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Elimination of a Cationic Dye (Crystal Violet) in Aqueous Medium by TiO_2/UV Oxidation Process

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The crystal violet, a cationic dye, could be discoloured by TiO_2/UV process. The experiments have shown on one hand that direct transformation at 365 nm has led to a feeble percentage of decolourization (≈ 25 % decoloured for a reaction time of 5 h and for a concentration of 3 ppm) and in another hand adsorption process has conducted, in absence of light, to a negligible amount of dye retention. By contrast, the treatment of the considered solution by TiO_2/UV at 365 nm has permitted to obtain a better efficiency of the bleaching process. It has been observed that the decolouration rate has varied with concentration of the substrate. Indeed, as the solution becomes more coloured, the colouration disappeared slowly. Moreover, in all cases, the discolouration process followed a first-order rate law. The influence of H_2O_2 has led to an improvement of this process marked thereby, by an acceleration of the bleaching rate. This fact could be attributed to the participation of the radicals $OH^•$, in these reactions. In this case too, the kinetics behaviour was well represented by first-order rate law. The effects of salts such as NaCl and Na_2SO_4 have been also investigated and the obtained results showed a decrease of the decolouration rate for both cases. The photocatalytic pathway has been well described by the Langmuir-Hinshelwood kinetics model. The values of the rate constant (k) and adsorption equilibrium constant (K) are 1.76 M min^{-1} and 7.07 M^{-1}, respectively.

Key Words: Violet crystal, TiO_2/UV, Hydrogen peroxide, Salts, Alcohol.

INTRODUCTION

The discharge of the effluents coming from the textile industries in the aqueous medium is a serious threat for it. Indeed, the coloured wastewaters are causing severe damage to aquatic life (fauna and flora) by impeaching penetration of solar light which is vital to its metabolism. Conventional

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techniques such as: Adsorption on activated carbon, ion exchange, biodegradation, *etc.* have been used. However these methods are not sufficient because they transfer pollution to one phase to another needing therefore more additional cost effective treatment to destroy these pollutants (*e.g.*, incineration or landfilling). In recent years, increasing attention has been focused on new systems of depletion, such as: photolysis[1,2], electrochemical degradation[3] and advanced oxidation processes (AOPs) used as well as in homogeneous as in heterogeneous medium[4-6]. For this latter process, its ability to destroy pollutants is linked to highly reactive entity: the hydroxyl radical. Once produced by the system on both mediums, they can react rapidly and without any discrimination with most organic compounds and with a second order rate constant[7] ranging from 10^7 to 10^{10} M^{-1} s^{-1}. In these conditions, mineralization becomes possible, mainly in term of CO_2 and H_2O.

In this work, the degradation of crystal violet either by direct photolysis at 365 nm and in absence of TiO_2 or by the TiO_2/UV system and at the same wavelength are presented. The effect of some parameters *viz.*, initial concentration of the substrate, addition of H_2O_2 and alcohol will be investigated. This will allow to choose the better degree of the efficiency either of TiO_2/UV or direct UV photolysis. The kinetic behaviour of the bleaching process of this dye will be studied on the basis of the experimental results.

EXPERIMENTAL

Crystal violet (Fig. 1) solutions were prepared in distilled water by dissolving appropriate amounts of dye. The concentrations were ranging from 1 to 5 ppm. The dilution of these solutions has been done according to the experimental condition. The pH was adjusted by NaOH or H_2SO_4, to reach the desired values. All reagents used in this work were analytical grade purity and used without further purification.

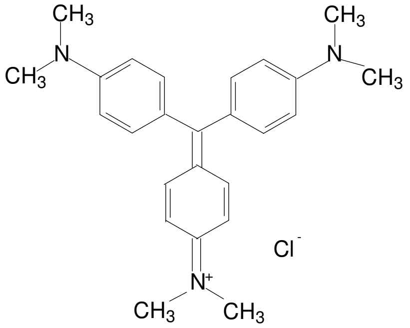

Fig. 1. Structure of crystal violet

Most of experiments were carried out with titanium dioxide (TiO_2, P25 Degussa). It predominantly forms anatase (80 % anatase, 20 % rutile), with a surface area of 50 ± 5 $m^2 g^{-1}$ and small amounts of SiO_2 and Al_2O_3.

Reactor and light source: The device used for irradiation was constituted by a pressure mercury lamp (Philips TLAD 15W/05) located along one of the focal axes of cylindrical enclosure with an elliptic base. The lamp had a maximum emission at 365 nm with a 50 nm half-width. The reactor, in Pyrex, was located along the other focal axis of the mirror. Its temperature was maintained constant by a circulation of thermostated water at 20 °C in the jacket. A magnetic stirrer, maintained TiO_2 in suspension. The reaction mixture is composed with 20 mL of crystal violet and 0.02 g of TiO_2 (in this condition, the concentration of 0.02 g/20 mL or 1 g/L was used). Light intensity received by the reactor was evaluated with potassium ferrioxalate to be about 4.10^{15} photons $cm^{-3} s^{-1}$.

Analysis procedure: The UV-visible absorption spectrum were recorded on double beam spectrophotometer "Unicam Helios α". Kinetics studies were monitored by measuring the absorption of all residuals concentrations, at maximum wavelength which was 592 nm for present substrate.

RESULTS AND DISCUSSION

Spectrum of the dye: The absorption spectrum of the crystal violet (10^{-5} M, pH = 6.80) in aqueous medium exhibits three bands where the most intense is located at 592 nm (ε = 101270.52 L $mol^{-1} cm^{-1}$ (Fig. 2). At 365 nm which is the wavelength emitted by the used lamp, the absorption of this dye was negligible.

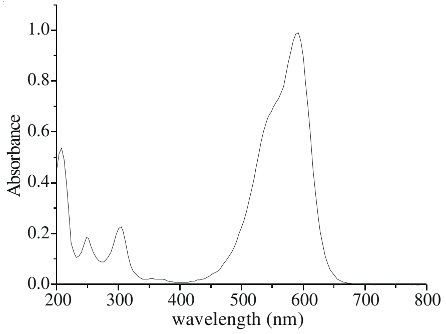

Fig. 2. Spectrum of crystal violet (10^{-5} M and pH = 6.8)

Kinetic study of the bleaching process: Suspensions containing TiO_2 (2 g/L) and crystal violet (3 ppm) were first put in contact and then irradiated at 365 nm.The results depicted in Fig. 3 showed that disappearance of the dye is much faster with TiO_2/UV than with UV alone (direct transformation) for the considered reaction time (5 h). This could be due to the very weak absorption of the substrate at this wavelength. It was also initially observed that no adsorption of crystal violet occurred in presence of TiO_2 alone.

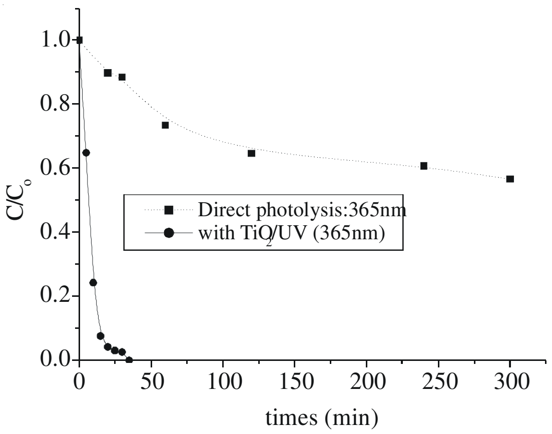

Fig. 3. Decolouration process of crystal violet by direct photolysis (365 nm) and by TiO_2/UV ($[TiO_2]_o$ = 1 g/L, λ = 365 nm and pH = 6.9)

Effect of mass catalyst: Experiments were conducted with different values of the mass catalyst. It has been observed that rate of decolouration increases as the mass of the catalyst increases until a certain range of concentration (1-2 g/L) where it remained constant. Thus, an augmentation to a limited extent of the catalyst concentration may favour the adsorption of the dye molecules and an activation of TiO_2 particles, involving in these conditions an enhancement of the discolouration rate. Nevertheless, a high dose on catalyst can affect the light diffusion in the solution implying therefore, a decrease of its photoactivity and in that way the diminution of the decolouration rate (Fig. 4). The concentration at 1 g/L was taken in all experiments since this value corroborated well with that reported by bibliographic data[8].

Effect of initial concentration: The kinetics of decolouration is reported in Fig. 5. It demonstrates that the photodegradation rate depends highly on the initial concentration.

Under present experimental conditions and on the basis of the pseudo first order homogeneous kinetics model, a diminution of the rate constant (k_{cv}) as the concentration of the substrate increases was observed (Fig. 6 and Table-1). This feature can be explained by a less accessibility of photons as the solution gets more coloured and thus to a less participation of radical $OH^{\bullet}$, issued from the photoactivity of the photocatalyst, to the degradation process.

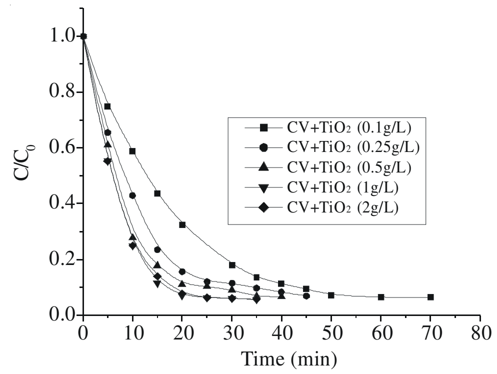

Fig. 4. Influence of mass catalyst on decolouration process by TiO_2/UV ($\lambda = 365$ nm and pH = 6.9)

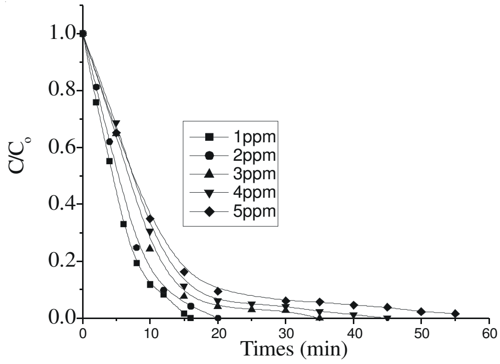

Fig. 5. Influence of the initial concentration of the dye during decolourization process ($[TiO_2]_o = 1$ g/L, $\lambda = 365$ nm and pH = 6.9)

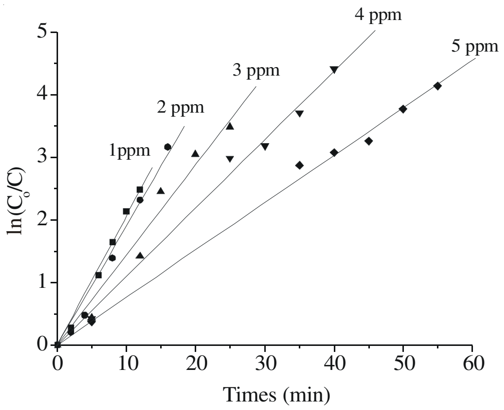

Fig. 6. Kinetics study of photocatalytic decolouration (ln C_o/C *vs.* time) of the crystal violet ($[TiO_2]_o = 1$ g/L, $\lambda = 365$ nm and pH = 6.9)

TABLE-1
VALUES OF RATE CONSTANT (k_{cv}) AT VARIOUS CONCENTRATION THE DYE

Substrate concentration (ppm)	Rate constant k_{cv} (min^{-1})	Correlation coefficient (R)
1	0.200	0.99737
2	0.190	0.99564
3	0.140	0.98631
4	0.110	0.99694
5	0.076	0.99782

The fact that the discolouration process was studied in heterogeneous medium, the modified Langmuir-Hinshelwood kinetics model is considered, which takes into account reactions occurring at the solid-liquid interface:

$$v_o = K'\theta = \frac{kK'C_o}{1+KC} \tag{1}$$

where v_o = initial rate, θ = fraction of the covered photocatalyst surface, k = rate constant of the disappearance of the dye, K' = equilibrium constant for adsorption.

The plot of $1/v_o$ *vs.* $1/C_o$ allows the determination of k and K' (Fig. 7). Thus, the deduced values from the linear representation are: k = 1.76 M min^{-1} and K' = 7.07 M^{-1}.

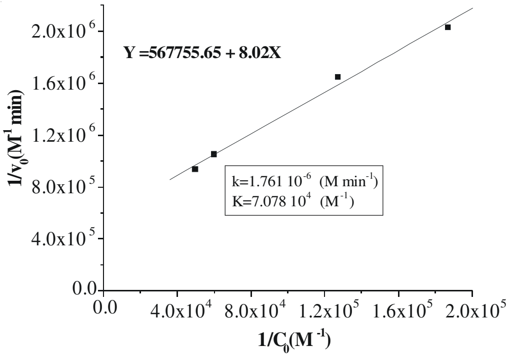

Fig. 7. Linearization of the modified Langmuir-Hinshelwood kinetic model ($1/v_o$ *vs.* $1/C_o$)

Effect of different factors: H_2O_2, pH, alcohols and salts

Effect of H_2O_2: The photocatalytic degradation of crystal violet has been studied at various hydrogen peroxide concentrations (10^{-1}, 10^{-2} and 10^{-3} M). The results depicted in Fig. 8 showed that the rate of discolouration process of the substrate increases with the rise of the concentration of H_2O_2. This acceleration could be related to the inhibition of the electron-hole recombination and also by the production of more radicals $^{\bullet}OH$ in the medium[5,9-12]:

$$TiO_2 + h\nu \rightarrow TiO_2 + e^- + h^+ \tag{1}$$

$$H_2O_2 + e^- \rightarrow HO^{\bullet} + OH^- \tag{2}$$

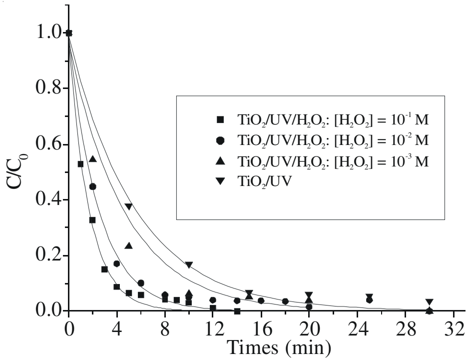

Fig. 8. Effect of the concentration of H_2O_2 on bleaching process of crystal violet ($[TiO_2]_o$ = 1 g/L, λ = 365 nm and pH = 6.9)

According to present experimental results depicted in Fig. 9, the decolourization process was well described by pseudo-first rate constant, demonstrating thus, the positive role played by H_2O_2. An increase of this apparent rate constant was noted as the concentration of H_2O_2 increases (Table-2).

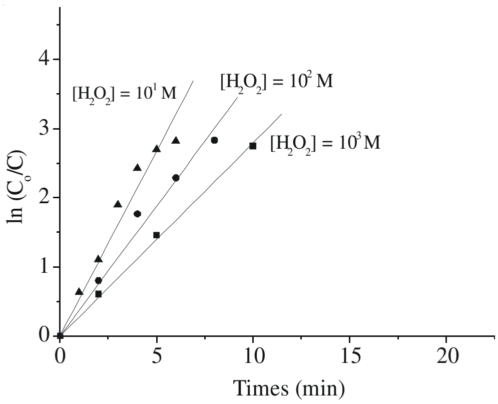

Fig. 9. Kinetics study of photocatalytic decolouration (ln C_o/C *vs.* time) of the crystal violet in presence of H_2O_2 ($[TiO_2]_o$ = 1 g/L,7 λ = 365 nm and pH = 6.9)

TABLE-2
VALUES OF APPARENT RATE CONSTANT (k'_{cv}) AT VARIOUS CONCENTRATION OF H_2O_2

$[H_2O_2]$ mol L^{-1}	Rate constant (k'_{cv}) (min^{-1})	Correlation coefficient (R)
10^{-3}	0.279	0.99935
10^{-2}	0.375	0.99181
10^{-1}	0.534	0.98083

Effect of pH: pH is an important influencing parameter since, it involves the ionization of the photocatalyst surface. Indeed, it becomes positively charged in acidic medium, negatively charged in basic medium and neutral at pH ≈ 6.5 in the case of TiO_2 (this point is also called the charge point zero or "cpz")[8]:

$$pH < 6.5 \quad Ti(OH)_2^+ \rightleftharpoons Ti(OH) + H^+ \tag{5}$$

$$pH > 6.5 \quad Ti(OH) \rightleftharpoons TiO^- + H^+ \tag{6}$$

Since, the dye has a cationic structure (*i.e.* charged positively) the decolouration process of this substrate has been favoured in basic medium, due on one hand to its adsorption on the surface of the photocatalyst by means of electrostatic forces and on the other hand to radicals $OH^•$ produced by the photoactivity of this support by the UV radiation at 365 nm (Fig. 10).

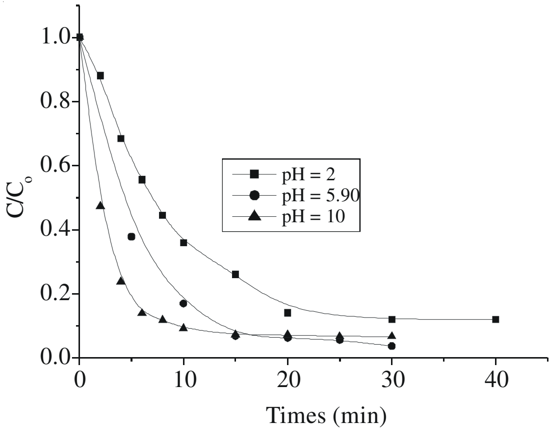

Fig. 10. Influence of pH on the discolouration process of the crystal violet

Effect of alcohol: Ethanol is habitually used as a scavenger for radicals $OH^•$ since the rate constant is of magnitude order of 1.9.109 M^{-1} s^{-1} with respect to these species[7]. Results represented in Fig. 11, showed the inhibition effect for low concentration of this alcohol (2 % v/v).Thus, one can conclude that the photodegradation process might occur within two routes: The first *via* radicals $OH^{\bullet}$ and which is the main one whereas the second through the positive holes (h^+) formed from the irradiation of the photocatalyst surface as reported by bibliographic data[12,13].

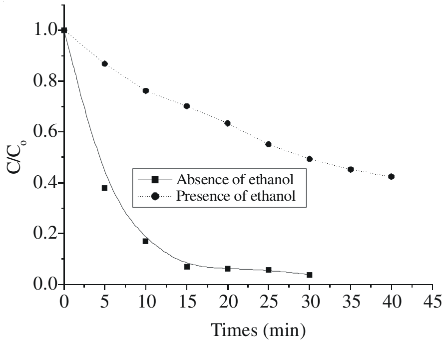

Fig. 11. Effect of ethanol (2% v/v) on decolouration of crystal violet ($[TiO_2]_o$ = 1 g/L, λ = 365 nm and pH = 6.9)

Effect of anions (chlorides and sulphates): Irradiations were performed in presence of various amounts of chloride and sulphate sodium. The results displayed in Fig. 12, demonstrate clearly that these amounts when they are elevated enough; they can diminish the discolouration rate of the dye. This fact could be attributed on one side to a competitive adsorption between the dye and both anions and on the other side on the quenching effect. This latter, is well illustrated by the chloride anions according to the following reaction[7]:

$$Cl^- + OH^{\bullet} \rightarrow Cl + OH^- \text{ with } k_{Cl^-} = 4.3.10^9 M^{-1}s^{-1}$$

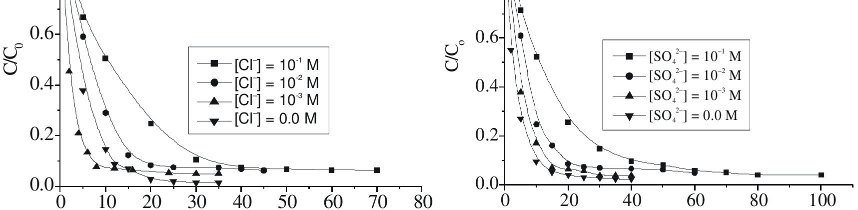

Fig. 12. Influence of salts at various concentrations ($[TiO_2]_o$ = 1 g/L, λ = 365 nm and pH = 6.9): (a) with chlorides (b) with sulphates

Conclusion

The results of this work proved that TiO_2/UV system has been more efficient than direct UV photolysis in the decolouration process at 365 nm. The discolouration rate of the crystal violet has been affected by factors like: pH, H_2O_2 and salts. It has been enhanced greatly in one part by addition of H_2O_2 but to a certain concentration limit to avoid the quenching effect and in basic medium and in another part decreased in presence of chlorides and sulphates in relatively large amounts. These two latter might act as scavenger for radicals $OH^{\bullet}$. The observed inhibition effect with ethanol suggested that bleaching process occurred within two routes: oxidation *via* radicals $OH^{\bullet}$ which is the main one and direct oxidation by positive holes (h^+) created on the photocatalyst surface during the irradiation. The modified kinetic model of Langmuir-Hishelwood fitted experimental results and allowed determination of both constants: rate of disappearance k and equilibrium constant K. The TiO_2 system could be considered as a promising way for the treatment of wastewaters.

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