Sciences &TechnologieA – **N°39** Juin. 2014, 23-30

PHOTOCATALYTIC DEGRADATION OF YELLOW ALIZARIN AZO DYE IN THE PRESENCE OFTIO_2SUSPENSION

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Reçu le 12/05/2014 – Accepté le 24/06/2014

Abstract

The present work involves the prospects of the kinetics study for photocatalyticdecolorization of an azo dye (Alizarin yellow) in aqueous solution with TiO_2 Degussa P25 as photocatalyst in slurry form using UV-A light at 365nm.The results showed that the adsorption of alizarin yellow on TiO_2 P25 was found negligible and discoloration of this dye by TiO_2/UV system is much faster than with direct UV photolysis. Additionally, the effects of various parameters such as initial dye concentration, catalyst dosage,H_2O_2 concentration, addition of alcohols and presence of inorganic salts on decolorization have been investigated. The removal rate of Alizarin yellow indicated an inverse dependence on the initial dye concentration. The optimal content of the catalyst was 1 g.L^{-1}. The disappearance kinetics was strongly enhanced in the presence of electron acceptors such as H_2O_2.However,the presence in the reacting system of Cl^-, SO_4^{2-} (Addition of dye assisting chemicals such as Cl^- and SO_4^{2-})inhibits the dye removal rate. The study of the effect of different type of TiO_2 on the decolorization reveals the following order of efficiency: TiO_2- P25> TiO_2Tiona PC.

Keywords: *Alizarin yellow, hydrogen peroxide, photocatalysis, TiO_2 Degussa P25.*

Résumé

Ce travail porte sur l'étude de la cinétique de décoloration photocatalytique d'un colorant azoïque, le jaune d'alizarine, en présence d'une suspension aqueuse de TiO_2Degussa P25 sous irradation UV-A à 365nm. Les résultats montrent que l'adsorption du jaune d'alizarine sur le TiO_2 P25 a été trouvée négligeable et la décoloration du colorant est beaucoup plus rapide avec TiO_2/UV qu'avec la photolyse directe UV. En outre, L'influence des paramètres tels que la concentration initiale du polluant, le chargement du catalyseur, la concentration en H_2O_2, l'addition alcools et la présence de sels inorganiques a été étudiée. Le taux de la décoloration du jaune d'alizarine, indique une dépendance inverse de la concentration initiale en colorant. La teneur optimale du catalyseur était de 1 g.L^{-1}. La cinétique de disparition a été fortement améliorée en présence d'accepteurs d'électrons, tels que H_2O_2. Cependant, la présence des Cl^- et SO_4^{2-} dans le système réactionnel inhibe le taux d'élimination de ce colorant. L'étude sur l'effet de différents types de TiO_2 sur la décoloration révèle l'ordre d'efficacité suivant: TiO_2-P25> TiO2 Tiona PC.

Mots Clés: *Jaune d'alizarine, peroxyde d'hydrogène, photocatalyse, TiO_2Degussa P25.*

ملخص.

هذا العمل يضم دراسة التفكك الضوئي المحفز للصبغ الأزويكي أصفر الأليزارينفيوجودمعلقمائي كان TiO_2Degussa P25 باستخدام الأشعة فوق البنفسجية عند 365 نانومتر.النتائج بينت لنا أن إدمصاص أصفرالأليزارين على TiO_2 P25مهمل، وأن إزالة الصبغ بواسطة التحفيز الضوئي أسرع بكثير من التفكك الضوئي المباشر. و أيضا تم دراسة تأثير العوامل مثل التركيز الابتدائي للصبغ ، تركيز المحفز، تركيز H_2O_2، إضافة الكحولات و وجود الأملاح اللاعضوية. بحيث وجدنا أن نسبة إزالة الصبغ للأصفر الأليزارين يتناسب عكسيا مع التركيز الأولي للصبغ. و المحتوى الأمثل للمحفز هو 1gL^{-1}. وقد تم تحسين حركية إختفاء الصبغ بقوة في وجود مستقبلات للإلكترونات مثلH_2O_2. لكن وجود الكلوريدات والكبريتات يؤخر معدل إزالة الصبغة. علاوة على ذلك، الدراسة حول تأثير مختلف أنواعTiO_2 في عملية إزالة الصبغ بينت ترتيب الفعالية كالتالي: TiO_2-P25> TiO_2Tiona PC.

أصفر الأليزرين,بيرو كسيد الهيدروجين, التحفيز الضوئي, **الكلمات المفتاحية:**TiO_2Degussa P25.

1. Introduction

Large amounts of the dyes used in the textile industry are lost to effluents during manufacturing operations and processing [1]. These colored dye effluents are causing severe damage to aquatic life (fauna and flora) by impeaching penetration of solar light which is vital to its metabolism [2,3]. Many of these dyes are toxic, non-biodegradable and potentially carcinogenic [4-6]. They may affect the environment in different ways. Among the important textile dyes, azoic dyes, which contribute to about 70% of all used dyes [7]. They are characterized by the presence of one or more azo group (-N=N-) bound to aromatic rings.

Azo dyes are difficult to degrade by biological treatment [8], methods due to their complex structure and the stability [7]. Conventional techniques like adsorption [9], flocculation [10] and coagulation [11] are not effective methods because they lead to solid waste, creating other environmental problems, requiring therefore further treatment [5].

Recent developments of advanced oxidation processes (AOPs), led to further improvements in the oxidative destruction of dyes and many other organic compounds in wastewater and effluents. These processes generally involve systems as Photo-Fenton, semi-conductor/ UV, UV/H_2O_2 or UV/O_3 for the oxidative degradation of contaminants, which gives encouraging results from the removal of the color reagent azo dye containing waters [12]. Among these processes, Semi-conductors photocatalysts appear to be very interesting of their high efficiency, availability of trade and high chemical stability [13].

Heterogeneous photocatalysis using titanium (TiO_2) dioxide as photocatalyst is highly regarded as a promising technology destructive for the treatment of polluted air and water due to a number of advantages [14-16]. Among of these advantages we can list: the process which may destroy the polluting compounds and also which may decompose it into non-toxic substances using the irradiation of light in UV or near UV region. Environmentally important materials can be also used as a photocatalyst semi-conductor, especially TiO_2, which is the most used. This method can be performed under mild conditions like: room temperature and atmospheric pressure. Finally, it may cause complete degradation of most organic contaminants without causing secondary pollution problems [17].

When TiO_2 is irradiated under wavelength at $\lambda<390$ nm, electrons are promoted from the valence band to the conduction band to give electron–hole pairs through the following reaction Eq.(1) [18,19]:

$$TiO_2 + h\upsilon\ (<390\text{nm}) \rightarrow e^- + h^+ \quad (1)$$

The valence band (h^+) potential is positive enough to generate hydroxyl radicals at the surface of TiO_2 and the conduction band (e−) potential is negative enough to reduce molecular oxygen as shown in Eqs. (2–6):

$$e^- + O_{2\,(ads)} \rightarrow {}^{\bullet}O_{2\,(ads)}^{-} \quad (2)$$
$$e^- + H_{(ads)}^{+} \rightarrow {}^{\bullet}H_{(ads)} \quad (3)$$

$${}^{\bullet}O_{2(ads)}^{-} + H^+ \rightarrow HOO^{\bullet} \quad (4)$$

$$2HOO^{\bullet} \rightarrow H_2O_2 + O_2 \quad (5)$$

$$H_2O_2 + {}^{\bullet}O_{2(ads)}^{-} \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad (6)$$

The hydroxyl radical is a strong oxidizing agent and will attack organic matter present in or near the surface of TiO_2. It causes, ultimately, the complete decomposition of toxic compounds into harmless species (CO_2, H_2O, …)[20-22].

The main objective of this work was to study the photocatalyticdecolorization of Alizarin Yellow at 365 nm (TiO_2/UV system). The effect of parameters such as: initial concentration of substrate and catalyst, addition of H_2O_2, alcohol and inorganic salts, was studied in order to illustrate the efficiency of this process.

2. Materials and methods

2.1. Materials

Alizarin yellow was purchased from Fluka chemical company and used without further purification; its molecular structure is shown in Fig1. Degussa P25 titanium dioxide was used as the reference photocatalyst. It is mostly in the form of anatase and has a BET surface area of 55m^2 g^{-1}, corresponding to a mean particle size of ca. 30 nm. Millennium PC500 titanium dioxide (100% anatase, specific surface area of 320 m^2 g^{-1}) [23] and other Millennium catalyst powders namely PC50, PC100 and PC105 were used for comparative study. Hydrogen peroxide solution (30%) was obtained from Labosi, ethanol (99%) and ter- butanol (99%) provided by Prolabo, sodium chloride (99.5%) provided by Labosi and sodium sulfate (99%) provided by Aldrich. Besides, pH was adjusted with NaOH or HCl to reach the desired value.

Fig.1. Structure of Alizarin yellow.

2.2. Procedure and analysis

The irradiation device used in the photocatalyst consists of a fluorescent tube « Philips TLAD 15 W/05 » placed at the location of one of the focal axes of an elliptical base metal cylinder. The emission spectrum of this lamp has a maximum at about 365 nm and a bandwidth of 50 nm at half maximum. The pyrex reactor with double cover, allowing circulation of water, is placed along the other focal axis. The homogeneity of the medium is provided by a magnetic stirrer.

The irradiation experiments were carried out with 50 ml of Alizarin yellow solution with a desired concentration of dye and TiO_2 at natural pH and 20°C. This mixture has been agitated in the dark for 30 minutes before illumination in order to reach the absorption equilibrium reaction. TiO_2 particles are removed by filtration on Millipore filters, 0.45 µm prior to analysis.

The UV-visible absorption spectrum was 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 428 nm for present substrate.

3. Results and discussion

3.1. UV–vis spectrum of Alizarin yellow

The UV-Vis spectrum of Alizarin yellow at natural pH (6.1) and dilute medium (50ppm), shows that it consists of two bands of variable intensity and located respectively at 257 nm and 428 nm(ε=3735 $l.mol^{-1}.cm^{-1}$). The pH influenced the behavior of Alizarin yellow in basic medium (pH = 11.5), where we observed a color change of the solution (turning into purplish red) with a displacement of the most intense band (λ= 428nm to 528nm) and an apparition of a new band (λ = 334nm) accompanied with a relatively important increase in the absorption coefficient (ε=6875$l.mol^{-1}.cm^{-1}$). By contrast, in acidic medium (pH =1.7), we observed no change in color or band positions (Fig2).

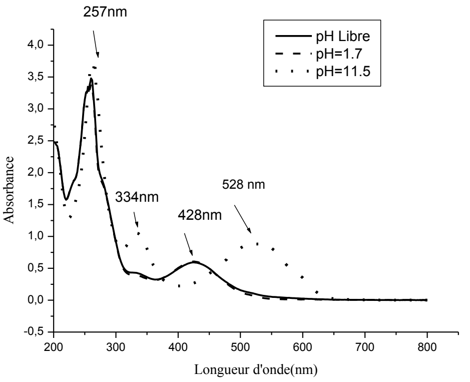

Fig.2. Spectrum of Alizarin yellow (50ppm). Influence of pH (50ppm).

3.2. Adsorption of alizarin yellow onto TiO_2 surface

Before proceeding to the study of the photocatalytic of Alizarin yellow decolorization by TiO_2/UV, it was useful to check first, the adsorption capacity of TiO_2 towards the substrate in the absence of UV irradiation. To do this, we followed the evolution of this process for a time of 180 minutes and for the following experimental conditions: [dye] = 70 ppm, T = 20°C, pH=6.5 and [TiO_2] = 1g/L.

The results showed that the adsorption of Alizarin yellow on the semiconductor was low for this reaction time (Fig3). Therefore, the adsorption of Alizarin yellow on the TiO_2 is negligible. This will allows us, to situate clearly the proper efficiency of TiO_2 / UV system.

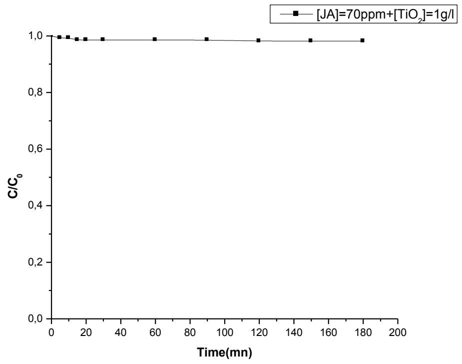

Fig.3. Adsorption of Alizarin yellow (70ppm) on TiO_2 (1 g/L)

3.3.Preliminary experiments: photolysis and photocatalysis of Alizarin yellow

Suspensions containing TiO_2 (1g/L) and Alizarin yellow (70 ppm) were first put in contact and then irradiated at 365 nm. The results presented in Fig 4, showed that disappearance of the dye is much faster with TiO_2/UV than with direct UV photolysis alone for the considered reaction time (6 h). This could be due to a very feeble adsorption of substrate to this wavelength and also to the very weak quantum yield of photolysis (photolysis alone). It was initially observed too, that no adsorption of Alizarin yellow occurred in presence of TiO_2 alone. However, the decolorization of the dye solution is accelerated in presence of the photocatalysis process. This feature could be due to the presence of hydroxyl radicals.

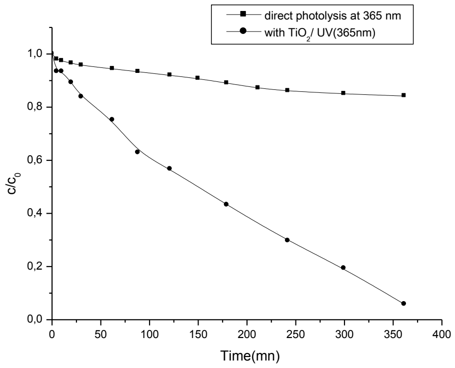

Fig.4. Decolorization process of Alizarin yellow by direct photolysis (365 nm)and by TiO_2/UV ($[TiO_2]_o$ = 1 g/L, λ = 365 nm andpH = 6.9).

This result demonstrates that the photocatalytic experiments occurred in a pure photocatalytic regime where photochemical processes can be neglected[23],and appear the degree of effectiveness of heterogeneous photocatalysis.

3.4. Effect of photocatalyst dosage

The effect of catalyst loading on the degradation of Alizarin yellow was investigated using Degussa P-25 from 0.1to 2 g/L keeping all other parameters constant.. The results obtained show that the rate of decolorization increase with TiO_2 concentration and reach a maximum at 1 g/l for TiO_2 catalyst.

Similar findings, have been reported for the photocatalytic oxidation of other dyes [24,25]. The reached plateau depends from more factors such as: geometry and operating conditions of the reactor, wavelength and intensity of the light source corresponding to the point where the entire catalytic surface is fully illuminated [26]. The optimum catalyst loading is found to be dependent on initial solute concentration because of the increase of catalyst dosage and also the total increase of the active surface; hence we deduce an availability of more active sites on catalyst surface [27,28]. At high concentrations of catalysts, particle aggregation may also reduce the catalytic activity by reducing the specific surface.

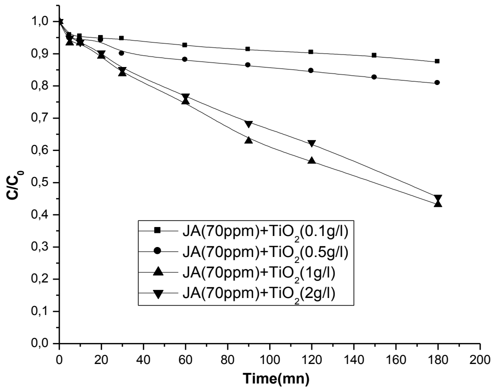

Fig.5. Effect of TiO_2 concentration on the photocatalytic degradation of dye.(λ = 365 nm and pH = 6.9)

3.5. Effect of initial dye concentration:

The pollutant concentration is a very important parameter in wastewater treatment.The effect of initial concentration of Alizarin yellow was studied at natural pH, at ambient temperature and catalyst loading of 1g/L. The kinetics of decolorization reported in Fig.6,showsthat the removal rate of Alizarin yellow, depends strongly on the initial concentration. This is attributed to the amount of $^{\bullet}OH$ and $O_2^{\cdot-}$ .Indeed, this amount does not increase because the surface of the TiO_2 (taken at 1g/L) remains constant. However, their quantity decreases with increasing the concentration of the substrate.

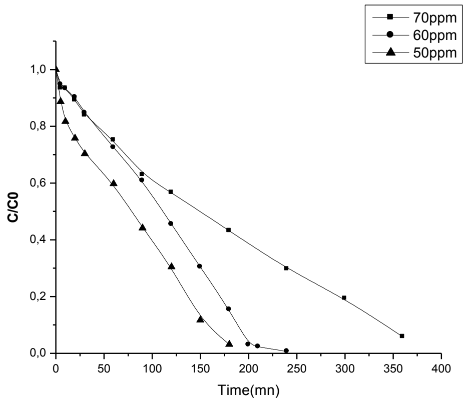

Fig. 6. Effect of initial Alizarin yellow concentration on the photocatalytic degradationby TiO_2/UV :($[TiO_2]_o$ = 1 g/L, λ = 365 nm and pH = 6.9).

3.6. Effect of addition of H_2O_2

The effect of addition of H_2O_2(10^{-1}, 10^{-2} and 10^{-3}M)on the photocatalytic oxidation has been carried. Hydrogen peroxide accelerates the photodegradation of organic compounds due to its strong oxidizing and character of dissociation hydroxyl radicals. This can be explained by three-way:

$H_2O_2 + e^- \rightarrow HO^\bullet + OH^-$(7)
$H_2O_2 + HO^\bullet \rightarrow HO^\bullet_2 + H_2O$ (8)
$H_2O_2 + HO^\bullet_2 \rightarrow HO^\bullet + H_2O + O_2$ (9)

Fig.7. shows that the addition of H_2O_2 in TiO_2/UV system accelerates the initial rate of disappearance of Alizarin yellow. The total elimination was reached in 60 minutes under irradiation at 365nm and in the following experimental conditions: 10^{-1}M on H_2O_2 and 1 g/L of TiO_2. Increasing rate can be attributed to an increase in the concentration of $^\bullet$OH radicals at the surface of TiO_2.

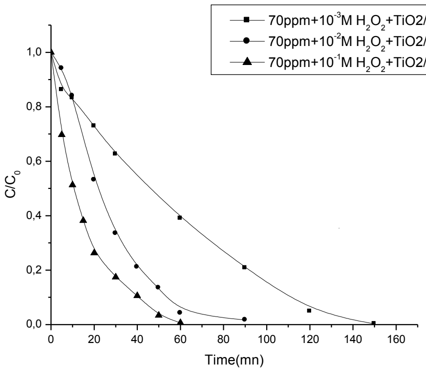

Fig.7. Effect of hydrogen peroxide concentration on the photocatalytic degradation of Alizarin yellow (70ppm) in the presence of TiO_2 (1g/l) and λ= 365 nm and pH = 6.9).

According to present experimental results represented in Fig. 8, the decolorization 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.1).

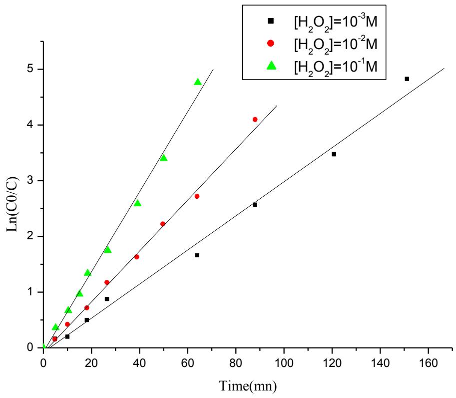

Fig. 8. Kinetic study of the process of photocatalytic discoloration of yellow Alizarin in presence of H_2O_2 ($[TiO_2]_o$ = 1 g/L, λ = 365 nm and pH = 6.9).

Table.1: Values of apparent rate constant at various concentration of H_2O_2 on the photocatalytic degradation of Alizarin yellow.

$[H_2O_2]$ M	Rate constant (mn^{-1})	Correlation coefficient (R)
10^{-3}	3,06 10^{-2}	0,99203
10^{-2}	4 ,57 10^{-2}	0,99612
10^{-1}	7,182 10^{-2}	0,99396

3.7. Effect of the addition of alcohols

Literature data indicate that the choice is usually worn on ethanol, isopropanol and tertiobutanol as a result of their high reactivity towards hydroxyl radicals (rate constant elevated of the order of 10^9-10^{10} $M^{-1}s^{-1}$[29] whereas tertiobutanol is a little lower [30]. Alizarin yellow solution was irradiated in the presence of tertiobutanol and ethanol (2%) in order to evaluate the participation of $^\bullet$OH radicals during photocatalytic degradation of the dye. Results represented in Fig.9, showed the inhibition effect for low concentration of these alcohols (2%).Thus, one can conclude that the photodegradation process might occur within two routes: The first viaradicals $^\bullet$OH 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 [31,32].

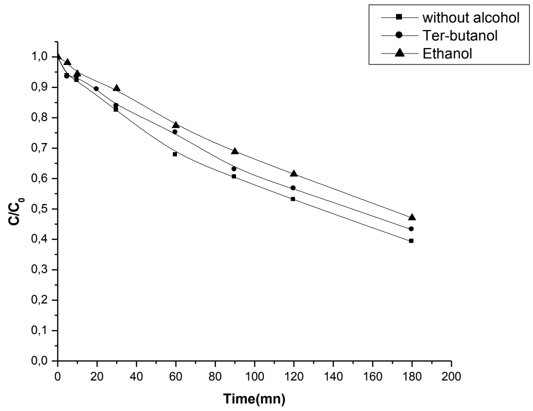

Fig.9. Effect of ethanol and tertiobutanol (2%) on decolorization of Alizarin yellow ($[TiO_2]_o$= 1g/L, pH = 6.9andλ = 365 nm).

3.8. Effect of anions (chlorides and sulphates)

The physicochemical water analysis often revealed the presence of Cl^-, SO_4^{2-}, NO_3^- and HCO_3^- ions with values depending on the nature of the effluent, and the site where taken the samples [33]. Therefore, to evaluate the importance of the presence of anions in the medium, a mixture of TiO_2 (1g/L) and Alizarin yellow (70ppm) was irradiated in the presence of various amounts of chloride and sulphate sodium.

The results displayed in Fig.10, demonstrate clearly that these amounts when they are elevated enough; they can diminish the decolorization rate of the dye. Therefore, the sulphates and the chlorides ions have an inhibiting effect on the decolorization of the photocatalytic reaction of the substrate. This fact could be attributed to the adsorption of these ions to the catalyst surface (the adsorption causes blocking of the active sites of the photocatalyst) and/or to their competition with the pollutant to react with the generated radicals.

Thus, for the chlorides which strongly inhibit the kinetics of degradation, it was reported that these ions trap oxidizing hydroxyl radicals (Eq.10)[34]:

$$Cl^- + HO^\bullet \rightarrow Cl + OH^- \qquad (10)$$

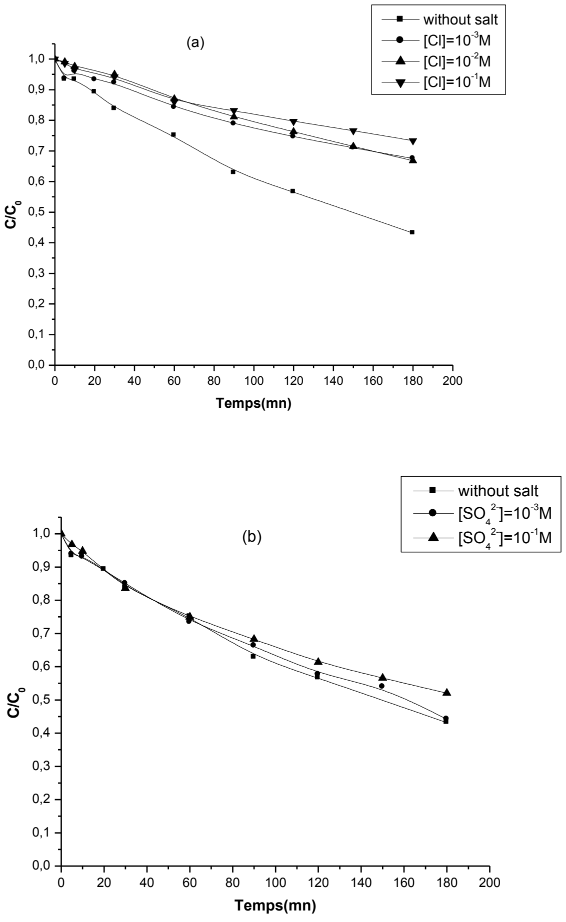

Fig.10. Influence of salts at various concentrations ($[TiO_2]_o$ = 1 g/L, pH = 6.9,λ = 365 nm): (a) with chlorides, (b) with sulphates.

3.9. Comparison of photocatalytic activity of different types of TiO2

The effects of various photocatalyst such as TiO_2-P25, PC50, PC100 and PC105 were studied on decolorization at1g/L.keeping all other parameters constant.Fig.11, shows the disappearance of alizarin yellow in the presence of different types of titanium dioxide.It appears that the TiO2 Degussa P25 has better photocatalytic activity than those of TiO_2 Tiona PC, despite the fact that Tiona PC have greater specific surface than the Degussa P25. Therefore, titanium dioxide (Degussa P25) is the most effective Millennium photocatalyst contain mainly anatase while P25 consists on 70% of anatase and 30% on rutile (Table.2) [23]. These results confirm that the specific surface is not the only factor affecting the photocatalytic activity but the structure and the condition of the surface have a fundamental role. Increasing the density of surface for example, can promote the electron-hole recombination and reduce the performance of these types of semi-conductor.

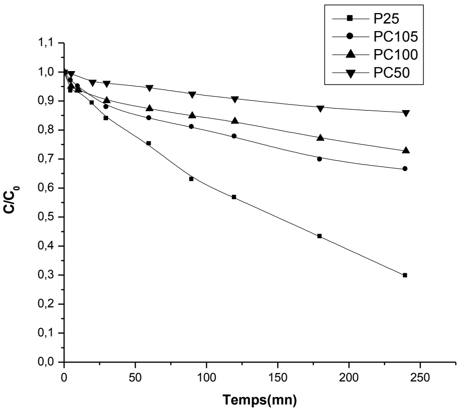

Fig. 11. Kinetics of photodegradation of alizarin yellow by different types of TiO_2 (1g/L); (pH = 6.9,λ = 365 nm)

Table2: Chemical and physical properties of the photocatalysts.

Catalyst	Composition (%) Anatase /rutile	Specific surface (m^2 g^{-1})	Particle size (nm)	Density (kg m^{-3})
P25	70 / 30	55	30	3800
PC50	100	45 ± 5	20-30	-
PC100	100	80-100	15-25	600-900
PC105	100	250>	5-10	-

4. Conclusion

The results of this work show that:

- TiO_2/UV system is more efficient than direct UV photolysis in the decolorization process of yellow Alizarin at 365 nm.
- Disappearancerate increases with the catalyst loadingin the medium, but the dosage is not necessary to improve the activity of the photocatalyst. Indeed, this activity is limited by photonic absorbance and aggregation of these particles.
- The presence of anions such as chlorides and sulphates, leads to partial inhibition of decolorization of alizarin yellow. This result is attributed to either a competition reaction of the

dye and the ion with respect to hydroxyl radicals or to an adsorption of the pollutant and competition of these ions

- The addition of H_2O_2 improves the performance of depollution technology of photocatalysis.
- Alcohols act as traps for the $^{\bullet}$OHradicals in the transformations that occur in a heterogeneous medium, associated with radiation.
- TiO_2-P25 is the most efficient despite its slowest specific surface. That is why we worked in this study with TiO_2 Degussa P25.
- Photocatalysis could be useful as a pretreatment technique to reduce the toxicity of polluted water .

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