

PHOTOCATALYTIC DEGRADATION OF CRYSTAL VIOLET USING TiO₂-IMMOBILIZED UNDER UV IRRADIATION

Djellabi R., Ghorab M.F.

Laboratory of Water Treatment and Valorization of Industrial Wastes, Chemistry Department, Faculty of Sciences, Badji-Mokhtar University, BP12, 23000, Annaba, Algeria

E-mail: rida.djellabi@yahoo.fr

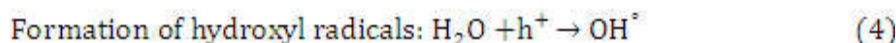
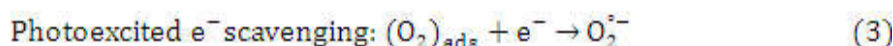
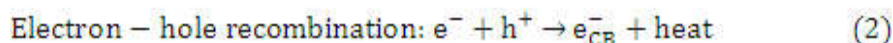
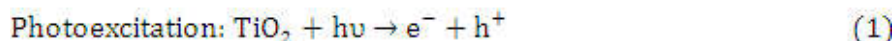
Abstract - The objective of this work was to assess the use of TiO₂-immobilized into glass plates for the degradation of Crystal Violet (CV) under UV irradiation (365 nm). The commercial Degussa P25 TiO₂ was used as a photocatalyst in this study. The P25 TiO₂ deposition process was carried out using acetone as precursor followed by drying at 110°C. The efficiency of P25 TiO₂-immobilized was compared to that of P25 TiO₂-dispersed under artificial UV. The degradation extents were 100% ($k = 0.0174 \text{ min}^{-1}$) and 92.2% ($k = 0.0070 \text{ min}^{-1}$) for the TiO₂-dispersed (0.5 g/L) and TiO₂-immobilized (2 plates = 0.4 g/L) respectively. The effect of the number of TiO₂P25-immobilized plates impregnated in the solution was studied. It was found that the process get better with the increasing of number of plates. Finally, the study of the reuse of TiO₂P25-immobilized showed that it could be reused several times.

Keywords: Photocatalysis, TiO₂P25-immobilized, Crystal Violet, Degradation, Water Treatment.

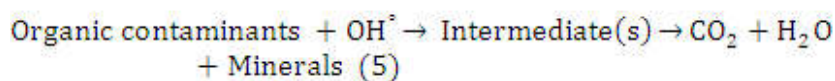
INTRODUCTION

TiO₂ photocatalysis has been extensively studied over the last three decades. The origin of the vast majority of these efforts is due to the fact that the material has an almost unique set of properties that allows for an effective direct transfer of light into highly reactive chemical species. These features can be exploited to tackle several contemporary global challenges involving pollutant degradation, photo organic synthesis and hydrogen production [1-2].

TiO₂ has been widely utilized as a photocatalyst for inducing a series of reductive and oxidative reactions on its surface. This is solely contributed by the distinct lone electron characteristic in its outer orbital. When photon energy ($h\nu$) of greater than or equals to the band gap energy of TiO₂ is illuminated onto its surface, the lone electron will be photoexcited to the empty conduction band in femtoseconds. The main oxidative-reductive reactions that occur at the photon activated surface were widely postulated as follows and also shown in Fig. 1 [3]:



The liquid phase organic compounds are degraded to its corresponding intermediates and further mineralized to carbon dioxide, water and minerals as follows:



Furthermore, it can reduce heavy metals to lower or metallic states.

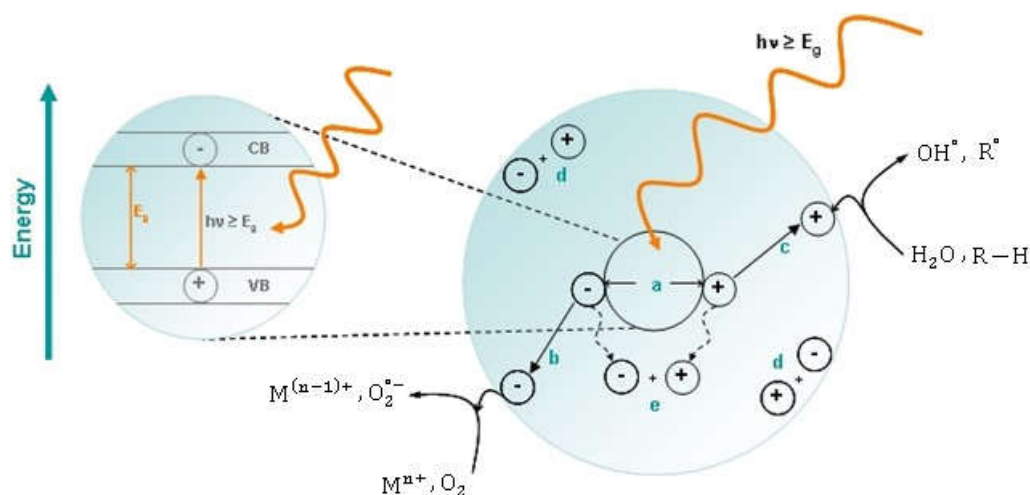
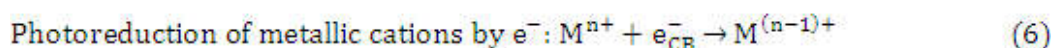


Fig. 1: Main processes occurring on a semiconductor particle: (a) photogeneration of electron/hole pair; (b) diffusion of the electron acceptor and reduction at the surface of the semiconductor; (c) oxidation of the electron donor on the surface of the semiconductor particle; (d) and (e) electron/hole recombination at the surface and in the bulk, respectively.

Regarding the catalyst configuration two main operating modes for photocatalysis can be distinguished: first the catalyst is applied in suspended form and second, the catalyst is immobilized on a substrate. The use of TiO₂ in suspension is efficient due to the large surface area of catalyst available for reaction and due to the absence of mass transfer limitations [4]. However, the need for a solid-liquid separation step to retrieve the catalyst after the reaction is a severe and expensive disadvantage of this system compared to the application of an immobilized TiO₂ system. On the other hand, the penetration depth of light is limited in slurries and the immobilized photocatalyst shows an inherent decrease in the specific surface area available for reactions [5, 6]. Assessing all the advantages and disadvantages for the different methods it can be said that the immobilized system shows more advantages mainly due to the cheaper running costs [7,8].

In the present work, the photodegradation of Crystal Violet (CV) was investigated using TiO₂P25-immobilized onto glass plates under UV irradiation (365nm). The performance of TiO₂P25-immobilized and in suspension was compared. The effect of the number of TiO₂P25-immobilized plates on the photodegradation extent and the reuse of the TiO₂P25-immobilized were investigated.

MATERIALS AND METHODS

Materials

P25 Titanium dioxide (Degussa AG Company) was used in this study. Its polycrystalline structure is composed of approximately 80% anatase and 20% rutile. It has a BET surface area of 50 m²/g and is approximately 21 nm as primary particles [9]. Acetone (Aldrich, 99.99%) was used for fixing P25 TiO₂ on glass plates. CV (MW = 408.979 g/mol, Fluka) of analytical grade was used without further treatment. Sample solutions of CV were prepared using double distilled water and protected from light. Its structure and absorption spectrum are shown in Fig. 2. A UV lamp TLD with a maximum emission located at 365 nm was used as an irradiation source.

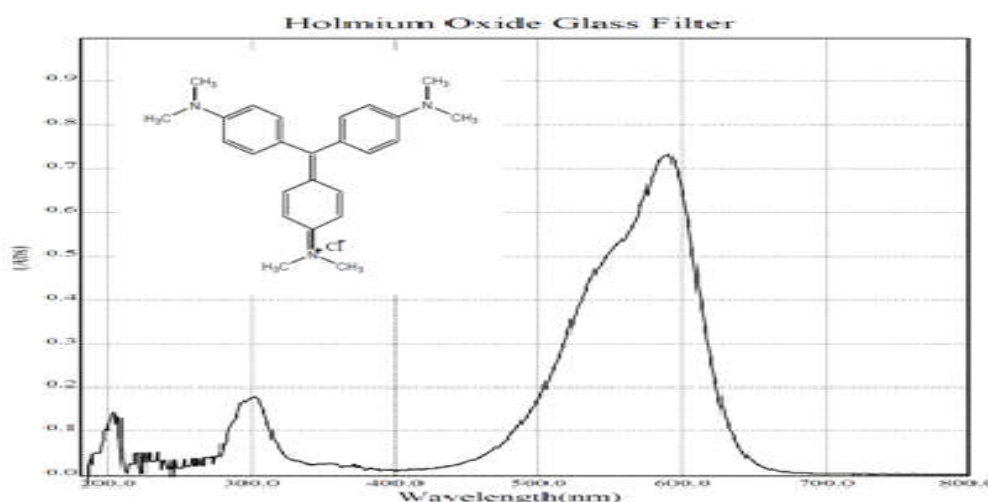


Fig. 2: Chemical structure and visible absorption spectrum of CV at [CV] = 10⁻⁵M, pH: 5.7.

Preparation of TiO₂P25-immobilized

The P25 TiO₂-immobilized used in this study was prepared by depositing P25 TiO₂ on glass plates (2.6 × 7.6 cm) according to a slightly modified method used by Bianchi et al. [10] and Tusnelda et al. [11]. Prior to their use, the glass slides were cleaned with double distilled water and acetone. A mixture of P25 TiO₂ and acetone (approximately 0.6 g TiO₂/30 mL acetone) was homogenized by mixing for 30 min then poured onto horizontally disposed glass slides and left until complete evaporation of the solvent. The plates were then dried overnight at 110°C to ensure strong fixation of TiO₂. This procedure enabled the formation of a thin layer of TiO₂, the mass of which on each glass slide was approximately 0.050 g.

Experimental procedure

The photocatalytic decolourization experiments of CV were performed using a static batch reactor consisting of 250 mL-Pyrex beaker, a UV lamp emitting in the range 300–400 nm with a maximum emission located at 365 nm was placed in a vertical position at 10 cm from the beaker. The intensity of the UV lamp measured at $\lambda = 365$ nm using a VLX-3W radiometer (France) with a cell diameter of 1 cm was around 0.3 mW/cm², measured at a

distance of 10 cm. The TiO₂ glass plates were kept in a slight inclination inside the beaker. During the experiments, samples (4 mL) were collected at selected time intervals. In the case of P25 TiO₂-dispersed, the samples were filtered through 0.45 µm-pore size membrane filters (Millipore Corp.). The decolorization of CV (maximum absorption at λ_{max}= 590 nm) was monitored using a UV-vis spectrophotometer (JENWAY 6405). The degradation extent of CV was calculated using Eq.7. The kinetics of the degradation process was investigated using a pseudo-first-order reaction according to a Langmuir-Hinshelwood kinetic model (Eq.8).

$$\text{Degradation extent (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (7)$$

$$\ln \frac{C_t}{C_0} = -kt \quad (8)$$

Where C_0 and C_t represent the CV concentration (M) before and after the treatment, t is the irradiation time (min), k is the apparent rate constant.

RESULTS AND DISCUSSION

Photodegradation of CV under UV (365nm)

Fig. 3 shows the photodegradation of crystal violet using both immobilized and dispersed photocatalysts under UV irradiation. The figure presents also the kinetic study based on pseudo-first-order reaction kinetics. The contribution of the direct photolysis of CV under UV irradiation (without photocatalyst) was around 10 % after 6 h. From this result we observe that the TiO₂ in suspension is more efficient than the immobilized. The removal extents were 100% ($k = 0.0174 \text{ min}^{-1}$) and 92.2% ($k = 0.0070 \text{ min}^{-1}$) for the dispersed and the immobilized photocatalysts respectively. This is due to the large surface area of catalyst available for the reaction between the substrate and P25 TiO₂-suspension. Although the P25 TiO₂-suspension is more efficient than the P25 TiO₂-immobilized, it is worth recalling the main drawback associated with the use of the former, namely the post filtration step, the tedious recuperation of photocatalyst [12]. Besides, the quantity of P25 TiO₂-dispersed (0.5 g/L) is relatively larger than the P25 TiO₂-immobilized (0.05 g/slide corresponding to approximately 0.4 g/L of TiO₂). Taking into account these considerations, the use of P25 TiO₂-immobilized in the CV photocatalytic decolorization confirms the relatively higher efficiency that offers this method for wastewater treatment.

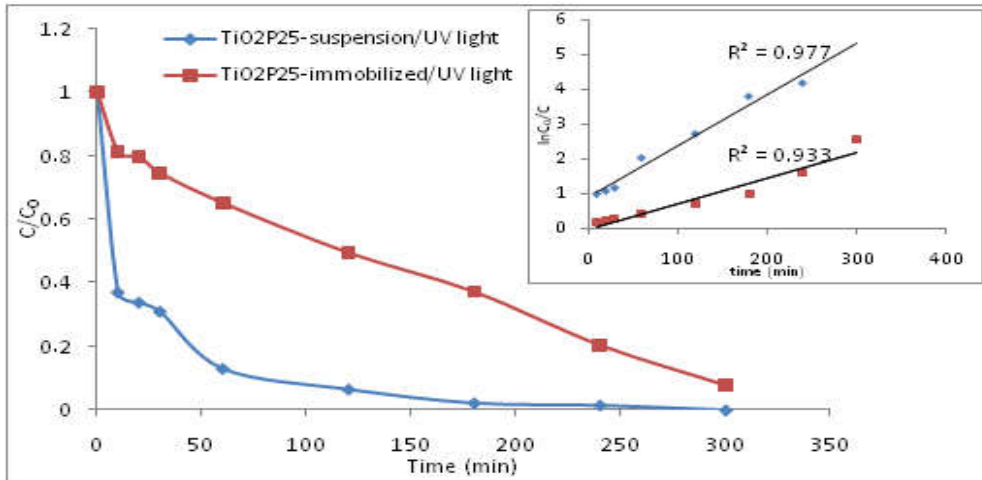


Fig. 3: Photodegradation of CV using TiO₂P25- immobilized and in suspension under UV irradiation (365 nm). Conditions: [CV]: 10⁻⁵M, pH: 5.7, [TiO₂P25-suspension]: 0.5g/L, number of plates of TiO₂P25-immobilized: 2.

Effect of plates number of TiO₂P25-immobilized

The [catalyst]/[pollutant] ratio is an important parametre in the photocatalytic treatment. Fig. 4 shows the dependence of the number of the P25 TiO₂-immobilized plates on the CV photocatalytic decolourization. From this figure, it can be noticed that, as anticipated, the process of CV decolourization increases with the number of plates impregnated in the solution. This enhancement is most probably due to the production of more oxidizing species when the number of plates increases leading to a faster decolourization process. The pseudo-first-order decolourization also applies under these conditions. The apparent rate constants increase proportionally to the number of slides used.

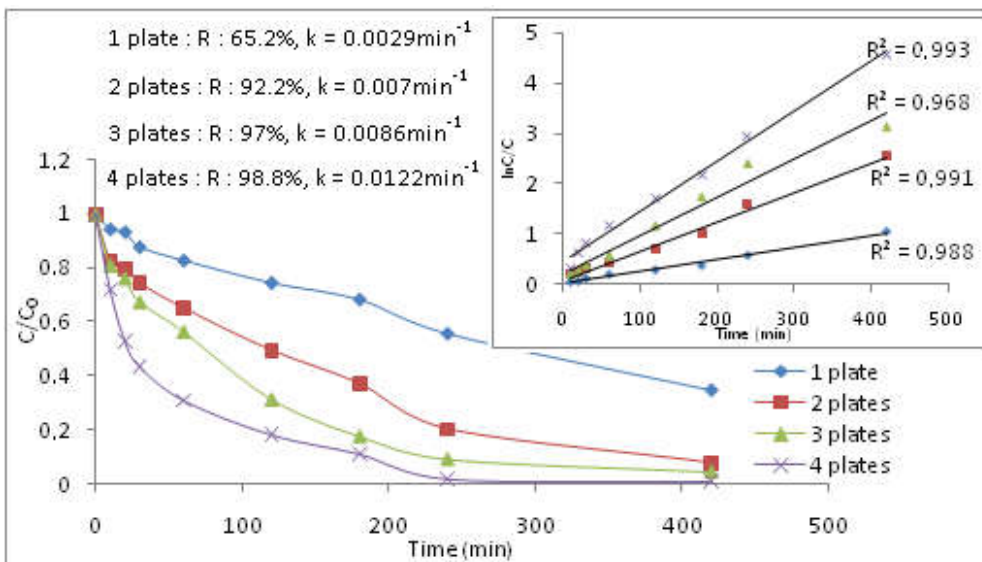


Fig. 4: Effect of number plates of TiO₂P25- immobilized on the CV photodegradation under UV irradiation Conditions: pH: 5.7, [CV]: 10⁻⁵M.

Reuse of TiO₂P25- immobilized

One of the main drawbacks of the photocatalytic processes that use dispersed photocatalysts is the relatively high cost of step of TiO₂ recuperation. Consequently, it is interesting to reduce the cost of this process by making reuse of the supported photocatalyst. In this study, the reuse of the TiO₂P25- immobilized was tested under the same working conditions for 6 times. Prior to its reuse, the plate of the TiO₂P25-immobilized was washed with double distilled water then dried for 2 h at 110°C. The results show that the TiO₂P25-immobilized can be used several times with a decreasing in the degradation extents of crystal violet (Fig. 5). The ratio of the loss of the removal rate calculated for six uses of the same plate is around 6 % / use. This decreasing in the efficiency may be due to the adsorption of by-products of the CV decolourization on the photocatalyst surface together with some loss of TiO₂ particles. However, considering the simple method of deposition of TiO₂, this result indicates a relatively good stability after six usages of the TiO₂.

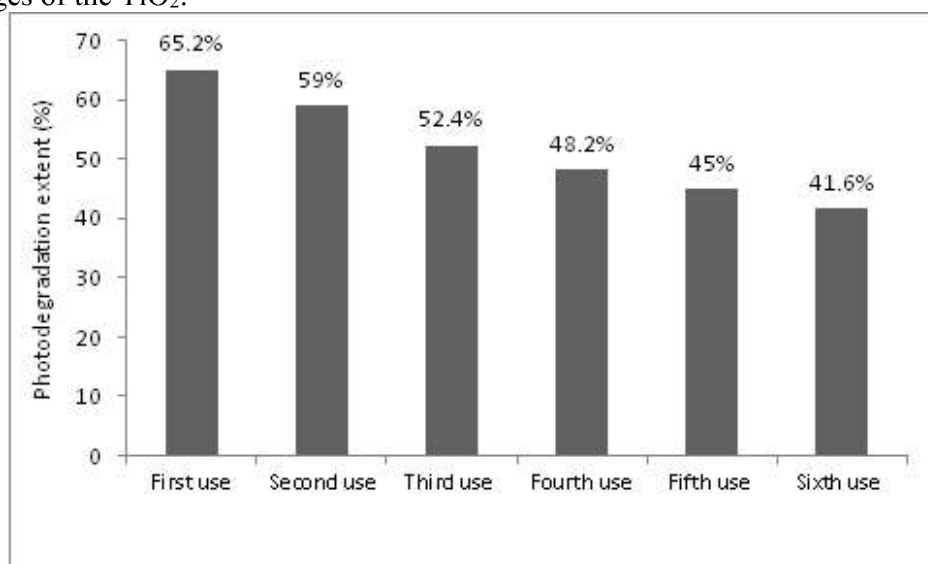


Fig. 5: Reuse of the TiO₂P25-supported for the degradation of CV under UV. Conditions: [CV]: 10⁻⁵M, pH: 5.7, number of TiO₂P25- immobilized plates: 1, Time: 6 h.

CONCLUSION

The application of TiO₂-immobilized on glass plates has been proven to be effective for the crystal violet decolourization under UV irradiation. The decolourization process increases with the increase in the number of TiO₂ glass plates. The reuse of TiO₂-immobilized illustrates a relatively good stability of the TiO₂ particles on the glass slide using a simple deposition method. The use of TiO₂-immobilized presents numerous economical advantages such as relatively small quantity of TiO₂ used, absence of filtration and possibility of its reuse.

ACKNOWLEDGEMENTS

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