ (h^+ + e^-) \tag{1}$$

$$e^- + O_2 \rightarrow O_2^{o-} \tag{2}$$

In this reaction, h^+ and e- are powerful oxidizing and reducing agents, respectively. The decomposition of organic steps are expressed as:

$$h^+\ organic \rightarrow CO_2 + ... \tag{3}$$

$$h^+ + H_2O \rightarrow HO^o + H^+ \tag{4}$$

$$HO^o + organic \rightarrow CO_2 + ... \tag{5}$$

In this study, we report the photo-oxidation of Methyl Orange in aqueous media using thin layers of titanium dioxide in order to avoid the expensive step of filtration when using TiO_2 in suspension. We used two different supports and their effect on the photooxidation process will be discussed. H_2O_2 and $S_2O_8^{2-}$ have been reported as electron acceptors having a higher activity and efficiency in this role than oxygen for titania conduction-band electrons (Fernandez *et al.*, 2004; Konstantinou and Albanis, 2004) as shown below:

$$e_{cb}^- + H_2O_2 \rightarrow OH^- + OH^o \tag{6}$$

$$S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^{2-} + SO_4^{o-} \tag{7}$$

$$SO_4^{o-} + H_2O \rightarrow SO_4^{2-} + HO^o + H^+ \tag{8}$$

These reactions inhibit electron-hole recombination at the semi-conductor surface. Hydrogen peroxide also increases OH^o radical production when absorbing light during photolysis (Saquib *et al.*, 2003; So *et al.*, 2002) according to the equation below:

$$H_2O_2 + hv \rightarrow OH^o + OH^o \tag{9}$$

Considering these reported reactions, H_2O_2 or $S_2O_8^{2-}$ addition seems beneficial to the photooxidation of dyes. The effect of H_2O_2 and $S_2O_8^{2-}$ ions will be discussed.

The objectives of this research were to determine (i) How the system (UV/TiO$_2$/SS) differs from the system UV/TiO$_2$/SnO$_2$: F and (ii) How these photocatalytic degradation pathways differ from the corresponding system in the presence of oxidants such as H_2O_2 and $S_2O_8^{2-}$.

MATERIALS AND METHODS

Materials: Titanium dioxide P-25 from Degussa is used in this study as purchased. For thin layer preparation, acetylaceton and polyethylen glycol tert-octylphenyl ether (Triton X -100) from Fluka and distillated water are used to prepare a first suspension which was then diluted with analytical grade methanol. TiO$_2$ P-25 was deposited on three conducting supports such as stainless steel 304 L and conducting glass from Solems France. Methyl orange $C_{14}H_{14}N_3SO_3Na$, used as model pollutant was obtained from Acros organic without any purification. Indigo Carmine (indigo disulphonic-5, 5 acid) was supplied by Acros Organics and was used as purchased. The molecular schemes of the two dyes are presented below.

Thin layer preparation: Thin layers were prepared by electrophoresis method. The conducting glass, stainless steel or aluminum used as substrates was first cleaned using a solution of sulfuric acid (75%) and oxygen peroxide (25%) and washed several times with distilled water. A DC voltage of 10 V was applied between a stainless steel anode and a cathode (conducting glass SnO$_2$: F or stainless steel), immersed in a colloidal suspension (50 g L^{-1} of photocatalyst in methanol). The distance between the electrodes was 1 cm and the deposition time used was 20 sec. Layers so obtained were dried at room temperature and then treated in an oven at 450°C (5°C min^{-1}) for one hour.

Photocatalytic reactor and photodegradation studies: Photocatalysis experiments were performed in a flow loop reactor open to air, provided by a 240 cm^2 surface of thin photocatalyst layer, volume of treatment 0.9 L solution.

A UV-A Black light Blue Lamp, (15 W, 365 nm) was used as light source under continuous flow conditions. The optical path through the solution was 1 cm and the temperature was kept at ca. 29-31°C. A New Jet pump was used for solution circulation during all the experiment.

The disappearance of the MO was measured using a Digitron Elvi 675 spectrophotometer. All experiments were performed at room temperature and atmospheric pressure. The photocatalytic degradation experiments were carried out by loading 900 mL of dye solution in the reactor. The scheme of the reactor is shown in Fig. 1.

Langmuir-Hinshelwood model: For azo dye photooxidation using AOPs, it is well known that the discoloration rate obeys the Langmuir-Hinshelwood (L-H) kinetic model (Tang and An, 1995):

$$r = \frac{dC}{dt} = \frac{kKC}{1+KC} \qquad (10)$$

where, r is the oxidation rate of the reactant, C the concentration of the reactant, t the illumination time, k the reaction rate constant and K is the adsorption coefficient of the reactant. When the chemical concentration C_o is a millimolar solution (C_o small) the equation can be simplified to an apparent first-order equation:
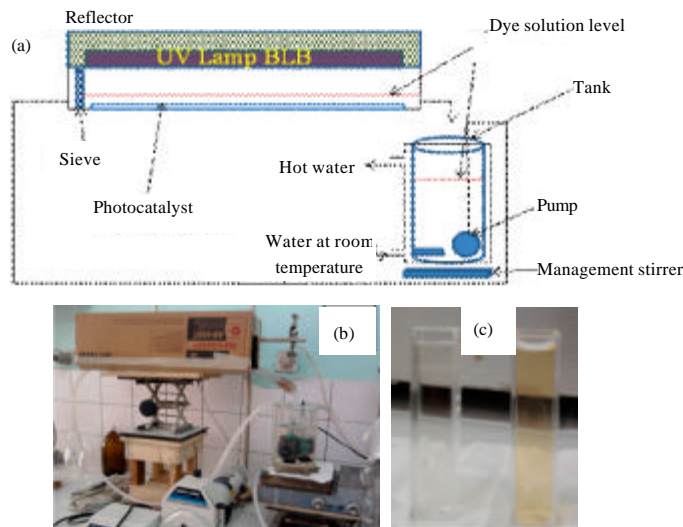
Fig. 1(a-c): (a) Schematic diagram of photocatalytic flow loop reactor, (b) Photograph of real reactor (c), Initial solution of MO (1 mM) and the resulting solution after photodegradation (t = 60 min) using $S_2O_8^{2-}$ (0.2 M)+UV+TiO_2/SS

$$Ln\frac{C_0}{C}=Ln(\frac{A_0}{A})=kK \times t=k_{app} \times t \text{ or } C=C_0 \exp(-k_{app} \times t) \qquad (11)$$

where, A_0 and A are the initial absorption and absorption at illumination time t, k_{app} equals the apparent first-order rate constant (Tchatchueng *et al.*, 2009). For comparison of different conditions, this kinetic model is used to depict the pseudo-first order, k_{app}, that corresponds to the slope of the straight line of the curve $Ln(C_0/C)$ vs. time, t corresponding to 50% discoloration. Also, we used the discoloration percentage calculated as follows Sarnthima and Khammuang 2008:

$$\text{Model Pollutant (\%)}=\frac{C_0\text{-}C_t}{C_0}\times100=\frac{A_0\text{-}A_t}{A_0}\times100 \qquad (12)$$

RESULTS

Photodegradation of Methyl Orange: effect of photocatalyst support: Most studies related to such photodegradation reactions have been carried out using suspensions of powdered TiO_2 (usually Degussa P-25) in a polluted aqueous solution. However, from a practical point of view it may not be possible to use catalyst suspensions in slurry photoreactors because of the filtration problems linked to the small size of the titania particles (Fernandez *et al.*, 1995). For this reason, attempts have been made to immobilize the catalyst on rigid supports (Acevedo-Pena *et al.*, 2009; Villarreal *et al.*, 2004; Wagner *et al.*, 2008). In this study, we used two metallic substrates (stainless steel and conducting glass SnO_2: F) to deposit TiO_2 by electrophoresis. The discoloration of MO 0.01 mM on TiO_2 deposited on these substrates was performed at free pH 6.1. Figure 2 shows the photodegradation rate in these conditions. The rate of photodegradation was greater when TiO_2 was
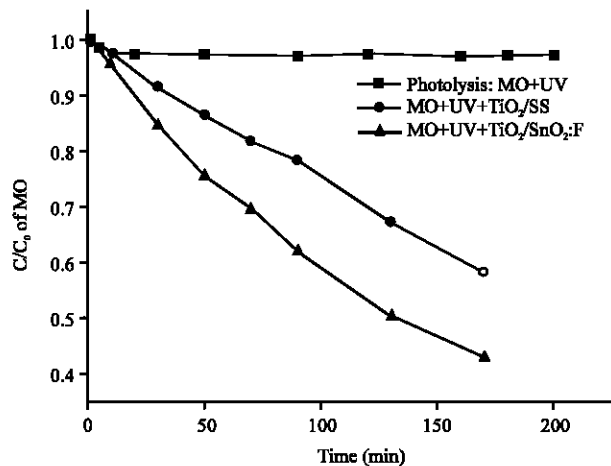
Fig. 2: Kinetics of the disappearance of methyl orange (1 mM), UV irradiation with or without TiO_2/SS or TiO_2/SnO_2: F
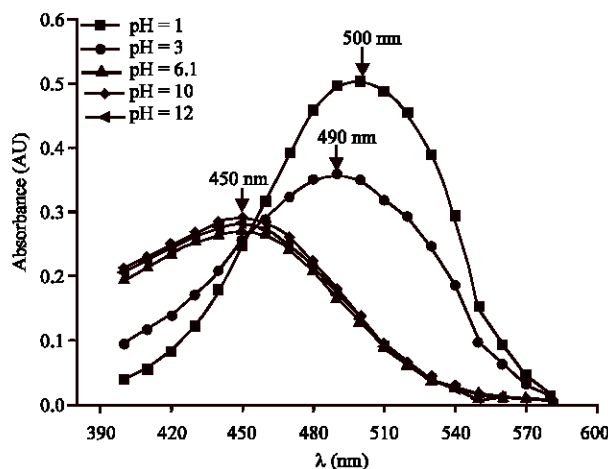

Fig. 3: Absorbance of methyl orange (1 mM) versus wavelength, effect of pH

supported on conducting glass. The rate constants were 0.00315 and 0.00508 min^{-1}, respectively with TiO_2/SS and TiO_2/SnO_2: F. We noted also that there was no significant photooxidation of MO using only UV light (15 W). However, due to the greater expense of the conducting glass than stainless steel, the latter substrate was used in all experiments.

Effect of pH on photodegradation of Methyl Orange: In Chemistry, pH is an important factor in many reactions. Particularly in photocatalysis, pH has some influence such as: - ionization state of the surface of TiO_2; -effect on the structure of dye component by ion exchange;-reaction between hydroxide ion and positive hole. So, it is important to know and to control the pH in order to enhance the rate of degradation. Five pH values (1; 3; 6.1; 10; 12) were chosen for our experiment to determine their effect on photodegradation rate of MO. Firstly, we measured the absorption of MO over the wavelength 400 to 650 nm to determine the maximum absorption peak. Figure 3
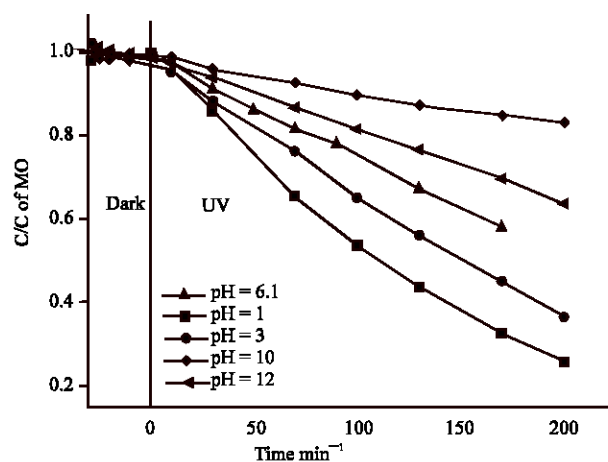
Fig. 4: Kinetics of the disappearance of methyl orange (1 mM) under UV irradiation with or without TiO_2/SS at different pH (1; 3; 6.1; 10; 12)
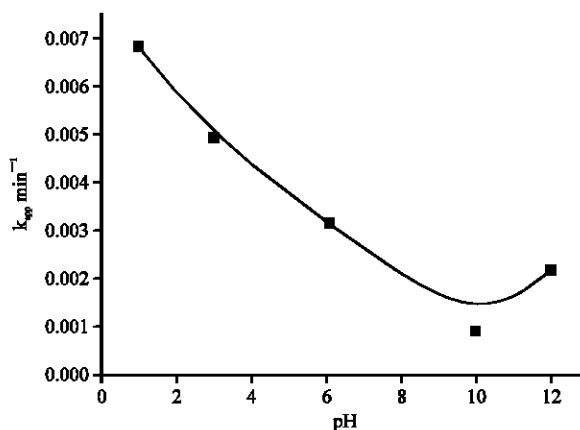

Fig. 5: Evolution of the apparent first order kinetic constant (k_{app}) with change in pH of MO solution

shows a plot of the absorption of MO versus wavelength. The maximum absorption peak depends on the pH. From natural pH to pH = 12, the maximum peak didn't change and was 450 nm while it was 490 and 500 nm, respectively for pH = 3 and 1. For the MO photodegradation studies, we used 450 nm when the pH was higher than 6, 490 nm when the pH varied from 2 to 3 and 500 nm when the pH was under 1.

The photodegradation of MO was studied at these different pH values (Fig. 4). The rate of disappearance of MO strongly depends on pH. The rate increases when pH decreases. The evolution of the pseudo-first order constant illustrated these phenomena well (Fig. 5). pH = 1 was more favorable for the photodegradation of MO in our conditions. The adsorptions calculated were 3.3, 2.9, 0.4, 0.3 and 0.8% for pH (1; 3; 6.1; 10; 12), respectively.

Effect of H_2O_2 on photodegradation of MO: Electron/hole recombination is one of the main drawbacks in the application of TiO_2 photocatalysis as it causes a waste of energy. In the absence of a suitable electron acceptor or donor, the recombination step is predominant and limits quantum
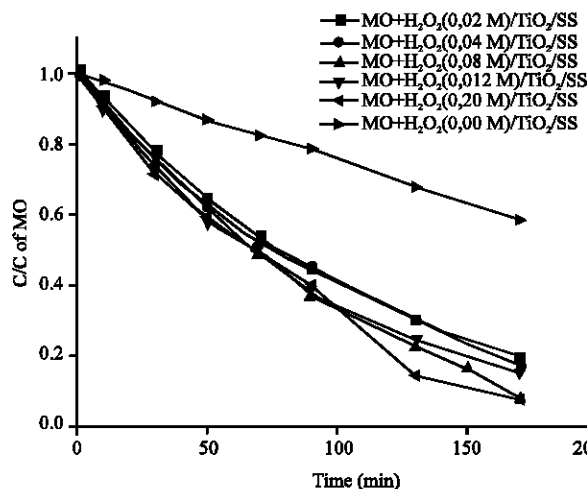
Fig. 6: Influence of H_2O_2 on photodegradation rate of methyl orange (1 mM)
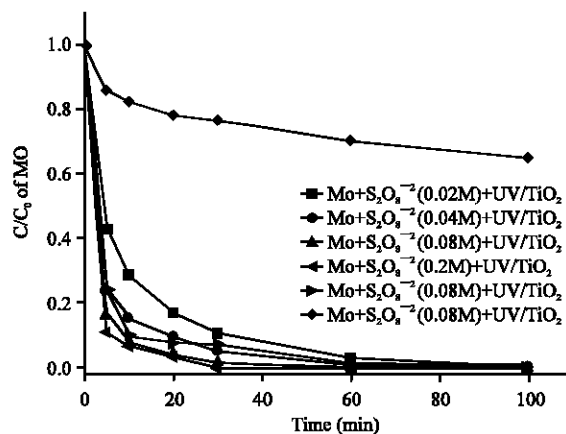

Fig. 7: Photooxidation of methyl orange (1 mM) under UV light: effect of peroxodisulfate ions on the rate of oxidation

yield. Thus, it is crucial to prevent electron-hole recombination to ensure efficient photocatalysis. Molecular oxygen is generally used as an electron acceptor in heterogeneous photocatalytic reactions (Nam *et al.*, 2002). Addition of external oxidant/electron acceptors to a semiconductor suspension has been shown to improve the photocatalytic degradation of organic contaminants by (1) Removing the electron-hole recombination by accepting the conduction band electron; (2) Increasing the hydroxyl radical concentration and oxidation rate of intermediate compounds and (3) Generating more radicals and other oxidizing species to accelerate the degradation efficiency of intermediate compounds (Ahmed *et al.*, 2010). Figure 6 shows the discoloration curves for MO 0.01 mM for different hydrogen peroxide concentrations. The discoloration rate increased in the presence of H_2O_2. Increasing the concentration of H_2O_2 did not significantly affect degradation rate.

Effect of peroxodisulfate ions $S_2O_8^{2-}$ on photodegradation of MO: Figure 7 reports the discoloration rate of MO under UV light in the presence of persulfate at different concentrations. $S_2O_8^{2-}$ had a strong positive effect on the rate of photodegradation of Methyl Orange. The rate of oxidation was also significant when $S_2O_8^{2-}$ was used without TiO_2 but under UV light. In all cases,
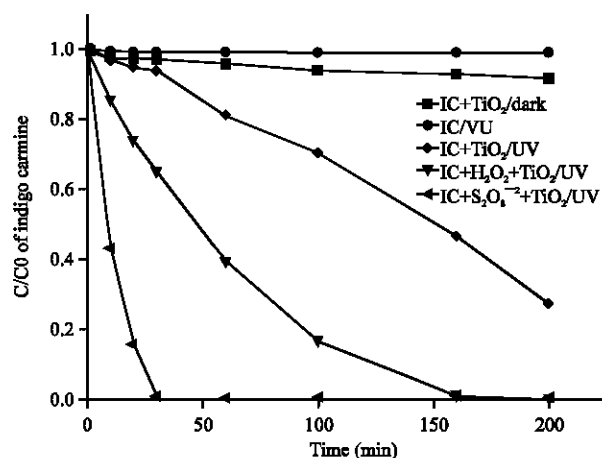
Fig. 8: Photolysis, adsorption and photocatalytic degradation of Indigo Carmine (0.03 mM) under UV light, effect of hydrogen peroxide and peroxodisulfate ions

peroxodisulfate ions strongly affected photodegradation rate than did H_2O_2. When persulfate ions were added to the MO solution, the pH decreased. The initial pH values were 3.6; 3.1; 2.8; 2.6; 2.5, respectively for initial concentration of $S_2O_8^{2-}$ equal to 0.02; 0.04, 0.08; 0.12; 0.2 M.

Photodegradation of indigo carmine (IC): The decrease in the concentration of the dyes was observed from the characteristic absorption at 610 nm for indigo carmine in water. The adsorption and photolysis of Indigo Carmine was studied to determine the exact effect of UV/TiO$_2$/SS. We used the best conditions of MO photodegradation using the oxidants H_2O_2 and $S_2O_8^{2-}$. Figure 8 presents the kinetics of IC degradation under these conditions. The initial pH and the conductivity of the IC (0.03 mM) solution were 4.64 and 22.9 μS cm^{-1}, respectively. After 200 min of photocatalytic experimentation under UV without any addition, the pH decreased slightly to 4.1 while the conductivity increased to 44.7 μS cm^{-1}. The curves in Fig. 8 indicate that there is no disappearance of IC under UV light without TiO$_2$ and the adsorption of IC reached 7.8% after 200 min. A strong adsorption of Indigo Carmine has also been reported in the literature (Barka *et al.*, 2008; Vautier *et al.*, 2001). Addition of H_2O_2 and $S_2O_8^{2-}$ was very beneficial to the rate of the degradation but peroxodisulfate ions had a strong effect as we ready found in the case of MO. The apparent first order kinetic constants obtained according to Langmuir-Hinshelwood's law of adsorption, photocatalytic degradation with C only, photocatalytic degradation in the presence of H_2O_2 or $S_2O_8^{2-}$ are 3.57×10^{-4}, 6×10^{-3}, 17.55×10^{-3} and 172.52×10^{-3} min^{-1}, respectively. In photocatalytic degradation without oxidant addition, the rate of degradation of IC was two times bigger than the MO one but the effect of $S_2O_8^{2-}$ although strong, was reduced in the case of IC.

DISCUSSION

Discussions of the interface reaction between a photocatalyst layer and a substrate, and the effect of the interface reaction on the structure and properties of the catalyst are important because the interface reaction could have a great influence on the properties of the photocatalyst. According to the method of deposition, here by electrophoresis that needs a conducting substrate, the elementary composition of the substrate can be detrimental or beneficial to activity of the photocatalyst. As shown in Fig. 2, the photodegradation of MO under the same condition was

greater with conducting glass (SnO_2: F) than with Stainless Steel (SS). The rate of degradation is enhanced about 1.6 times with conducting glass according to kapp (Table 1). Our previous work showed that annealing the conducting glass at 450°C did not affect its stability while for stainless steel the XRD patterns showed the diffusion of iron (Fe) leading to the formation of iron oxides (Kodom, 2011). Zhu *et al.* (2001) also reported the diffusion of Fe, Cr and Ni in the TiO_2 surface layer during the annealing treatment of stainless steel (Zhu *et al.*, 2001). The presence of these elements in the thin layer probably has a negative effect on the activity of TiO_2 resulting in less degradation of MO in the case of TiO_2/SS. These impurities may act as electron-hole recombination centers. The photoactivity of TiO_2 is more preserved when it is deposited on conducting glass. However stainless steel has some advantages such as its low coast and abundance.

Taking account only of the photoactivity of titanium dioxide, it could be enhanced in the presence of some oxidant or metallic cation. In this project, we report on the influence of pH, H_2O_2, S_2O_8.

pH is an important variable influencing the rate of degradation of some organic compounds in photocatalytic processes. Analyzing our result, the rate of degradation of MO is greater in acid medium. The result shows that high apparent first order was obtained at pH 1 probably because of the adsorption which was also high at this pH. One important consideration in the TiO_2-photocatalyzed reactions is the adsorption of the organic compounds on the surface of semiconductor particles (Qourzal *et al.*, 2006). Many investigations have observed similar trends in the discoloration of azo dyes (Sakthivel *et al.*, 2003; Nam *et al.*, 2002). However, according to the curve of k_{app} versus pH, one can clearly see that the rate tends to increase at pH 12 compared with pH 10.

All these observations can be explained: i) in terms of the location of the point of zero charge (about pH 6.5) of the TiO_2; ii) hydroxide ions (OH^-) in the solution inducing the generation of hydroxyl free radicals ($OH°$), from the photooxidation of OH^- by holes formed on the surface of TiO_2 particles. So, in acid media, the surface of TiO_2 is electropositive (Xu *et al.*, 2009). which favors the adsorption of MO (negatively charged) related to degradation by photoproduced holes. In alkaline media, negatively charged surface of TiO_2 does not favor the adsorption of MO but the high concentration of hydroxyl ions probably favors the production of hydroxyl radicals which oxidize MO in solution.

Hydrogen peroxide concentration, the intensity of UV irradiation, pH, dye structure and dye bath composition are the key factors influencing photodegradation rate when H_2O_2 is used. Here, we focused our research on the effect of hydrogen peroxide concentration using TiO_2/SS illuminated by UV light (15 W). As shown in Fig. 6 and 7, the discoloration rate increased significantly in the presence of H_2O_2. Regarding the apparent first order constant, the rate of degradation increased about 3 times in the presence of H_2O_2 (20 mM). This might be because hydrogen peroxide was reduced by photo-electrons in the conduction band of TiO_2 as shown in Eq. 6. Also, hydrogen peroxide can be activated by UV light resulting in the formation hydroxyl radicals Eq. 9. (Fatimah *et al.*, 2009). From the rate constant values in Table 1 it may be noted that the reaction rate doesn't increase significantly when the concentration of H_2O_2 was increased from 0.02 to 0.2 M. Also, the reaction rate began to decrease with the concentration of 0.2 M H_2O_2. This may be because the excess H_2O_2 becomes a scavenger of photo-electrons in the TiO_2 conduction band (Daneshvar *et al.*, 2003). Without TiO_2, the 0.08 M hydrogen peroxide induces the degradation of MO. H_2O_2 is decomposed by UV light to produce hydroxyl radicals Eq. 9. which oxidize the dye molecule in solution. The rate of oxidation with H_2O_2 is similar to rate obtained with TiO_2/SS

Table 1: Apparent first order constant, k_{app}, depicted according to Langmuir-Hinshelwood law

		H_2O_2 0,02 M	H_2O_2 0,04 M	H_2O_2 0,08 M	H_2O_2 0,12 M	H_2O_2 0,2 M	$S_2O_8^{2-}$ 0,02 M	$S_2O_8^{2-}$ 0,04 M	$S_2O_8^{2-}$ 0,08 M	$S_2O_8^{2-}$ 0,2 M
k_{app}	With TiO$_2$/SS	0.00909	0.00911	0.01017	0.01063	0.01025	0.12495	0.28711	0.43611	0.44317
	Without TiO$_2$/SS	-	-	0.00348					0.23328	

indicating the efficiency of this advanced oxidation (H_2O_2/UV). The presence of hydrogen peroxide decreases the pH of the solution and favors the rate of degradation of MO in the presence of TiO$_2$.

As for hydrogen peroxide, peroxodisulfate ions in solution are a strong oxidant species which can accelerate the oxidation of organic dyes. Figure 7 very well shows its action which is much better than the action of H_2O_2. In the presence of $S_2O_8^{2-}$ (0.08 M), 1 h is sufficient to obtain the total discoloration of Methyl Orange whereas in this time only 45% discoloration is obtained with H_2O_2 (0.08 M). Augugliaro *et al.* (2002) have also reported on the fast discoloration of MO with the system (MO+$S_2O_8^{2-}$+UV)/TiO$_2$. We remark also that without a photocatalyst, the action of peroxodisulfate ions was still strong (Fig. 7). But in this case Augugliaro *et al.* (2002) observed that there is no mineralization. In the presence of $S_2O_8^{2-}$ pH decreases in the course of the reaction to 3 for all the runs due to the formation of hydrogen ions according to Eq. 8. So, the fast degradation is attributed both to the pH and the action of the oxidant.

Most of the organic pollutants in water can be completely decomposed and mineralized at the surface of UV-excited TiO$_2$ photocatalysts. However, many factors have been monitored during the photodegradation of organic compounds using TiO$_2$. Nevertheless, the discussion about the group of compounds is rarely mentioned in the literature. Here, we transpose the best condition of Methyl Orange, an azo-dye, photodegradation to Indigo Carmine, an indigoid dye Fig. 8. The result shows that the addition of H_2O_2 or $S_2O_8^{2-}$ has a strong positive effect on the rate of IC disappearance. However, under the same condition H_2O_2 gives a positive effect during IC degradation than it does in the case of MO degradation. Also, we observe that the presence of $S_2O_8^{2-}$ in the same concentration increases the rate of MO than IC degradation. The mechanisms of photodegradation of these dyes are significantly different probably because of their chromophore group. Also, due to their structure, the reactions of the hydroxyl radical (HO°) or photoproduced holes (h$^+$) are different. In addition, the adsorption, negligible for MO, was about 7.8% for IC. This factor is important in photocatalysis considering direct mechanism reaction (adsorbed organic compound attacked by holes) which will be enhanced in the case of IC. Comparing the apparent first order kinetic constants, one clearly sees that the rate of IC with the TiO$_2$/UV system is two times greater because adsorption is better.

CONCLUSION

The results of our study have shown that the degradation of Methyl Orange dye was successfully carried out using coated TiO$_2$ on stainless steel. pH, H_2O_2 and $S_2O_8^{2-}$ have a strong effect on the rate of MO degradation. The major degradation of the dye was achieved for pH less than the free pH of MO (1 mM), but the maximum rate was obtained for pH 1. A complete discoloration was obtained in a few minutes (~30 min) in the presence of peroxodisulfate in MO or IC solution. H_2O_2 has a positive effect on the rate of degradation of the two dyes but its influence is less significant than with $S_2O_8^{2-}$ ions, the strongest oxidant that increases reaction rate.

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