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Photocatalytic treatment of colored wastewater from medical laboratories: Photocatalytic oxidation of hematoxylin

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Abstract

The decolorization and organic content reduction of a synthetic Harris' Hematoxylin (SHH) solution, which is widely used in biochemical and biomedical laboratories, by the use of heterogeneous and homogeneous photocatalytic methods under artificial irradiation has been studied. In the case of heterogeneous photocatalysis the effect of two different commercial TiO_2 products with oxidants such as H_2O_2 on the decolorisation and the organic content reduction (COD) of the wastewater was examined. Reuse experiments had shown that TiO_2 P-25 retains its activity nine times concerning the decolorization of the solution and four times concerning the COD reduction. The Photo-Fenton process activated by using UV-A or visible light appears to be more efficient for this type of wastewater in comparison to the TiO_2/oxidant system. The apparent initial photonic efficiency (ζ) of decolorization, as well as mineralization under various experimental conditions has been calculated.

Keywords: Hematoxylin; Hematein; Biomedical wastewater; Photocatalysis; TiO_2; Photo-Fenton

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1. Introduction

Biological stains such as Hematoxylin, Eosin Y, Rose Bengal and Auramine O are widely used in biomedical research laboratories and also for diagnostic purposes. Some of these stains are known to be toxic or mutagenic for human and animals [1]. Although the volume of the stain solutions used in these kind of laboratories is relatively small, the very high concentration of dyes in them ($1\,g\,L^{-1}$ Hematoxylin, $\sim 10\,g\,L^{-1}$ Eosin Y or $5\,g\,L^{-1}$ Rhodamine B in Auramine-Rhodamine Fluorescence solution [2,3]) and the presence of various harmful additives, results in the formation of wastewater of high toxicity, low light transparency and high organic carbon content.

According to our knowledge, the methodology that is mainly used for the removal of these biological stains from their solutions is their sorption either on activated carbon or on a polymeric resin (i.e. Amberlite XAD-16) [1]. However the problem is not solved with these methods, but is just moved from the liquid to the solid phase. In addition, the recovery efficiency is not the same for all biological stains and in some cases, a large amount of adsorbent is necessary for their complete removal.

The photocatalytic treatment of solutions containing organic dyes have been reviewed. Decolorization and reduction of the organic content of these dyes in the presence of natural or artificial near UV (UV-A) [4–7] or visible light [8,9] has been shown to be promising.

Concerning the previous mentioned problem, a research program was designed on the application of heterogeneous photocatalysis, as well as of Photo-Fenton's reagent, for the oxidation and decolorization of wastewaters from biochemical and biomedical laboratories. Its main objective was to eliminate the more dangerous pollutants in a chemical stage before their environmental release.

In the present paper, we report for the first time the photocatalytic decolorization and oxidation of simulated wastewater from biomedical laboratories, containing Hematoxylin as a model dye, which is the most world widely used counterstain in routine staining of histological tissue sections [2,3].

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2. Experimental

2.1. Reagents

TiO_2 P-25 of Degussa (anatase/rutile = 3.6/1, surface area 56 $m^2\,g^{-1}$ nonporous) and a commercially available TiO_2 (A) (Tronox A, McGee, 100% anatase, surface area 11.7 $m^2\,g^{-1}$) were used for all heterogeneous photocatalytic experiments. The TiO_2 (A) was chosen due to its considerably good photocatalytic properties and because of its lower price, in relation to TiO_2 P-25. All other reagent-grade chemicals, such as $FeCl_3 \cdot 6H_2O$ and H_2O_2 were purchased through Merck and were used without further purification.

2.2. Simulated Harris' Hematoxylin solution (SHH)

The conversion of Hematoxylin ($C_{16}H_{14}O_6$, Fig. 1A), which is not a dye itself, to the dye Hematein ($C_{16}H_{12}O_6$, Fig. 1B) is accomplished after exposure of the solution to atmospheric oxygen or by the use of oxidants such as $NaIO_3$, HgO and $KMnO_4$. Hematein itself has a low affinity for tissues, but in combination with alum ($AlK(SO_4)_2$), it is converted to a strong anionic chelate dye.

Depending on the oxidizing agent and the various additives, there are several types of Hematein solutions, the most important are Harris' Hematoxylin, Mayer's Hematoxylin και Delafield's Hematoxylin. In the case of Harris' Hematoxylin and Mayer's Hematoxylin solutions, HgO and $NaIO_3$ are used as oxidizing agents respectively, while for Delafield's Hematoxylin the oxidation is simply done by exposure to atmospheric oxygen. In the present study Harris' Hematoxylin was chosen as a model solution for homogeneous and heterogeneous photocatalytic experiments. Hematein was used instead of Hematoxylin for the experiments without HgO. The initial solution of the simulated Harris' Hematoxylin used in all experiments has the composition shown in Table 1 [3].

Hematein ($C_{16}H_{12}O_6$) a product of Sigma Chemie GmbH was used as received. $AlK(SO_4)_2 \cdot 12H_2O$, ethyl alcohol and acetic acid were purchased through Merck and were used without further purification.

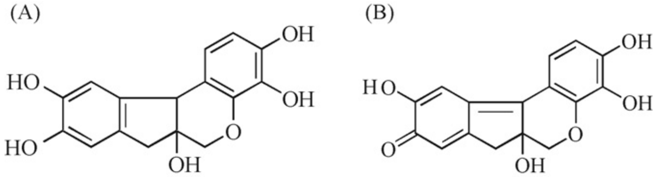

Fig. 1. Molecular structure of Hematoxylin (A) and Hematein (B).

Table 1
Simulated Harris' Hematoxylin solution (SHH)

Composition	C ($g\,L^{-1}$)
Hematein	1
$AlK(SO_4)_2 \cdot 12H_2O$	20
Ethyl alcohol	7.9
Acetic acid	4.2

This simulated Harris' Hematoxylin solution (SHH) gives a mean dissolved organic carbon (DOC) concentration of about 5.6 $g\,L^{-1}$ (13.75 $g\,L^{-1}$ COD). For the experiments conducted in this paper a 1:20 dilution of the initial SHH solution was used, with an initial Hematein concentration of 50 $mg\,L^{-1}$ and an initial organic content expressed as COD, of 690 $mg\,L^{-1}$ (280 $mg\,L^{-1}$ DOC).

2.3. Procedures and analysis

Experiments were performed in a closed Pyrex cell of 500 mL capacity. The reaction mixture in the cell was maintained homogeneous by magnetic stirring. The reaction vessel was fitted with a central 9 W lamp and had inlet and outlet ports for bubbling the desired gas under which the reaction was taking place. The spectral response of the irradiation source (Osram Dulux S 9W/78, UVA) according to the producer, ranged between 350 and 400 nm with a maximum at 366 nm and two additional weak lines in the visible region. For the experiments with Photo-Fenton reagent except for UV-A irradiation a visible light irradiation source with exactly geometry was used. The spectral response of this irradiation source (Osram Dulux S 9W/71, Vis) according to the producer, ranged between 400 and 520 nm. The photon flow per unit volume of the incident light was determined by chemical actinometry using potassium ferrioxalate [10]. The incident photon flow of UV-A light, under exactly the same conditions as in the photocatalytic experiments, was estimated to be 6.3×10^{-4} Einstein $L^{-1}\,min^{-1}$, while the incident photon flow of the visible light was estimated to be 5.8×10^{-4} Einstein $L^{-1}\,min^{-1}$.

In all cases during the experiments 450 mL of the SHH solution containing the appropriate quantity of the catalysts (TiO_2 or Fe^{3+}/H_2O_2) was magnetically stirred, before and during the illumination, while the solution was purged with CO_2 free air. In the case of heterogeneous photocatalysis, the suspension was left for 30 min in the dark in order to achieve the maximum adsorption of the dye onto the semiconductor surface. At specific time intervals samples of 10 mL were withdrawn. To remove the TiO_2 particles, the solution was filtered through a 0.45 μm filter (Schleicher and Schuell). Changes in the concentration of Hematein were observed from its characteristic absorption band using a UV–vis spectrophotometer (Perkin-Elmer, Lamba 3, UV–vis spectrophotometer). Since a linear dependence between the initial concentration of the dye and the absorption at 559 nm is observed, during the experimental procedure the photodecomposition was monitored spectrophotometrically at this wavelength.

In order to determine the extent of mineralization, samples were taken out at regular time intervals and the chemical oxygen demand (COD) was measured according to standard methods [11]. In order to avoid any mistakes during the COD measurement, due to residual H_2O_2, the samples were treated with catalase from *Aspergillus niger* for 8 h.

All photocatalytic experiments, were carried out at the natural pH value of 3.1 and the reaction temperature was kept constant at 25 ± 0.1 °C.

Some photocatalytic experiments were repeated three times in order to check the reproducibility of the experimental results. The accuracy of the optical density values was within ±5%, while that of chemical oxygen demand (COD) reduction during the mineralization experiments was ±10%.

2.4. Calculation of the apparent initial photonic efficiency ζ (%)

The photonic efficiency [12] describing the effectiveness of light conversion to product in heterogeneous, light scattering systems is directly proportional to the quantum yield, and may be considered to be the lower limit of this more commonly used measure of light efficiency. In our case of decolorization the following equation has been used for calculation of the apparent initial photonic efficiency,

$$\zeta_0(\%) = r_0 I_{h\nu}^{-1} \times 100 \tag{1}$$

where r_0 is the initial reaction rate of the decolorization [mol L^{-1} min^{-1}] and $I_{h\nu}$ the incident photon flux per unit volume [mol photons L^{-1} min^{-1} = E(instein) L^{-1} min^{-1}], while for the mineralization process the photonic efficiency, ζ_{COD}, per oxygen molecule, can be calculated using the following equation.

$$\zeta_{COD}(\%) = r_{COD}(32 I_{h\nu})^{-1} \times 100 \tag{2}$$

where r_{COD} is the initial rate of chemical oxygen demand reduction [mol O_2 L^{-1} min^{-1}].

3. Results and discussion

3.1. Photodegradation experiments in the presence of TiO_2

A general description of heterogeneous photocatalysis under artificial or solar irradiation is included in several excellent review articles [13–15]. A brief summary is presented here only for the sake of completeness. It has been demonstrated that semiconducting materials mediating photocatalytic oxidation of organic compounds can be an alternative to conventional methods for the removal of organic pollutants from water and air. The illumination of these particles with light energy greater than the bandgap energy of the semiconductor ($h\nu > E_g$) produces excited high energy states of electron and hole pairs (e^-/h^+) that can migrate to the surface of the particle and initiate a wide range of chemical redox reactions, which can lead to complete mineralization of the organic pollutants. The disappearance of these compounds could take place via formation of partially oxidized intermediates that could be even more toxic than the original pollutants. Advantages of the photocatalytic process are its mild operating conditions and the fact that it can be powered by sunlight, thus reducing significantly the electric power required and therefore the operating costs [16,17]. Among various semiconducting materials (oxides, sulphides, etc.) research has focused on TiO_2 (anatase), because of its high photocatalytic activity, resistance to photocorrosion, biological immunity and low cost.

At first, experiments concerning the photocatalytic decomposition of 50 mg L^{-1} (1.67×10^{-4} M) Hematein in a SHH solution were performed, in the presence of semiconducting catalysts as TiO_2 P-25 and TiO_2 (A).

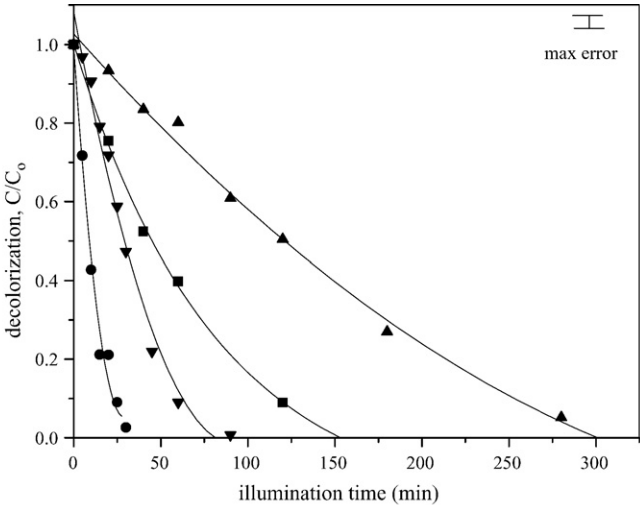

Fig. 2. Photocatalytic decolorization of a 50 mg L^{-1} Hematein solution as a function of illumination time in the presence of (■) 1 g L^{-1} TiO_2 P-25, (●) 1 g L^{-1} TiO_2 P-25 + 1 g L^{-1} H_2O_2, (▲)1 g L^{-1} TiO_2 (A) and (▼) 1 g L^{-1} TiO_2 (A) + 1 g L^{-1} H_2O_2.

Results of the photocatalytic decolorization of a SHH solution containing 50 mg L^{-1} Hematein in the presence of 1 g L^{-1} TiO_2 P-25 or 1 g L^{-1} TiO_2-A alone and in synergy with H_2O_2 are shown in Fig. 2. The amount of Hematein present in the supernatant is plotted as a function of irradiation time. From Fig. 2 it is clear that the photolysis of an air equilibrated Hematein solution in the presence of the semiconducting powders leads to disappearance of the compound, while the synergetic action of H_2O_2 in both cases accelerates the decolorization process.

Under these experimental conditions and after 120 min of light exposure in the presence of 1 g L^{-1} TiO_2 P-25 the decolorization of the solution was almost complete, while by using 1 g L^{-1} TiO_2-(A), as is shown in Fig. 2, after the same time of illumination 50% of the initial concentration of Hematein remains in the solution.

The addition of 1 g L^{-1} H_2O_2, an amount which represents 47% of the theoretically necessary hydrogen peroxide concentration for 100% mineralization of the organic content in the SHH solution (1 g L^{-1} COD = 2.125 g L^{-1} H_2O_2) [18], results in a significant acceleration of the decolorization process, as well as in a significant reduction of the initial organic content. Addition of H_2O_2 was necessary because of the high initial organic content mainly due to the organic additives in the SHH wastewater (see Table 1).

Fig. 3 shows a 65% COD reduction within 5 h of illumination of TiO_2 P-25 and a 35% with TiO_2-A. The respective initial photonic efficiencies (ζ_0) of decolorization, as well as COD reduction (ζ_{COD}) under the above mentioned conditions are presented in Table 2.

The superiority of TiO_2 P-25 may be attributed to the morphology of crystallites, which was proposed to be one of the most critical properties for the photocatalytic efficiency of P-25 among various grades of TiO_2. Crystallographic studies show that it consists of multiphases of amorphous, anatase and rutile

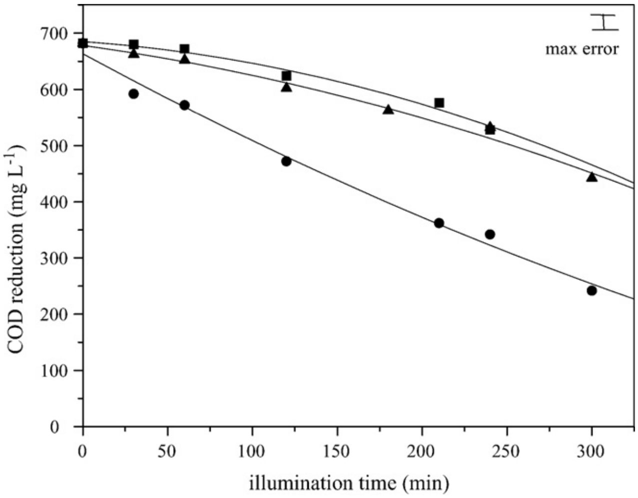

Fig. 3. Photocatalytic COD reduction of a SHH solution containing 50 mg L^{-1} Hematein as a function of illumination time in the presence of (■) 1 g L^{-1} TiO_2 P-25, (●) 1 g L^{-1} TiO_2 P-25 + 1 g L^{-1} H_2O_2 and (▲) 1 g L^{-1} TiO_2 (A) + 1 g L^{-1} H_2O_2.

forms. The close proximity of these phases and in some cases the overlapping of forms makes it difficult to differentiate and it has been documented to be the reason for long lasting excitation of electrons from the valence band to the conductive bands, allowing for efficient and effective degradation of organic compounds [19,20]. Recently, Hurum et al. had shown that in the case of TiO_2 P-25 a transfer of the photogenerated electrons from rutile to anatase particles takes place leading to stabilization of the charge separation and therefore lowering the recombination of the photogenerated carriers, which determine the efficiency of most photocatalysts. Additionally the small size of the rutile particles in this formulation and their close proximity to anatase particles are crucial to enhancing the catalyst activity [21].

Table 2
Apparent initial photonic efficiencies of the photocatalytic decolorization (ζ_0) and COD reduction (ζ_{COD}) of a of a SHH solution containing 50 mg L^{-1} Hematein

Experimental conditions	Apparent initial photonic efficiency of decolorization ζ_0 (%)	Apparent initial photonic efficiency of COD reduction ζ_{COD} (%)
1 g L^{-1} TiO_2 P-25	0.21 ± 0.04	3.20 ± 0.31
1 g L^{-1} TiO_2 (A)	0.101 ± 0.003	–
1 g L^{-1} TiO_2 P-25 + 1 g L^{-1} H_2O_2	0.8878 ± 0.04	8.17 ± 0.9
1 g L^{-1} TiO_2 (A) + 1 g L^{-1} H_2O_2	0.503 ± 0.025	3.35 ± 0.17
56 mg L^{-1} Fe^{3+} + 1 g L^{-1} H_2O_2 UV-A illumination	–	47.96 ± 3.88
56 mg L^{-1} Fe^{3+} + 1 g L^{-1}H_2O_2 visible light illumination	–	45.26 ± 2.15

3.2. *Influence of the Hematein concentration on the reaction kinetics*

The influence of the initial concentration of the solute on the photocatalytic degradation rate of most organic compounds is described by a pseudo-first kinetic order, which is rationalized in terms of the Langmuir–Hinshelwood model (Eq. (1)), modified to accommodate reactions occurring at a solid–liquid interface [5,22].

$$r_0 = -\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_r K C_{eq}}{1 + K C_{eq}} \tag{3}$$

where r_0 is the initial rate of disappearance of the organic substrate and C_{eq} is the equilibrium bulk-solute concentration. K represents the equilibrium constant for adsorption of the organic substrate onto TiO_2 and k_r reflects the limiting rate constant of reaction at maximum coverage under the given experimental conditions. This equation can be used when data demonstrate linearity plotted as follows:

$$\frac{C_{eq}}{r_0} = \frac{1}{k_r K} + \frac{C_{eq}}{k_r} \tag{4}$$

The effect of altering the equilibrium concentration of Hematein on the initial reaction rate (r_0) of photodegradation is shown in Fig. 4. Due to the fact that Hematein is adsorbed quite strongly on the TiO_2 P-25 surface, the equilibrium concentration of the dye (C_{eq}), after 30 min equilibration in the dark, instead of the

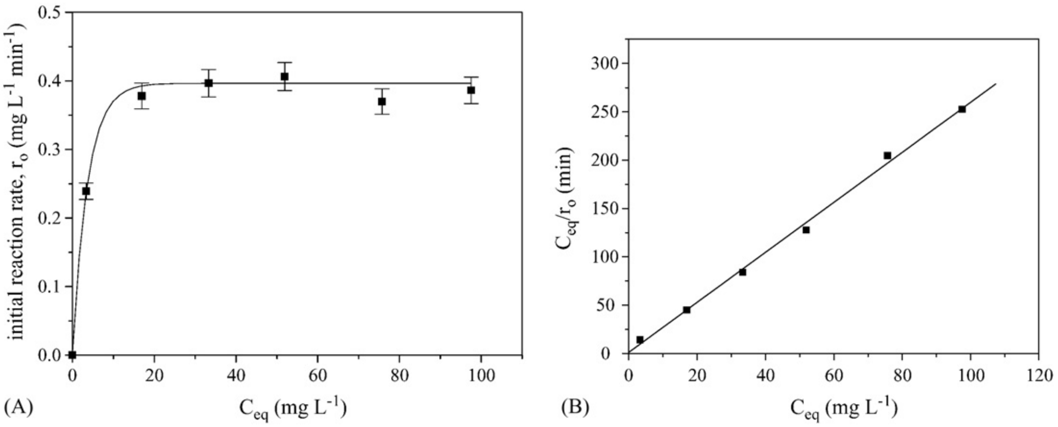

Fig. 4. (A) Plot of r_0 vs. C_{eq} for different initial concentrations of Hematein at constant concentration of TiO_2 P-25 at 1 g L^{-1} and (B) linear transform of C_{eq}/r_0 vs. C_{eq} according to Eq. (2). Data from Fig. 4A.

initial one (C_0), has been used in the kinetic study [22]. The curve is reminiscent of a Langmuir type isotherm, for which the rate value of decomposition first increases sharply and then reaches a saturation value at higher concentrations of Hematein. The r_0 values were independently obtained by a linear fit of the $C_{eq} - t$ data in the range of 10–120 mg L^{-1} initial Hematein concentration. Only the experimental data obtained during the first minutes of illumination, until 20% reduction was achieved, were used in calculating the initial reaction rates, in order to minimize variations as a result of the competitive effect of the organic additives and the intermediates. It is well known that the organic additives, as well as the intermediate products formed during photodegradation furthermore undergo photocatalytic oxidation, thus resulting in a change of the initial conditions.

The dependence of C_{eq}/r_0 values on the respective equilibrium concentrations of Hematein for constant concentration of TiO_2 P-25 at 1 g L^{-1} is shown in inset of Fig. 4B. The k_r and K values calculated according to Eq. (2) from the slope of the straight line ($R^2 = 0.99$) and from the intercept with the C_{eq}/r_0 axis were 0.39 mg L^{-1} min^{-1} (1.3×10^{-6} M min^{-1}) and 2.36 mg^{-1} L (2.23×10^5 M^{-1}), respectively.

As already mentioned, K represents the equilibrium constant for the adsorption of Hematein onto TiO_2 and k_r reflects the limiting rate of reaction at maximum coverage for the given experimental conditions and accordingly has no absolute meaning.

3.3. Influence of the amount of catalyst and H_2O_2 on the photooxidation

TiO_2 dosage in slurry photocatalytic processes is an important factor, that can influence strongly the degradation of the organic compound. The optimum quantity depends on the nature of the organic compound, as well as the photoreactor geometry [23,24]. The effect of varying the concentration of TiO_2 P-25 on the observed initial reaction rate (r_0) of decolorization of Hematein is presented in Fig. 5. As the TiO_2 concentration increases from 0.25 to 2 g L^{-1} the r_0 of photodecomposition of Hematein increases by a factor of 2. The curve is reminiscent of a Langmuir type isotherm suggesting that r_0 may reach a saturation value at higher TiO_2 concentrations, as has been reported in similar cases [5,23].

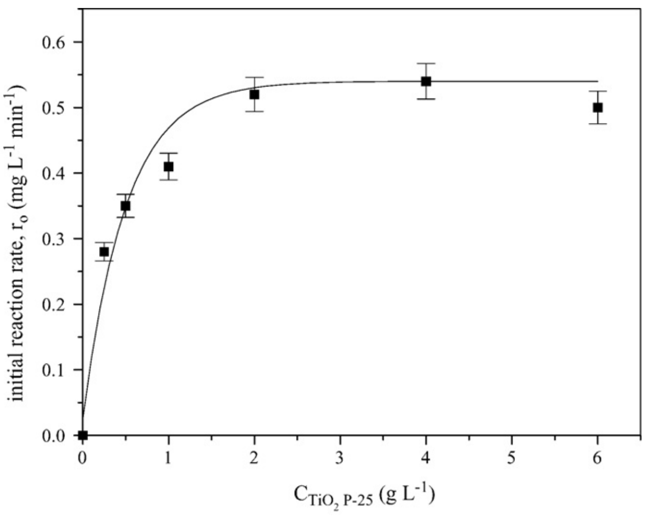

Fig. 5. Dependence of the initial reaction rate of decolorization, r_0, of a SHH solution containing 50 mg L^{-1} Hematein, on the concentration of the TiO_2 P-25.

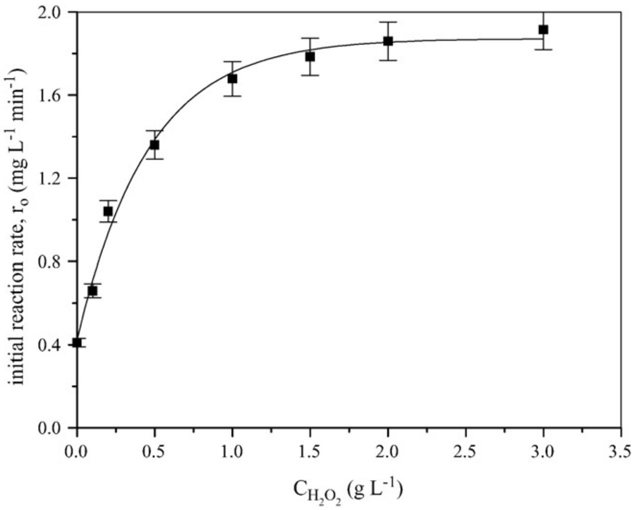

Fig. 6. Dependence of the initial reaction rate of decolorization, r_0, of a SHH solution containing 50 mg L^{-1} Hematein, on the initial concentration of H_2O_2 at constant 1 g L^{-1} TiO_2 P-25.

The addition of other powerful oxidizing species such as hydrogen peroxide (H_2O_2) and potassium peroxydisulfate ($K_2S_2O_8$) to TiO_2 suspensions is a well-known procedure and in many cases leads to an increase in the rate of photooxidation [5,25,26]. The role of H_2O_2 in the process of photocatalytic degradation is dual. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation and it also forms OH radicals via superoxide, while a possible reaction of H_2O_2 with the photogenerated intermediates cannot be excluded.

In our case the photocatalytic degradation of 50 mg L^{-1} Hematein, contained in the SHH solution in the presence of 1 g L^{-1} TiO_2 P-25 has been studied at different H_2O_2 initial concentrations, to find out the optimal concentration of H_2O_2 for the maximum effect.

The effect of the amount of H_2O_2 on the initial reaction rate can be seen in Fig. 6. An increase in the concentration of H_2O_2 from 0.1 to 3 g L^{-1} leads to an increase in the reaction rate of decolorization (∼4.5-fold the initial one without H_2O_2 in the case of 3 g L^{-1} H_2O_2). In contrast to similar reports [27,28], we did not observe any decrease in the reaction rate at these H_2O_2 concentrations, which probably happens with higher H_2O_2 doses.

3.4. Reuse experiments

The catalyst's lifetime is an important parameter of the photocatalytic process, due to the fact that its use for longer period of time leads to a significant reduction in the treatment cost. For this reason the photocatalytic decolorization experiments were repeated nine times with the same amount of TiO_2 P-25

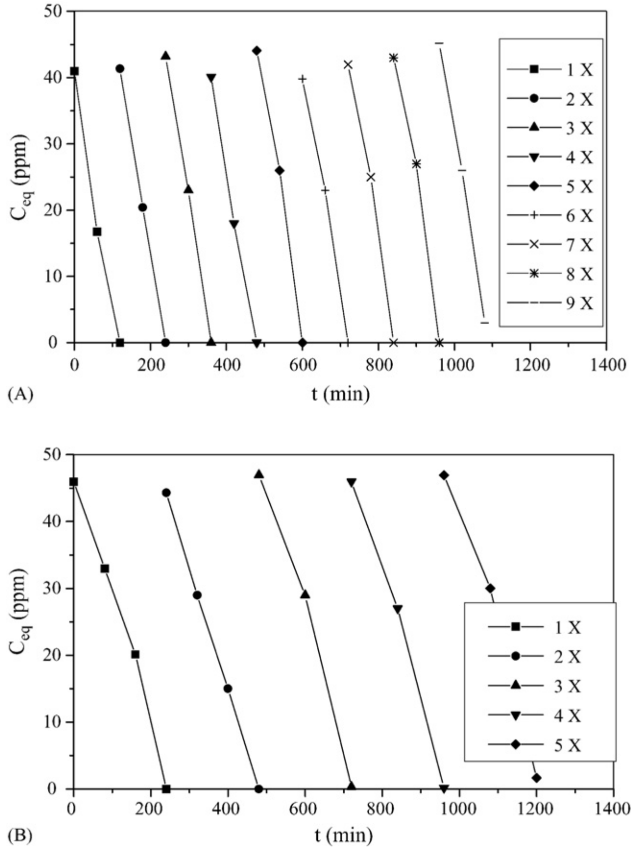

Fig. 7. Photocatalytic decolorization experiments of a SHH solution containing 50 mg L^{-1} Hematein with the same amount of catalyst: (A) 1 g L^{-1} TiO_2 P-25 and (B) 1 g L^{-1} TiO_2 (A).

as catalyst and five times with TiO_2 (A), with the use of a new initial SHH solution in each experiment. In Fig. 7A and B the most characteristic of the above results are shown. The parallel decreasing lines indicate that the catalyst reactivity during the nine times reuse experiments with TiO_2 P-25 and the five times reuse experiments with TiO_2-A remains almost constant. Some reuse experiments in the presence of catalysts and H_2O_2 were performed in order to study the organic content reduction. In this case the catalysts had lost their reactivity after four reuse experiments. The catalysts deactivation after a certain reaction time, according to several reports, could be explained as a result of the production of intermediates (e.g. aromatic aldehydes or carboxylic acids) not easily oxidizable, in comparison to the parent compounds. These intermediates accumulate onto catalyst surface and inhibit further photocatalytic processes [29,30].

3.5. Experiments with the Photo-Fenton reagent

The Fenton reagent, a mixture of hydrogen peroxide and ferrous salt, has been proved to be a powerful oxidant of organic compounds. This reagent, which produces in a very simple way $OH^\bullet$ (Eq. (5)), is an attractive oxidative system for wastewater treatment, due to the fact that iron is an abundant and non toxic element and hydrogen peroxide is easy to handle and environmentally safe. The hydroxyl radical is generally invoked as the primary reactive species generated according to Eq. (5), although metal-based oxidant intermediates, such as peroxo ($Fe(OOH)^{\bullet +}$) and ferry1 (FeO'^{+}) complexes have also been proposed. Furthermore it was found that the reaction could be enhanced by UV–vis light (artificial or natural), thus producing additional $OH^\bullet$ and leading to the regeneration of the catalyst (Eq. (6)) (Photo-Fenton reaction) [31–33].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad (5)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + OH^\bullet \quad (6)$$

These reactions are known to be the primary forces of photochemical self-cleaning of the atmospheric and aquatic environment [34].

The decolorization process of a SHH solution containing 50 mg L^{-1} Hematein, by using the Fenton reagent in the dark is a very fast process. In a period of 8 min before the illumination started, the decolorization was almost complete. For this reason in the homogeneous photocatalytic experiments only the organic content reduction was studied.

In Fig. 8 the initial reaction rate of the COD reduction of the synthetic Harris' Hematoxylin solution by the use of Photo-Fenton reagent ($Fe^{3+} + H_2O_2$) under UV-A illumination, in the presence of 1 g L^{-1} H_2O_2 and various initial Fe^{3+} concentrations are given. As shown in Fig. 8, there is a significant increase in the reaction rate of mineralization, while Fe^{3+} concentration is increased. By raising the Fe^{3+} concentration to 56 mg L^{-1} (1 mM) a nine-fold increase of the reaction rate can be observed in comparison to the mere presence of H_2O_2. From Fig. 8 it can also be seen that the efficiency of mineralization attains a plateau by an additional increase of the Fe^{3+} concentration. This could be due to the excessive formation of Fe^{2+}, which can compete with the organic carbon for $OH^{\cdot}$ Radicals. There is also a possibility that the fixed H_2O_2 concentration becomes the limiting factor of the reaction, when high concentration of Fe^{3+} is used [35].

In Fig. 9 the dependence of the initial reaction rate of the COD reduction on H_2O_2 concentration at the optimal Fe^{3+} con-

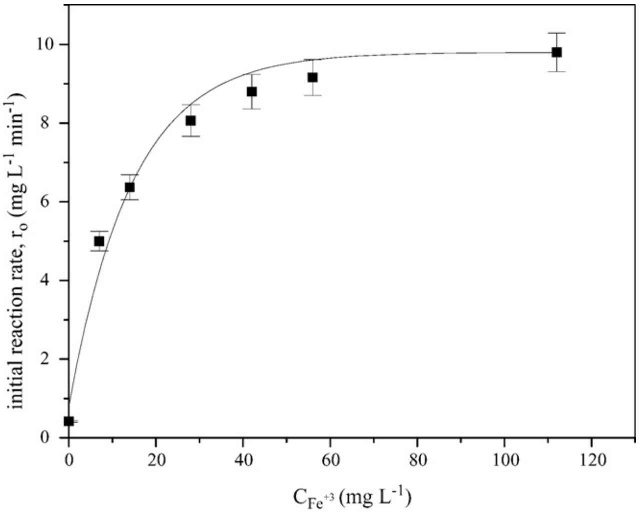

Fig. 8. Dependence of the initial reaction rate of COD reduction, r_{COD}, of a SHH solution containing 50 mg L^{-1} Hematein, on the initial concentration of Fe^{3+}. The initial H_2O_2 concentration is 1 g L^{-1}.

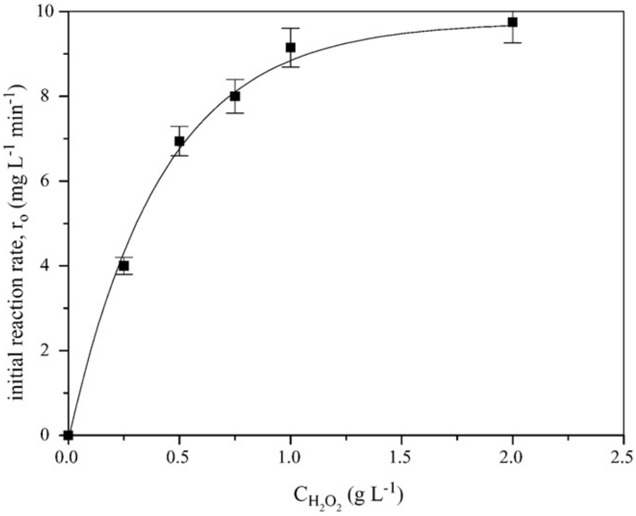

Fig. 9. Dependence of the initial reaction rate of COD reduction, r_{COD}, of a SHH solution containing 50 mg L^{-1} Hematein, on the initial concentration of H_2O_2. The initial Fe^{3+} concentration is 56 mg L^{-1}.

centration of 56 mg L^{-1}, as determined previously, is given. As can be seen in Fig. 9 a significant enhancement of the mineralization can be observed by increasing H_2O_2 concentration. The optimum concentration of H_2O_2, ranged between 1 and 2 g L^{-1}. This is in agreement to the 1.445 g L^{-1} H_2O_2, which represents the theoretically necessary hydrogen peroxide concentration for 100% mineralization of the organic content in the given simulated wastewater (1 g L^{-1} COD = 2.125 g L^{-1} H_2O_2) [18].

Taking into account that the Photo-Fenton reaction can be also initiated with light from the visible spectrum [36,37], some experiments have been done by using an irradiation source with exactly the same geometry as the UV-A source, emitting above 400 nm.

In Fig. 10 the comparison of COD reduction of a SHH solution containing 50 mg L^{-1} Hematein by using the Photo-Fenton reagent in the presence of UV-A and visible light ($h\nu > 400$ nm) is given, as well as the corresponding COD reduction by using the heterogeneous photocatalytic oxidation. As presented in Fig. 10 and in Table 2 the efficiency of photo-Fenton reaction in the presence of light of the visible part of the spectrum is similar to that in the presence of UV-A, concerning the COD reduction. Oxidation in the presence of TiO_2/H_2O_2 is a slower process in comparison to photo-Fenton, although after 6 h of illumination a 65% reduction of the initial COD value is achieved.

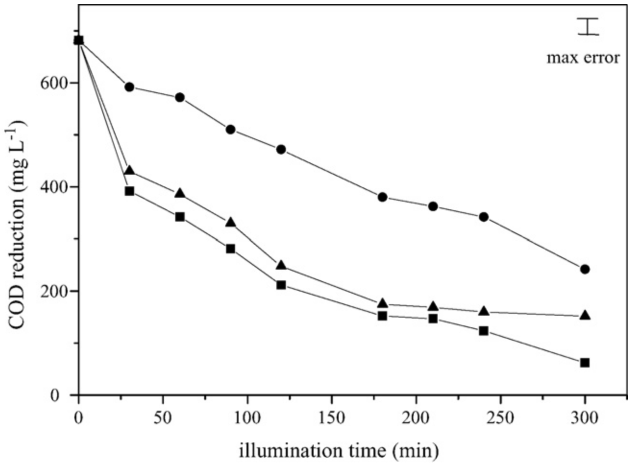

Fig. 10. Photocatalytic COD reduction of a SHH solution containing 50 mg L^{-1} Hematein as a function of illumination time in the presence of (●) 1 g L^{-1} TiO_2 P-25 + 1 g L^{-1} H_2O_2 (UV-A), (■) 56 mg L^{-1} Fe^{3+} + 1 g L^{-1} H_2O_2 (UV-A) and (▲) 56 mg L^{-1} Fe^{3+} + 1 g L^{-1} H_2O_2 (visible light, $h\nu > 400$ nm).

4. Conclusions

In the present study the decolorization and the reduction of the organic content of a synthetic Harris' Hematoxylin solution has been successfully carried out by applying a heterogeneous and a homogeneous photocatalytic method. From the results reported above it is clear that, under the specific experimental conditions of this work,

(a) The synergetic action of both modifications of TiO_2 with H_2O_2 leads to a substantial increase in the initial reaction rate and the extent of mineralization in comparison to TiO_2 alone, while the presence of H_2O_2 makes possible a multiple use of TiO_2.
(b) An advantage of the heterogeneous photocatalytic treatment of real Harris' Hematoxylin wastewater is also the ability of TiO_2 to remove in addition to color and organic content, the dissolved mercury ions as a result of their reduction from the photogenerated electrons [38].
(c) Photo-Fenton reagent in the presence of UV-A or visible light was considerably faster than those with TiO_2, but a detailed experimental and economical analysis has to be made in order to arrive at a conclusion about the most appropriate method for application.

From the results of the present work one could claim that the photocatalytic treatment of colored wastewater of medical laboratories could be employed as a powerful alternative tool for the decolorization and the organic content reduction of this liquid waste and can offer economically reasonable and practical solutions to its processing.

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