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Mineralization of organic compounds in photochemical and photocatalytic systems
Comparative analysis for the example of methylviologen photooxidation

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Abstract

A comparative study of the activity of different homogeneous photochemical and heterogeneous photocatalytic systems in oxidation of methylviologen in aqueous solutions is done. The photochemical systems used contained hydrogen peroxide or a mixture of hydrogen peroxide and potassium ferrioxalate or iron(III) chloride additives. The photocatalytic systems contained TiO_2 with or without hydrogen peroxide additives. The system activities were compared by the initial quantum yield of the process, the initial rate of the fall in the optical density of the organic component as well as the kinetics of carbon dioxide evolution during complete mineralization of methylviologen molecules. The homogeneous photochemical systems with pH=3 are shown to be much more active than the heterogeneous photocatalytic systems. As pH grows to 10, the photocatalytic system activity significantly increases in initial oxidation stage; however, in final stage the process becomes slow. At optimal pH=3 the activity of the homogeneous system is twice as high as the activity of the photocatalytic system at its optimal pH=10. © 1997 Elsevier Science B.V.

Keywords: Photocatalysis; TiO_2; Photo-Fenton; Water purification

1. Introduction

Deep oxidation of organic compounds up to their complete mineralization is a way to remove them from aqueous solutions. Presently a number of ways to accomplish such processes are known. Light-based photochemical and photocatalytic processes are especially appealing [1]. It is well known that light can stimulate decomposition of compounds to radicals which are usually extremely active and, consequently, can react with most organic compounds. One of the most active radicals present in aqueous medium and oxidizing most organic compounds is $OH^{\bullet}$ [2]. This radical is produced effectively from hydrogen peroxide on exposure of aqueous H_2O_2 to light with $\lambda<250$ nm. Lighting of organic solutions in the presence of hydrogen peroxide leads to an intense oxidation organic compound. However, the main drawbacks of the photochemical system containing only H_2O_2 are a necessity to use rigid ultraviolet (deficient in the sunlight) and low extinction of H_2O_2 (at $\lambda=250$ nm it is 18.5 M^{-1} cm^{-1} [3]). Nevertheless, today more than

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200 examples of practical (commercial) use of the H_2O_2/UV system are known [4].

Addition of potassium ferrioxalate or iron(III) chloride to a solution containing hydrogen peroxide significantly increases the activity of photochemical system [5]. However, in this case a subsequent removal of iron ions is required.

Photocatalytic systems with titanium dioxide as a heterogeneous photocatalyst [6–8] may be also used for water purification from organic impurities. Such photocatalytic systems have at least two obvious advantages, compared with photochemical systems. Photocatalytic oxidation of organic compounds requires only oxygen from the air, dissolved in water. Such oxygen is present in excess in the atmosphere. Moreover, a TiO_2 photocatalyst can be easily separated from purified water by filtration or precipitation. Using the photocatalyst in the form of 1 mm granules minimizes the difficulties of its separation [9]. Nevertheless, the method of photocatalytic purification has some difficulties. The most serious failing of this method, compared with a mentioned homogeneous photochemical method, is a low quantum yield of the oxidation process. However, one should note that such comparison was performed for acidic medium at the pH optimal for the photochemical system operation, while the solution pH optimal for the photocatalytic system operation may lie far in the alkali region [10].

In this connection, in the present studies we have tried to compare the activities of photochemical and photocatalytic systems for water purification from organic impurities both at identical pH and pH optimal for each system.

2. Experimental

2.1. Reagents and materials

Solutions were prepared from distilled water, doubly recrystallized methylviologen dichloride (1,1′-dimethyl-4,4′-bipyridine dichloride) $MVCl_2$ (chemical purity grade (c.p.g.)), perchloric acid $HClO_4$ (c.p.g.), sodium hydroxide NaOH (purity grade (p.g.)), hydrogen peroxide H_2O_2 (p.g.), iron(III) chloride $FeCl_3 \cdot 6H_2O$ (p.g.), potassium ferrioxalate $K_3Fe(C_2O_4)_3$ (p.g.). TiO_2 has been used as powder ("Degussa P25" grade) with a surface area of 55 $m^2\,g^{-1}$ [7]; this kind of TiO_2 is considered to be one of the most active photocatalysts for organic compounds oxidation.

2.2. Solution preparation

The samples for illumination were prepared as follows. A methylviologen solution was added to distilled water, and $MVCl_2$ concentration was adjusted to 5×10^{-5} M. Then the necessary amount of TiO_2 suspension, hydrogen peroxide, iron(III) chloride and potassium ferrioxalate were added. A required initial pH of the solution was adjusted by means of perchloric acid or sodium hydroxide solution. The pH value was controlled by a pH-meter "pH-673" (the former USSR).

2.3. Procedures

All experiments were carried out at room temperature on continuous agitation by a magnetic stirrer "MM-2A". Solution absorption was measured by a spectrophotometer "Shimadzu UV-300" (Japan). The amount of carbon dioxide over the solution was determined by means of a gas chromatograph LKhM 8 MD (Russia) with a methanator and flame-ionization detector (Institute of Catalysis). The samples were exposed to the incident light of a high-pressure mercury lamp DRSH-1000 (Russia). When required, an appropriate interference filter was used to separate certain spectrum lines. Light intensity was measured by a power meter LM2 (K. Zeiss, former GDR). The absorption path in the reactor was 3 cm.

Methylviologen destruction was performed in the presence of dissolved oxygen from the air in several systems: only on exposure to the incident light of the high-pressure mercury lamp ("$h\nu$"), on lighting of the samples containing hydrogen peroxide ("$h\nu+H_2O_2$"), photocatalyst – titanium dioxide ("$h\nu+TiO_2$"), titanium dioxide and hydrogen peroxide ("$h\nu+TiO_2+H_2O_2$"), iron(III) chloride and hydrogen peroxide ("$h\nu+FeCl_3+H_2O_2$"), potassium ferrioxalate and hydrogen peroxide ("$h\nu+K_3Fe(C_2O_4)_3+H_2O_2$"). The concentrations of these compounds in the final solution were as follows: $[H_2O_2]=4\times10^{-4}$ M, $[TiO_2]=0.02$ g l^{-1}, $[FeCl_3]=3\times10^{-4}$ M, $[K_3Fe(C_2O_4)_3]=10^{-4}$ M. The absorption spectra for titanium dioxide, iron(III) chloride and potassium ferrioxalate of the above concentrations at pH=3 are shown in Fig. 1.

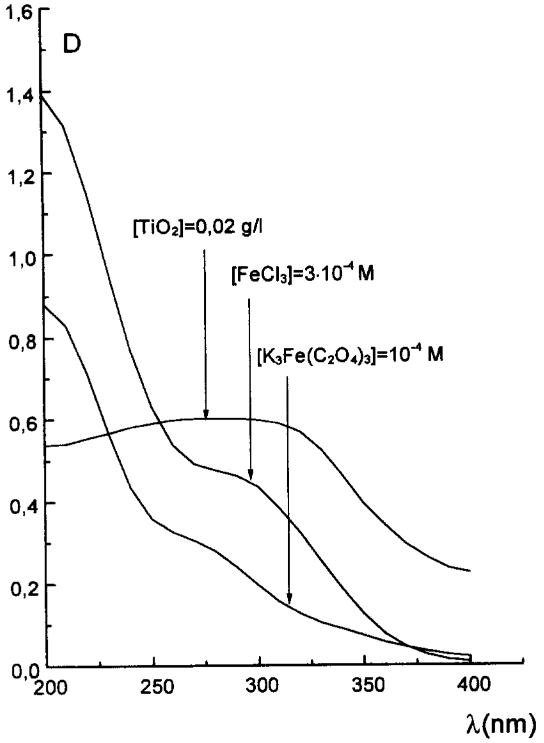

Fig. 1. Absorption spectra of TiO_2 ("Degussa P25") suspension, $FeCl_3$ and $K_3Fe(C_2O_4)_3$ solutions at pH=3 ($HClO_4$) and l=1 cm.

Illumination of methylviologen solutions (both in the presence and absence of various additives) is accompanied by a gradual decrease in the optical density of the sample at λ=250 nm and by a change in the spectrum shape. These changes may result from variation in the absorption both of the organic component of the solution during methylviologen destruction and TiO_2 or iron complexes on their irradiation.

In order to distinguish changes in the optical density caused by the organic molecules destruction, we carried out two experiments. In the first we irradiated the methylviologen solution containing appropriate additives. In the second, control, experiment we lighted the solution of the same composition, not containing methylviologen (blank solution). In both cases the rate of optical density variation with time was determined. The difference in these two kinetic functions was used later.

The optical density of the solution was measured, as the reaction proceeded, by two ways. When the reaction rate was low, so that for building up a kinetic curve it was sufficient to measure the optical density every 5 min only, the measurements were performed on continuous lighting. In this case we took a required amount of the solution at regular intervals and measured its absorption. In the case of rapid reaction proceeding, lighting was interrupted every 10 or 20 s, and the absorption spectrum was recorded. The same procedure was used when it was necessary to control the pH of the solution during the process.

The initial rate of the optical density decrease was determined by the four first points of the kinetic curve. The quantum yield of methylviologen destruction, referred to incident light, φ_{inc}, was calculated from the data on the initial rate of variation in the optical density of the organic component with allowance for possible absorption by the products of primary methylviologen oxidation (the calculation procedure was taken from [10]).

3. Experimental results

Fig. 2 shows the initial rates of the decrease in the optical density of the organic component of the solution in methylviologen destruction at pH=3. One can see that a maximal rate is achieved when a mixture of potassium ferrioxalate and hydrogen peroxide is used as additives. The lower rate is observed in the iron(III) chloride+hydrogen peroxide system. At the same pH, the activity of the systems containing photocatalyst TiO_2 and/or H_2O_2 is much lower (less than 10%) than that of the ferrioxalate containing system. Nevertheless, one can see that in the acidic medium the activity of the "hν+TiO_2" system is close to that of the practically realized "hν+H_2O_2" system. On carrying out the reaction in the basic medium (at pH=10) the pattern somewhat differs (Fig. 3). Under these conditions, iron(III) chloride and potassium ferrioxalate are converted into iron hydroxide, which cannot photocatalyze the methylviologen oxidation. At the same time, the activity of the systems containing TiO_2 drastically increases (Fig. 3). Note that in the basic medium the activity of the photocatalytic "hν+TiO_2" system is significantly higher than that of the "hν+H_2O_2" system.

Table 1 lists the obtained initial rates of the decrease in the optical density of the organic component at λ=250 nm on the samples exposure to full

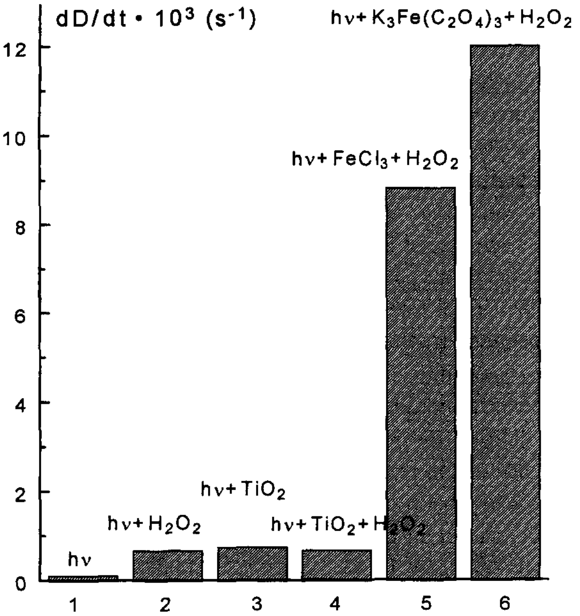

Fig. 2. Initial rate of the decrease in the optical density D of the organic component at λ=250 nm on irradiation of methylviologen solution ($[MVCl_2]_0=5\times10^{-5}$ M) under full light of DRSH-1000 in the presence of additives: $[TiO_2]$=0.02 g l^{-1}, $[H_2O_2]=4\times10^{-3}$ M, $[FeCl_3]=3\times10^{-4}$ M, $[K_3Fe(C_2O_4)_3]=10^{-4}$ M. pH=3 (adjusted by means of $HClO_4$), V=40 ml and T=20°C.

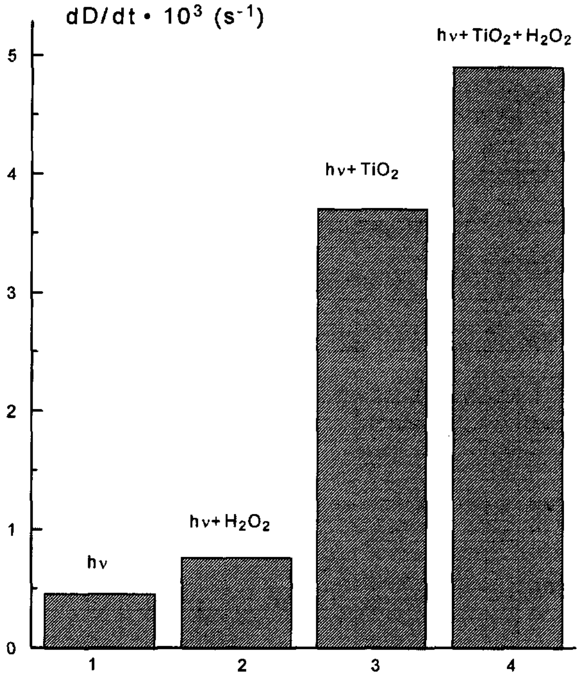

Fig. 3. Initial rate of the decrease in the optical density D of the organic component at λ=250 nm on irradiation of methylviologen solution ($[MVCl_2]_0=5\times10^{-5}$ M) under full light of DRSH-1000 in the presence of additives: $[TiO_2]$=0.02 g l^{-1}, $[H_2O_2]=4\times10^{-3}$ M, $[FeCl_3]=3\times10^{-4}$ M, $[K_3Fe(C_2O_4)_3]=10^{-4}$ M. pH=10 (adjusted by means of NaOH), V=40 ml and T=20°C.

light of the lamp DRSH-1000, as well as the quantum yield of methylviologen destruction referred to incident light with λ=302 nm (φ_{inc}). The quantum yield of the process referred to the absorbed light (φ_{abs}) is also given in the table. In some cases it was difficult to calculate the amount of light absorbed by the sample,

Table 1
Initial rates of the variation in the optical density of the organic component, dD_{250}/dt, at illumination by the incident light of lamp DRSH-1000 (0.5 W) and the estimated quantum yields of methylviologen destruction, referred to incident light (φ_{inc}) and absorbed light (φ_{abs}) at illumination by the light with λ=302 nm (5 mW), under various conditions

pH	$[TiO_2]$= 0.02 g l^{-1}	$[H_2O_2]$= 4×10^{-3} M	$[FeCl_3]$= 3×10^{-4} M	$[K_3Fe(C_2O_4)_3]$ $=10^{-4}$ M	dD/dt (10^{-2} s^{-1})	φ_{inc} (%)	φ_{abs} (%)
3	—	—	—	—	0.1	0.096	?
3	—	+	—	—	0.66	0.46	?
3	+	—	—	—	0.73	0.83	0.83
3	+	+	—	—	0.65	0.4	0.4
3	—	+	+	—	8.8	10.6	10.9
3	—	+	+	—	0.035 (dark)	—	—
3	—	+	—	+	≈12	8.5	11.2
10	—	—	—	—	0.45	0.38	?
10	—	+	—	—	0.76	0.76	?
10	+	—	—	—	3.7	4.9	4.9
10	+	+	—	—	4.9	7.8	7.8

Remarks: In all experiments $[MVCl_2]_0=5\times10^{-5}$ M, V=40 ml and T=20°C.

since the absorption spectrum of methylviologen only partially overlapped with the filter spectrum. These cases are marked by the sign "?".

As the above d*D*/d*t* data show, when incident light is used, under optimal conditions (at pH=10 [10]) the activity of the "hv+TiO_2+H_2O_2" system is only half as high as the activity of the $K_3Fe(C_2O_4)_3$-containing system, maximal at pH=3 [11]. Moreover, the relative efficiency of the TiO_2-containing system increases on the sample illumination by monochromatic light with λ=302 nm. In this case the "hν+TiO_2+H_2O_2" system is only 1.4-fold less active than the system containing potassium ferrioxalate or $FeCl_3$ (Table 1).

Fig. 4 presents the kinetic curves for the optical density of the organic component on illumination of the sample containing a TiO_2 photocatalyst. The oxidation was performed under different conditions. In one experiment, the initial pH of the solution, equal to 10, was set by addition of sodium hydroxide solution. In this case, as the reaction proceeds, pH varies, probably, due to the formation of the methylviologen oxidation products. In the other experiment pH was adjusted to 10 (at every 5 min intervals) by addition of the required amount of NaOH solution. In both cases the rapid variation in the optical density in the initial stage and the drastic inhibition of the process on the sample lighting for more than 10 min are observed. It is worth noting that the process inhibition is more distinct at a maintained pH than in the case of its variation. At pH=3, the oxidation of methylviologen in initial stage is less rapid than at pH=10. However, in this case the reaction rate does not fall with time. For comparison, Fig. 4 shows the kinetic curves for the process on illumination of the methylviologen solution not containing the photocatalyst additives.

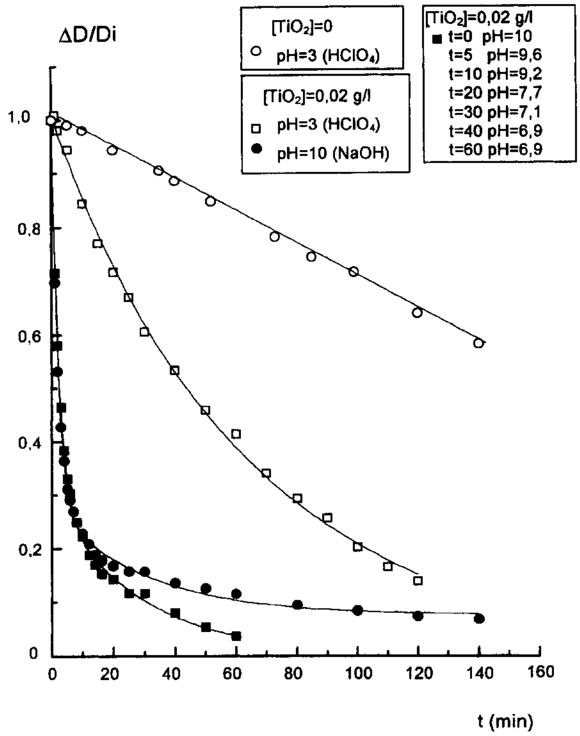

Fig. 4. Kinetic curves for decrease in the optical density *D* of the organic component at λ=250 nm on irradiation of methylviologen solution ($[MVCl_2]_0=5\times10^{-5}$ M) under full light of DRSH-1000 in the presence and absence of TiO_2 suspension. pH=10 maintained by means of NaOH (the case without NaOH addition see in the insertion). *V*=40 ml, *T*=20°C. D_i – initial optical density of the organic component.

Fig. 5 presents the kinetic curves for the optical density of the organic component for the "hν+$FeCl_3$+H_2O_2", "hν+$K_3Fe(C_2O_4)_3$+H_2O_2" systems at pH=3. Note that the process rate for the homogeneous systems is much higher than that for the TiO_2-containing systems under the same conditions. Thus, for example, for the $K_3Fe(C_2O_4)_3$-containing system the characteristic time the optical density takes to decrease 5-fold, is about 2 min. For the $FeCl_3$-containing system this time is 3 min. In the TiO_2-containing system at pH=3 the optical density becomes equal to 20% from the initial one after 100 min (which is 50-fold slower than that for the $K_3Fe(C_2O_4)_3$-containing system and about 30-fold slower than that for the $FeCl_3$-containing system). In the TiO_2-containing system at pH=10 the characteristic time is much lower – about 10 min, which is only 3-fold lower than that for the $FeCl_3$-containing system. When the time of the optical density decrease by 90% is chosen as characteristic time, the activity of the $K_3Fe(C_2O_4)_3$-containing system is significantly higher than that of the TiO_2-containing system. This results from the reaction inhibition in the "hν+TiO_2" system. A probable reason of this phenomenon will be discussed below.

Fig. 6 shows the kinetic curves for deep methylviologen oxidation in all studied systems. As expected from the data in Figs. 4 and 5, the reaction proceeds

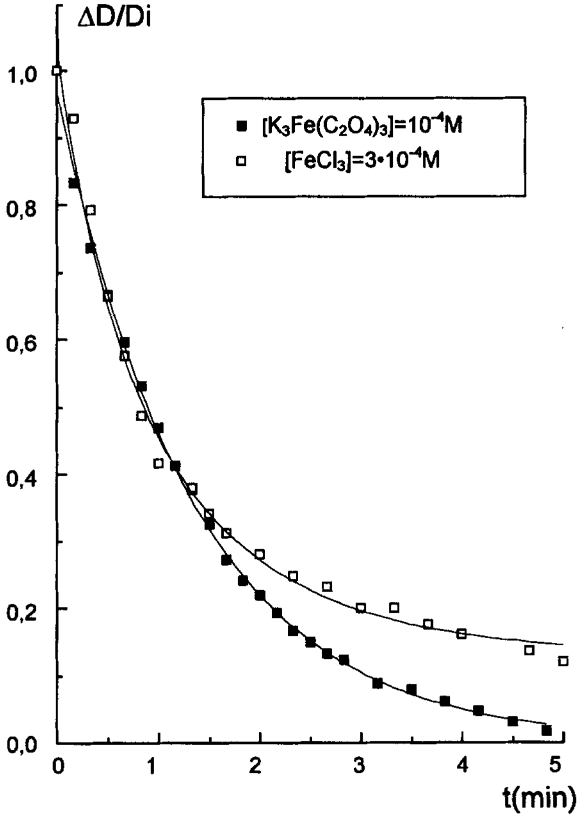

Fig. 5. Kinetic curves for decrease in the optical density D of the organic component at λ=250 nm on irradiation of methylviologen solution ($[MVCl_2]_0=5\times10^{-5}$ M) under full light of DRSH-1000 in the presence of additives. pH=3 (adjusted by means of $HClO_4$), V=40 ml, T=20°C. D_i – initial optical density of the organic component.

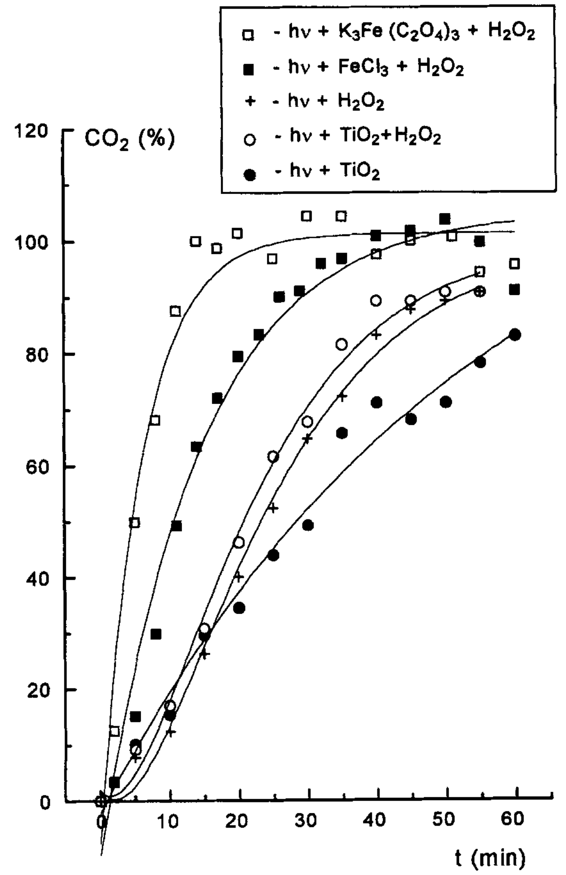

Fig. 6. Kinetic curves for CO_2 accumulation on the methylviologen oxidation ($[MVCl_2]_0=5\times10^{-5}$ M) in the presence of additives: $[TiO_2]=0.02$ g l^{-1}, $[H_2O_2]=4\times10^{-3}$ M, $[FeCl_3]=3\times10^{-4}$ M, $[K_3Fe(C_2O_4)_3]=10^{-4}$ M. pH=3 ($HClO_4$), V=20 ml, under full light of DRSH-1000.

most rapidly in the $K_3Fe(C_2O_4)_3$-containing system. However, on lighting potassium ferrioxalate decomposes with releasing carbon dioxide. Therefore, in this case the process kinetics is to be considered as a sum of the kinetics of CO_2 production from methylviologen and potassium ferrioxalate decomposition. Then the system activity falls in the series: "hν+$FeCl_3$+H_2O_2", "H_2O_2-containing systems", "hν+TiO_2".

4. Discussion

It is advisable to begin discussion of the obtained results from consideration of the used methods for determining the activity of the systems of deep oxidation of organic compounds.

In the present studies, the system activity was estimated by the rate of variation in the optical density of the organic component. It is obvious that during oxidation the initial reagents are constantly spent giving rise to other compounds. Therefore, the optical density of the organic component falls due to the disappearance of initial reagents and grows at the expense of the reaction products. As a result, in the initial reaction stage the optical density can both fall (when produced compounds have lower extinction than the initial ones) and grow (when the reaction products absorb light heavier than the initial compounds). However, during the reaction, large organic molecules containing strongly absorbing aromatic systems gradually decompose and turn into more simple compounds with much weaker absorption. This leads to a decrease in the organic component absorption during the reaction, in spite of its ambiguous variation in the initial stage. A total mineralization of the initial organic compound will ensure the total absence of absorption by some other organic compounds.

It is worth noting that absorption of organic component during oxidation of initial organic compound should disappear well before mineralization. Actually, in the ultraviolet radiation region, the organic compounds with π-bonds are the main light absorbers (due to π–π^*, n–π^* transitions). Saturated hydrocarbons, aldehydes, acids, e.g., formic and acetic acids, which are precursors of mineralization, have no such bonds and, therefore, make no contribution to the light absorption. Compounds containing aromatic rings are characterized by high extinction near $\lambda\sim250$ nm. Depending on the rings number and substituents, it varies from $\sim10^3$ to 10^4 M^{-1} cm^{-1}. The extinction of compounds having no aromatic rings is usually lower. For example, at $\lambda=265$ nm acetone extinction is 18.5 M^{-1} cm^{-1} when water is used as a solvent [11, p. 58]. Thus, by controlling variation in the absorption of methylviologen (at $\lambda=250$ nm its extinction is $\sim10^4$ M^{-1} cm^{-1} [10]), we follow the substitutions in its aromatic rings and aromatic compound destruction.

In some cases (when the composition of the products of primary oxidation and their extinction are known), the variation in optical density in the initial stage correlates with the rate of the oxidation of initial organic compound. In particular, by controlling the optical density of the organic component at $\lambda=270$ nm, it is possible to measure the initial rate of the methylviologen oxidation [10]. The quantum yield in the initial stage (φ_{inc}) may be estimated from the intensity of incident light.

Let us discuss the kinetic curve shape. Here a question arises: What are the reasons for the gradual inhibition of methylviologen oxidation in the presence of a photocatalyst, especially in the basic medium (Fig. 4)? Several explanations may be proposed. First, the products of the primary methylviologen (MV^{2+}) oxidation may be poorly absorbed on the photocatalyst surface and therefore much slowly oxidized than methylviologen. Second, probably, the oxidation of the products of the primary MV^{2+} oxidation proceeds rapidly but all produced aromatic compounds show the same extinction, therefore, the optical density of the solution does not change. Among these two hypotheses the first seems to be most preferred. Actually, the primary stages of methylviologen oxidation consist in substitution of hydrogen in the aromatic ring by –OH group [12] which can dissociate to $-O^-$ in basic medium, acidifying the solution and decreasing the positive charge of methylviologen molecule or even changing it to the negative charge. At the same time, in basic medium the titania surface is negatively charged due to the $Ti-O^-$ groups formation [6]. Thus, the methylviologen oxidation may give rise to the compounds poorly adsorbed and, consequently, slowly oxidized on the TiO_2 surface [10]. A decrease in pH should lead to reduction in the dissociation of the –OH groups of organic molecules and thus favor the adsorption of the latter and, consequently, accelerate the process. Actually, the spontaneous medium acidification in the initial stage of the MV^{2+} oxidation indicates the presence of extra H^+ that are probably produced in the dissociation of the primary reaction products. Moreover, as seen from Fig. 4, such acidification favors more rapid oxidation of the intermediate organic compounds than in the case of constant pH=10.

Thus, the data obtained show that photocatalytic oxidation of organic compounds is a selective process: the stronger is the absorption of compounds on the photocatalyst surface, the more intense is their oxidation. Therefore, in the stage of the formation of poorly adsorbed compounds photocatalytic oxidation is inhibited.

As follows from the experimental data, especially the kinetic curves for the decrease in the optical density of the organic component, the studied photochemical system is not selective. This is especially true for the "$h\nu+K_3Fe(C_2O_4)_3+H_2O_2$" system. Nevertheless, the "$h\nu+FeCl_3+H_2O_2$" system shows some decrease in the reaction rate (Fig. 5).

Practical use of the above systems for deep oxidation of organic compounds depends on peculiarities of the latter. The homogeneous photochemical systems seem to demonstrate higher activity than the heterogeneous photocatalytic ones. In other words, photochemical oxidation of organic compounds requires a less generation of light (when artificial light sources are used) and smaller oxidation reactors, which will reduce the costs of special setup construction. However, the process performance in homogeneous photochemical systems needs using consumable reagents. Thus, the $FeCl_3$- and $K_3Fe(C_2O_4)_3$-containing systems operate on hydrogen peroxide. Moreover, the latter system requires addition of soluble oxalates during the process. The iron ion concentration in the solution purified from organic compounds is about 10^{-4} M. Since these systems can efficiently operate only in acidic media [5], the purified solution contains also the traces of acid. It is obvious that the water purified by such a method is not of drinking quality without additional treatment.

Note that the "$h\nu+H_2O_2$" system is already in a widespread use, though it is homogeneous and requires H_2O_2 additions during the oxidation. The matter is that hydrogen peroxide can operate in a wide range of the medium acidity and is a thermally unstable compound. Therefore, unreacted H_2O_2 can be easily destructed over nontoxic iron or manganese oxides after the process completion.

The heterogeneous photocatalytic systems show much promise for practical use. These systems can operate in a wide pH range. At optimal pH the quantum yield of the methylviologen oxidation over TiO_2 in the H_2O_2 presence is 7.8%, which is only 1.4-fold lower than that for the ferrioxalate-containing system. The oxidation performed without H_2O_2 leads to the lower quantum yield – about 4.9%. This value is about 2.3-fold lower than that for the $K_3Fe(C_2O_4)_3$-containing system. Consequently, choosing the optimal medium acidity, sometimes it is possible to achieve equality in the activities of both photocatalytic and photochemical systems. Easy photocatalyst separation from the purified solution and using oxygen from the air or easily destructed hydrogen peroxide evidence in a perspectiveness of this system for removal of small concentrations of organics.

5. Conclusions

The activity of homogeneous photochemical systems in the methylviologen oxidation in acidic medium is higher by one order than that of the heterogeneous photocatalytic TiO_2-containing system. However, the comparison of the initial quantum yields at optimal pH for the studied systems has shown that the activity of the "$TiO_2+H_2O_2$" system comprises 71% from that of the most active $K_3Fe(C_2O_4)_3$-containing system.

Selection of the most reasonable oxidation procedure much depends on certain conditions controlled by customers. The nature of organic compound to be mineralized and its concentration as well as the initial pH of the solution, the spectrum of used light source and requirements to iron ion concentration in the final solution are the main affecting parameters. By using homogeneous photochemical systems, the organic impurities dissolved in water may be broken in acidic medium by sunlight without any limitations on iron ions discharge. Toxic impurities heavily adsorbed on TiO_2, which may be present in a solution with a high content of poorly adsorbed nontoxic organic compounds, can be oxidized in basic medium by means of the heterogeneous photocatalytic method, by using ultraviolet lamps or solar light.

Acknowledgements

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