

## Review Article

# Photocatalysis: Oxidative Processes in Water Treatment

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The efficiency of various homogeneous and heterogeneous systems photocatalytic processes destructive oxidation of organic compounds of different classes is considered. It is shown that photocatalytic methods can significantly increase the speed and depth (up to complete mineralization) of decomposition processes of toxicants. The use of photocatalysis (PC) in the creation of low-power water treatment technologies is a promising direction in addressing environmental problems of the hydrosphere.

## 1. Introduction

A global character of the human activity with respect to development of industry, agroindustrial complex, and transportation poses the ecological problems as the most topical. By the middle of the last century, the scale of the impact on the environment began to exceed the adaptive capacity of the biosphere which caused disturbances in a number of places natural evolution of the ecological balance, the deterioration of living conditions for living organisms, and eventually the disappearance of the biological species. Currently, anthropogenic factor was to play a decisive role in the genesis not only of continental but also of marine aquatic ecosystems.

In the anthropogenesis impacts, contamination of natural water by the nonpurified waste effluents of industrial and agricultural production, including water pollution by harmful microorganisms, plays an essential role. Under action of different external factors (light, temperature, humidity, etc.), there comes to pass degradation of toxicants and formation of new substances including the more toxic ones. Alongside with the biological processes, there run a number of the physicochemical processes in hydrosphere, namely, adsorption, ion exchange, oxidation-reduction reaction, catalysis, synthesis of new compounds, and so forth [1–3].

Great scientific and practical interest in the system under consideration in the environmental aspect is due to the possibility to carry out the oxidation of organic matter to a high degree of mineralization at relatively low temperatures,

especially in the presence of oxygen, ozone, and hydrogen peroxide with a significant reduction of energy consumption of the process when using sunlight [4].

Among photocatalytic processes that play an important role in the natural self-purification of water by solar light are those that are initiated by complexes of transition metal (TM) (iron, copper, chromium, etc.), for which photoreactivity is of crucial environmental importance. The main sources of TM compounds in surface waters are the processes of dissolution and destruction of rocks and minerals, waste of the steel, metal, and chemical plants, oil refineries, mines, and so forth. The use of waste water in agricultural engineering is also a threat of pollution of the biosphere. TM content in surface freshwater changes from a few to several hundred micrograms per liter. The most common TM pollutants of soils and natural waters include iron and copper, which are also in nutrients, due to the participation in the synthesis of proteins, enzymes, photosynthesis, and so forth.

Compounds of Fe(III) and Cu(II), as being thermodynamically more stable, are more common than Fe(II) and Cu(I). The coordination interaction of TM ions is particularly important in the photochemical processes of transformation of organic compounds in surface waters. In this case, there is usually extension to longer wavelengths of the spectral range of utilization of solar radiation reaching the Earth's surface [2].

Studies on the effect of ions on the kinetics of the TM and the mechanism of chemical transformation of the organic

component of the hydrosphere facilitates to suit different synergistic and antagonistic effects provide important information as to the environmental aspect and from the point of view of increasing the efficiency of the advanced oxidation process (AOP) technologies, based on the new photooxidation systems. The interactions of TM ions with organic pollutants in natural and waste waters play a significant role in the environmental photocatalysis. Under solar irradiation, TM ions are photoreduced by organic matter and reoxidized by molecular oxygen. The photoreduction is accompanied by simultaneous oxidation of organic matter. They also affect the efficiency of photooxidation methods used in water treatment technology. The kinetics of these processes are largely determined by the nature of the TM and organic substrate and physicochemical parameters of objects of the hydrosphere: pH, redox potential of the medium, and so forth.

Due to the increasing complexity of wastewater, in particular through the stubborn biological, toxic, and organic compounds, the most promising methods for water treatment are those based on the use of foremost photocatalytic oxidation processes.

The use of photocatalytic processes in the water treatment is a relatively new area with great features which will be implemented in the near future [5–9].

The photocatalytic oxidative degradation of anthropogenic and natural organic contaminants (pesticides, surfactants, organic fertilizers, humic matter, etc.) in the photic layer of surface waters is of great importance among the vast number of physicochemical transformations occurring in hydrosphere. The importance of environmental photochemical processes is ever growing due to intensification of the UV component of solar radiation reaching the Earth surface that is caused by growth of the ozone holes in the stratosphere.

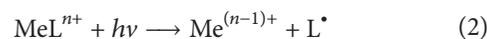
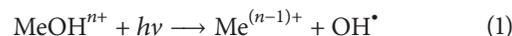
Modern homo- and heterogeneous photocatalytic methods of water purification from organic compounds—pollutants of natural and man-made origin—are based on the oxidation of the latter by molecular oxygen, ozone, and hydrogen peroxide under the influence of artificial UV light or sunlight in the presence of dissolved, suspended or immobilized PCs [10]. It is already known advantages that contribute to their promise, which include simplicity, efficiency, and the possibility of using solar light. Due to the ongoing depletion of world reserves of fossil fuel energy production, the application of photocatalytic processes occurring under the influence of solar radiation, of course, will be a priority in the development of technology and industry.

## 2. Homogeneous Photocatalysis

Among homogeneous photocatalytic processes that are of crucial environmental importance and play an important role in the natural self-purification of water by ultraviolet (UV) component of solar light are those that originated on hydrocomplexes of TM (iron, copper, chromium, etc.) in higher oxidation state [2, 5, 11].

Thus, generated hydroxyl radicals react with the substrate, which leads to accumulation in the solution of various organic radicals. One-channel flow photochemical process in this case is the oxidation of the substrate hydroxyl radicals

that are formed as a result of phototransfer charge in the hydraulic field inside the metal ions (Me) in a higher valence state. Consider



Under the action of atmospheric oxygen the original form of TM is regenerated with simultaneous formation of superoxide ions, peroxylic radicals, and radical oxidation of the substrate degradation products. Interactions of organic pollutants with hydroxyl radicals formed by the photoreaction (1), in the presence of molecular oxygen, are accompanied by the generation of hydrogen peroxide (Figure 1).

The photochemical process can be carried by photoinduced inner-sphere electron transfer from ligand to metal ion with the formation of organic radicals and reducing of TM ions (2). Formed in the early stages of the photoreaction, the reduced form of the metal, organic radicals, and radical ions are involved in the subsequent thermal reactions.

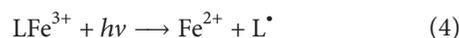
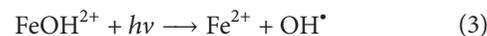
The formation of  $\text{H}_2\text{O}_2$  in the photooxidation of alcohols in the presence of molecular oxygen is independent of the method of generating  $\text{HO}^{\bullet}$  radicals, initiating the regeneration process under consideration.

Thus, accumulation of  $\text{H}_2\text{O}_2$  is observed during photooxidation of ethanol in aqueous solutions of salts of iron (III), in which  $\text{HO}^{\bullet}$  generation is effected by photoinduced electron inner-aqua  $\text{Fe}^{3+}$  ions [12–14].

This primarily includes oxidation of organic matter of hydrosphere in the system  $\text{Fe}^{2+}$  ( $\text{Fe}^{3+}$ )- $\text{H}_2\text{O}_2$ -UV (photo-Fenton system), which has been widely used in photochemical methods of water treatment [5].

Fenton's reagent oxidation with additional exposure to UV radiation is one of the most promising ways to clean heavily soiled AOP drains.

Substrates and intermediate destruction products forming complexes with  $\text{Fe}^{3+}$  may act as light-sensitizing agent. The effect of light is formed in the system of a relatively high concentration of the active catalyst  $\text{Fe}^{2+}$  ions due to photoreduction of trivalent iron complexes with aqua (3) and organic (4) ligands via intraspherical electron transfer with formation of secondary hydroxyl radicals with a quantum yield of  $\Phi = 0.14$  (313 nm) and 0.017 (360 nm)



The photoactive ions are  $\text{Fe}^{3+}$ ,  $\text{FeOH}^{2+}$ , and  $\text{Fe}_2(\text{OH})_2^{4+}$  whose contribution is determined by the pH value and the wavelength of the light source used.

When the quantum yield in the photooxidation of ligands is higher than in reaction (3), this process will predominate in the system as was the case in the oxidation of oxalic acid and 2,4-xylene. Photoreduction of  $\text{Fe}^{3+}$  in its complexes with citric and oxalic acids in the near-UV region is reported to proceed with high quantum yields.

In the processes occurring in the system  $\text{H}_2\text{O}_2$ - $\text{Fe}^{2+}$ - $h\nu$ , we must also consider proceeding with a high quantum

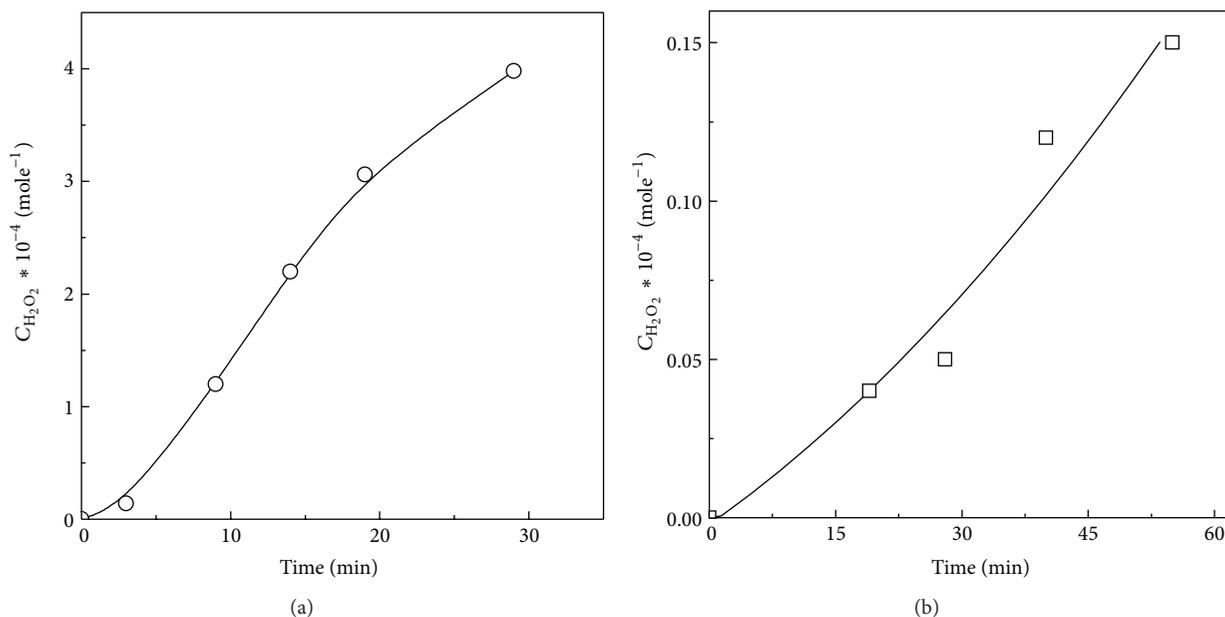
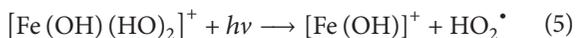


FIGURE 1: Generation of  $\text{H}_2\text{O}_2$  in the photooxidation of tert-butyl alcohol ( $\text{Co} = 1.0 \cdot 10^{-3} \text{ M}$ ) by  $\text{Fe}^{+3}$  ( $1.0 \cdot 10^{-4} \text{ mole}^{-1}$ ) (a), and  $\text{Cu}^{+2}$  ( $1.0 \cdot 10^{-3} \text{ mole}^{-1}$ ) (b) in an aqueous solution ( $1.18 \cdot 10^{-3} \text{ M HClO}_4$ ) under the action of UV light.

yield (1.32) photo-induced decomposition of complex ions  $[\text{Fe}(\text{OH})(\text{HO})_2]^+$  (5) to form hydroperoxide radicals, far inferior of hydroxyl radicals as oxidative agents:



This process competes with the oxidation of organic compounds by  $\text{Fe}^{3+}$  ions according to (4), which reduces the efficiency of the cleaning process itself.

Effect of various physicochemical factors on the efficiency of the oxidation process flowing in the photo-Fenton is system generally similar to that observed in the case of Fenton's reagent.

Destruction of toxic substances in both cases increases with the growth of the temperature and the drop of pH.

The increase of the degree of mineralization of pollutants contributes to the phased introduction in the system of hydrogen peroxide.

Application of photo-Fenton system provides more complete removal of several classes of organic compounds as compared with conventional oxidation methods. TOC removal degree in photochemical mineralization of 4-chlorophenol and waste water components using different dye oxidation systems is reduced in sequence  $\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+} > \text{UV}/\text{O}_3 > \text{UV}/\text{H}_2\text{O}_2 = \text{UV}/\text{TiO}_2$  [1, 11].

Interaction of pyridinecarboxylic (PA) and dichloropi-colinic (DCPA) acids with the hydrogen peroxide at pH 2–9 in the absence of iron ions does not cause oxidation said compound.

Under the action of  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2/\text{Fe}^{3+}$  systems oxidation of DCPA and PA at pH 4 effectively carried out; moreover, the reaction rate increases with increasing concentration of hydrogen peroxide and iron ions [15].

The presence of the oxidation products  $\text{NH}_4^+$  ions indicates the occurrence of deep destruction of DCPA and PA, degradation process cannot achieve a quantitative removal of these compounds from the reaction mixture.

Pyridinecarboxylic acid oxidation in Fenton system can be intensified by additional using of natural solar radiation ( $\lambda > 310 \text{ nm}$ ). The time required for substantially complete removal of these compounds is significantly reduced.

Destructive oxidation of acids proceeds by photocatalysis mechanism according to which the role of the solar radiation is in the regeneration of  $\text{Fe}^{2+}$  by photoreduction of  $\text{Fe}^{3+}$ , consequently, maintaining a certain ratio of the valence forms involved in catalytic decomposition of hydrogen peroxide.

Under the reaction conditions, the  $\text{Fe}^{2+}$  ions ( $\text{Fe}^{3+}$ ) form chelates with DCPA and PA, and therefore, it can be assumed that the latter plays an important role in photoreproduction of an active form of catalyst.

Under the reaction conditions, the formation of chelate compound of  $\text{Fe}^{2+}$  ( $\text{Fe}^{3+}$ ) ions with DCPA and PC takes place and therefore can suggest a role of these complexes in processes of photogenerated active form of the catalyst.

It was shown that irradiation in the absence of acid solutions of iron oxidation with hydrogen peroxide is not observed; therefore, the effect of radiation on the rate of degradation is only due to the influence of the catalyst. Improving the effectiveness of Fenton's reagent in the processes of oxidative degradation under the influence of solar radiation, as we observed in an example of pyridinecarboxylic acids, will expand the scope of this oxidation system.

Waste water from dyeing and finishing factories is a dangerous source of environmental contamination with pollutants characterized by high levels of chemical and biochemical oxygen demand, color, concentration of suspended solids

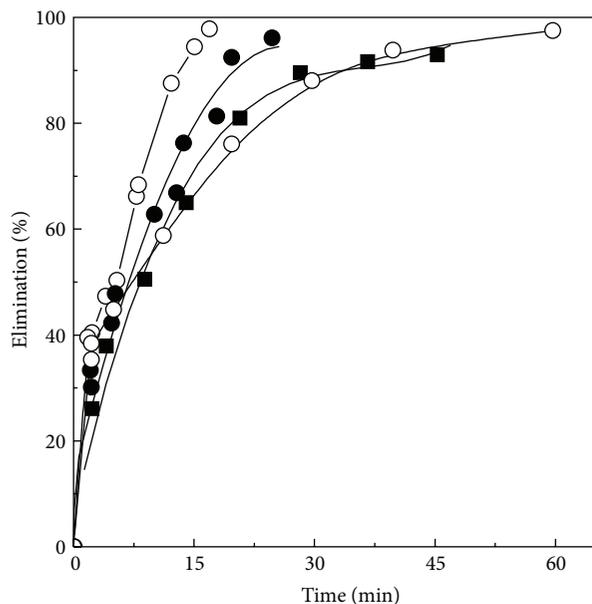


FIGURE 2: Sunlight influence on the AYL ( $5.8 \cdot 10^{-5}$  M) oxidation with Fenton's reagent  $[\text{H}_2\text{O}_2]_0$  (M):  $1 \cdot 10^{-3}$  (circle) (dark conditions);  $1 \cdot 10^{-3}$  (box);  $5 \cdot 10^{-4}$  (black circle) ( $\bullet$ ),  $3.3 \cdot 10^{-4}$  (black box) ( $\blacksquare$ ).

and so on. The reduction of color produced by residual dyes causes the most difficulties.

To intensify the bleaching of aqueous solutions of azo dyes by Fenton's reagent, we studied the effect of exposure to natural sunlight on the rate of discoloration of azo dye active yellow lightfastness AYL [6]. The results of experiments using solar radiation show the efficiency of such influence in the oxidation by Fenton's reagent (Figure 2).

Accelerating action of light to be seems apparently due to photoreduction of the  $\text{Fe}^{3+}$  ion in the system with renewal of  $\text{Fe}^{2+}$  ions, which, compared with the first, are more active catalysts of the hydrogen peroxide decomposition, resulting in formation of a hydroxyl radical.

The accelerating action of light, apparently, is due to photoreduction of  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  ions, that are more active catalysts of the hydrogen peroxide decomposition.

As a result the intensification of the process takes place as previously observed for a system substrate- $\text{H}_2\text{O}_2$ - $\text{Fe}^{2+}$ -sunlight, wherein the substrate was the components of sewage of waste water.

Increasing the speed of the process as previously observed for a system of substrate- $\text{H}_2\text{O}_2$ - $\text{Fe}^{2+}$ -sunlight, wherein the substrate, the components of sewage of textile production.

Thus, in this case, we have the rate increase as a result of photoreduction of  $\text{Fe}^{3+}(\text{L}) \rightarrow \text{Fe}^{2+}(\text{L}^*)$  for the substrate- $\text{H}_2\text{O}_2$ - $\text{Fe}^{2+}$ -sunlight system, where the substrate was 3,6-dichloropyridine-2-carboxylic acid or sewage components from textile factories.

These studies show that it is possible to reduce the specific consumption of  $\text{H}_2\text{O}_2$  to bleach azo dye solutions by selecting the appropriate initial concentration of the oxidizing agent.

Application of aeration at certain stages of the process reduces the hydrogen peroxide consumption and reduces

thereby the economic costs of this method in water treatment. Due to regeneration of  $\text{Fe}^{2+}$  ions in the reaction, original amount of the catalyst can be significantly reduced.

The  $\text{Cu}^{2+}$  ions in substrate- $\text{H}_2\text{O}_2$ - $\text{Cu}^{2+}$ -light system also can be photoreduced. Formed Cu(I) ions are also capable of catalyzing the formation of reactive hydroxyl radicals through the decomposition of hydrogen peroxide via Fenton-type reaction.

The principal vulnerabilities of photo-Fenton system include high costs of  $\text{H}_2\text{O}_2$  storage and of additional acidification and neutralization systems as well as usage of UV-lamps and electric power, and high salinity of the water under treatment because of addition of reagents used to adjust pH and formation of hydroxide slurries that need to be utilized or buried.

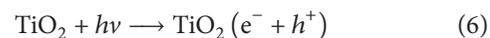
The costs of treatment by the methods under consideration can be reduced, for example, by on-site synthesis of  $\text{H}_2\text{O}_2$  by means of electrochemical reduction of oxygen and by replacing ultraviolet sources with solar light in oxidation by Fenton's reagent.

### 3. Heterogeneous Photocatalysis

Heterogeneous photocatalytic water treatment technologies are in the early stage of practical use. But known advantages that contribute to their promising future, which include simplicity, efficiency, and the possibility of using solar light.

The heterogenic photocatalysis on semiconductor materials has been used on the evergrowing scale in the processes of water purification of pollutants and contaminants of natural and man-made origin, artificial photosynthesis, developing methods of storing the energy of sunlight and photochemical water decomposition, and so forth [1, 16–18].

Most papers consider heterogenic systems based on high disperse titanium dioxide with a crystalline modification of anatase (Degussa, Hombikat, Aldrich, etc.). Practical use of other semiconductors ( $\text{WO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{CdS}$ ,  $\text{ZnS}$ ,  $\text{SnO}_2$ ,  $\text{SrTiO}_3$ , etc.) has been complicated by their solubility in water or toxicity thanks to which they are substantially inferior to titanium dioxide in terms of technology. Titanium dioxide is a highly active, cheap, nontoxic, and chemically stable product of heavy duty production. Photocatalytic properties of  $\text{TiO}_2$  are determined by the features of its electronic structure [17, 19], namely, the existence of a valence and conductance zones in it (Figure 3). When a quantum of light is absorbed—a free electron ( $e^-$ ) and an electronic vacancy—a hole are formed and they recombine or migrate in a semiconductor being partially localized on structural defective centers of its crystalline lattice:



Probability of electron transfer in PC-adsorbate (oxidant, substrate) system is determined by a relative position of the valence and conductance zones of PC and the value of the oxidation-reduction potential (ORP) of the oxidant and the substrate. The photogeneration of electrical charges is in dynamic equilibrium with their recombination substantially reducing the quantum yield of the photocatalytic process.

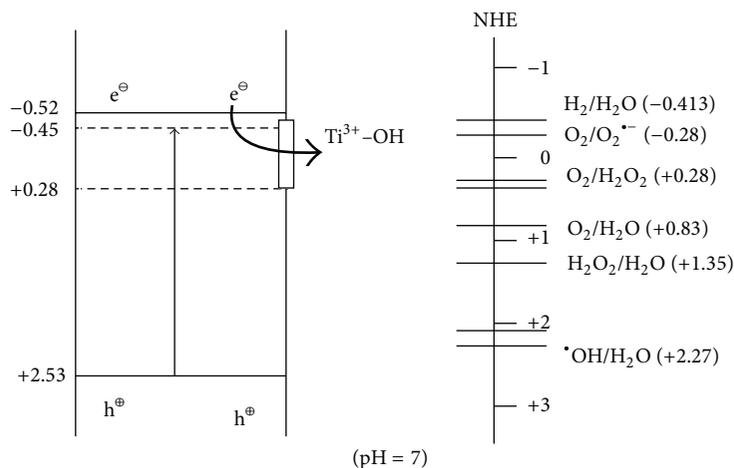
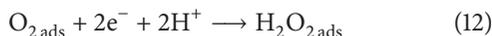
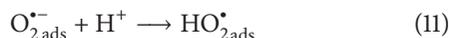


FIGURE 3: Schematic of photogenerating initial oxidizing agents on the  $\text{TiO}_2$  surface in the presence of electron-donor (D) and electron-acceptor (A) compounds.

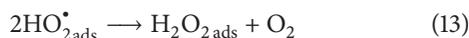
The ORP of water oxidation, the hydroxylic ions, and most organic compounds in a wide range of pH is below of the photogenerated holes (Figure 1), whereby the formation of hydroxyl radicals and organic cation radicals on the surface of PC are thermodynamically possible processes:



The redox potential for conduction band electrons equals  $-0.52$  V, which is negative enough to evolve hydrogen from water. However, even after trapping, a significant number of electrons are still able to reduce dioxygen to superoxide radicals  $\text{O}_2^{\bullet-}$  or to hydrogen peroxide. Depending upon the conditions, the holes,  $\text{OH}^{\bullet}$  and  $\text{O}_2^{\bullet-}$  radicals,  $\text{H}_2\text{O}_2$ , and  $\text{O}_2$  itself can all play important roles in the photocatalytic reaction mechanisms. Reduction of oxygen with electrons results in the formation of superoxide, hydroperoxide radicals, and hydrogen peroxide:



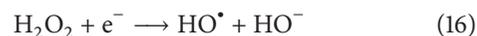
Hydrogen peroxide is also formed during interaction of hydroperoxide radicals and recombination of hydroxylic radicals:



Under the action of UV light, ( $<300$  nm) hydrogen peroxide dissociates with the formation of hydroxylic radicals:



Hydrogen peroxide is an effective scavenger of photogenerated electrons:



As in the case of homogenous photocatalytic systems used in the water treatment technologies, in the heterogeneous photocatalytic reactions, hydroxylic, hydroperoxide, and peroxide radicals are the main highly effective oxidizing agents.

The photocatalytic process is performed by the direct oxidation of the substrate by the holes of  $\text{TiO}_2$  on the surface of the latter's and by oxidation of the pollutant highly active oxygen radicals in the solution layer contiguous to  $\text{TiO}_2$  [20, 21].

In addition to the above energy factors of the rate of the photocatalytic process substantially depends on the specific surface of a catalyst, the nature of surface active centers, the localization degree of photogenerated charges and other parameters of the system, which are determined by a crystalline structure, the synthesis method, and subsequent treatment of  $\text{TiO}_2$ . Thanks to amphoteric properties of  $\text{TiO}_2$ , the rate of a photoreaction depends also on the acid-base equilibrium in the system.

The designing of new highly effective photocatalytic system based on semiconductor materials is possible only with the account of thermodynamic, crystallochemical, and photo- and electrophysical properties of PC on a molecular cluster level [19].

An increase of photocatalytic activity of semiconductor materials is achieved by doping them with TM (Pt, Pd, Au, Ni, Cr, Mo, Nb, W, Mn, Fe, Ce, Co, etc.), by grafting to the surface of PC polymers and dyes, by the use of mixed double and triple metal-oxide systems, nanosized  $\text{TiO}_2$ , and so forth.

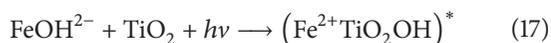
Nanodimensional particles of  $\text{TiO}_2$  in combination with oxides and sulfides of other elements (Si, Ce, Zr, Nb, etc.) are incorporated in the composition of the series of composites that possess higher photocatalytic properties and thermal and chemical stability as compared with initial  $\text{TiO}_2$ .

Sol-gel methods were developed for obtaining new nanostructural semiconductor composites based on silicate

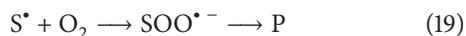
materials with incorporated nanoparticles of sulfides of silicon and zinc. A positive effect when using the above systems is determined by stabilization of electrons photogenerated in one of the component systems (e.g., CdS, ZnS, ZnSe, etc.) as a result of transition to a conductance zone of other component (e.g., TiO<sub>2</sub>, ZnO, etc.). Activity of TiO<sub>2</sub> increases after its preliminary thermal treatment (400–700°C) and also when ultrasound affects the medium being radiated [22, 23].

The rate of oxidizing photodestruction of organic pollutants substantially increases with simultaneous use of the homogenous (in the presence of Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Hg<sup>2+</sup>, Cr<sup>6+</sup>, Pt<sup>4+</sup>, Au<sup>3+</sup> ions, etc.) and heterogenous catalysis [1]. As the oxidizer ORP increases from some threshold (–0.3 V) the degree of substrate decomposition increases [17].

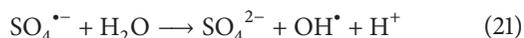
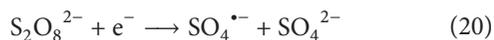
In result of phototransfer of charge in hydrocomplexes an excited cluster (Fe<sup>2+</sup>TiO<sub>2</sub>OH) containing hydroxyl radical is formed, which thus provides sensibilization of the heterogeneous-homogenous catalytic system:



Organic radicals, generated as a result of the transfer of the radical state from the excited cluster to the substrate (S), participate in further oxidizing processes leading to the formation of the products (P) of their mineralization through an intermediate buildup in the system of hydroperoxides:



When oxidizers (H<sub>2</sub>O<sub>2</sub>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, ClO<sup>-</sup>, O<sub>2</sub>, etc.) are introduced to the system, the rate of recombination of electron-hole pairs in PC decreases and additional channels for generating radicals from there:



Oxidation of substrate on the surface of PC goes on the two different mechanisms: that of Langmuir-Hinshelwood and that of Eley-Rideal. The Langmuir-Hinshelwood mechanism according to the process of substrate adsorption on the PC surface is followed by its oxidation with holes. The photoreaction rate ( $\nu$ ) is proportional to the degree of binding the PA adsorption centers with the substrate, which depends on the concentration of the latter (Cs) and the constant of adsorption equilibrium (K):

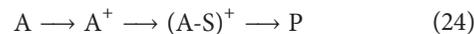
$$\nu = \frac{kKCs}{1 + KCs}, \quad (22)$$

where  $k$  is the constant of the photoreaction rate.

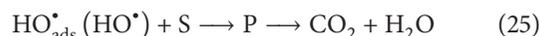
The product of substrate oxidation (S<sub>ads</sub><sup>+</sup>) is reduced with the electrons of the valence zone until the initial state or is transformed to reaction products:



According to the Eley-Rideal mechanism, oxidation is implemented through the initial stage of forming active centers (A<sup>+</sup>) as a result of capturing the holes with the defects of the catalyst surface (A) on which substrate chemisorption takes place:



Indirect oxidation is brought about during interaction of the substrate with hydroxylic radicals adsorbed and being in solution:



Adsorption properties of PC may be substantially increased by introducing it in the form of strutting off poles in the interlayer space of disperse aluminosilicates. The interlayer surface of the latter in most cases has a hydrophobic nature, which is conducive to adsorption and concentration of the substrate. A high degree of removing pollutants, especially at their low concentration, is achieved by TiO<sub>2</sub>, impregnated into mesoporous zeolite with a high specific surface (>100 m<sup>2</sup>/g). The shift of spectral bands being observed in the spectra of TiO<sub>2</sub> fixed clays with the particles size <10 nm is determined by the quantum-size effect resulting in the increase of PC activity.

In photoreactors, using suspended TiO<sub>2</sub>, the penetration depth of effective light in a great measure decreases due to absorption of radiation by the components of the medium. In addition, the use of the suspended PC in water treatment is linked with the necessity of its separation at the end of the technological cycle. The indicated drawbacks of the reactors of this type may be ruled out by using PC in the form of pallets or immobilized on various carriers (glass, ceramic, oxide metallic, fabric, etc.). Light penetration depth in the reactor increases when using a glass fiber as a carrier for TiO<sub>2</sub>.

The efficiency of the photodestruction process may be increased also by using combined methods of water treatment according to which water is preliminarily purified by filtering through membranes or photocatalytic decomposition of the pollutants precedes biological water treatment.

The vast majority of works devoted to the photocatalytic degradation of water pollutants here studied heterogeneous systems based on highly semiconductor PCs (mainly involving the dispersion of titanium dioxide). In practical terms, these systems are attractive because they can relatively easily achieve separation of the components, especially in the case of the PC supported on the stationary substrate.

Various physical and chemical factors (pH, the initial concentration of the oxygen pressure, the nature and amount of additives, the wavelength of the excitation light, etc.) have an impact on the efficiency of photocatalytic processes.

The maximum speed of the process achieved by the simultaneous presence of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>; small additions of TM ions (Fe<sup>3+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, etc.) increase the reaction rate. The highest speed of the process is observed in the presence of TiO<sub>2</sub> with doped zinc ions.

The efficiency of polycrystalline technical modification of titanium oxide (anatase) in DCPA destructive oxidation in

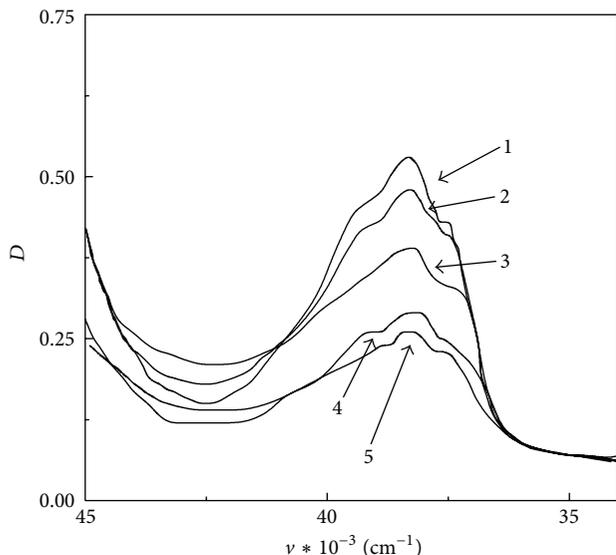


FIGURE 4: An effect of the photocatalyst ( $\text{TiO}_2$ ) on the photolysis kinetics of CPB: 1—spectrum of the feed solution; 2—the same after irradiating by UV light in the absence of  $\text{TiO}_2$ ; 3—the same by using the nonmodified  $\text{TiO}_2$ ; 4 and 5—the  $\text{TiO}_2$  samples alloyed by correspondingly iron and platinum.

aqueous media is commensurate with the reference sample Degussa P25.

Introduction TM ions  $\text{TiO}_2$  lattice (Fe, Cr, Ce, Mo, Nb, Ni, Mn, etc.), in most cases, allows to increase the efficiency of photocatalytic process by increasing chemisorption of pollutants on the surface of the photocatalyst and the expansion of the range of the spectral sensitivity of the latter in the long wavelength region of the spectrum.

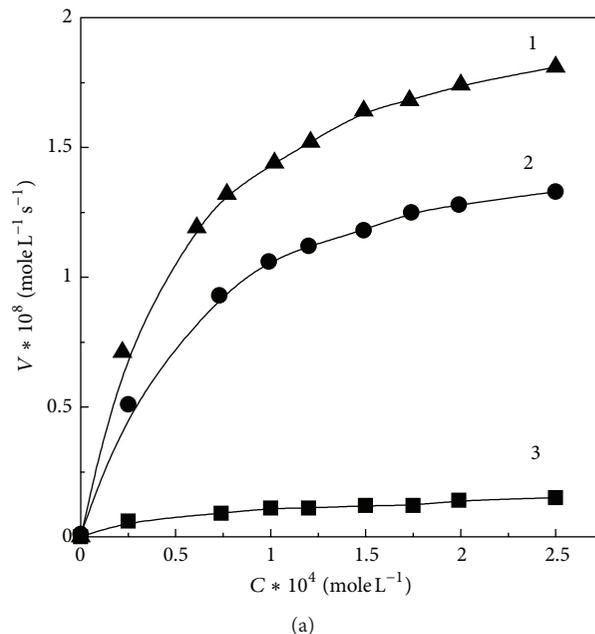
As shown in [1, 17], of the tested PC oxidative degradation (and recorded in the electronic spectrum of the products of its photolysis), DCPA is most effective in visible light polycrystalline technical modification of  $\text{TiO}_2$  doped with iron.

It is known that photodegradation of chlorinated hydrocarbons in the water under the action of ultraviolet irradiation is slow. This process proceeds efficiently in the presence of titanium dioxide and platinized titanium dioxide.

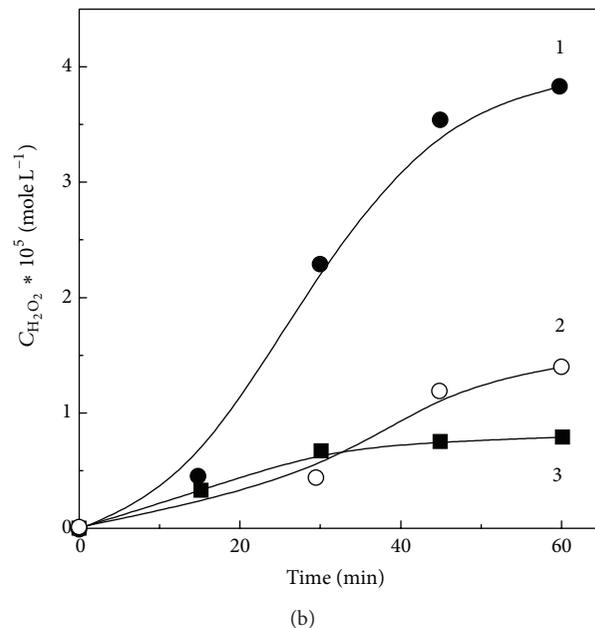
Doped with iron and platinum,  $\text{TiO}_2$  has a higher photocatalytic activity than pure PC (Figure 4). In the investigated processes, which are hydroxyl radicals, photogenerated by photoinduced transfer of electron between the ion-modifier element and a water molecule or a hydroxyl ion play an important role [14].

Introduction of cerium ions in the columns of the titanium dioxide in the interlayer space of montmorillonite increases photocatalytic activity of  $\text{TiO}_2$ -crosslinked decomposition of dichloromethane and 1,2-dichloroethane chlorinated methane and ethane [24]. As a result of photodegradation of these pollutants  $\text{CO}_2$ , HCl, and lower carboxylic acids are formed.

Introduction of cerium ions in the columns of titania in the preparation of  $\text{TiO}_2$ -fixed montmorillonite increases its



(a)



(b)

FIGURE 5: The dependence of the initial velocity ( $V$ ) of DCPA photocatalytic oxidation by atmospheric oxygen on initial concentration of the DCPA ( $C$ ) in the aqueous suspensions  $\text{Fe}_2\text{O}_3$  (0,5 wt.%)— $\text{TiO}_2$  (1),  $\text{TiO}_2$  (2), and  $\text{Fe}_2\text{O}_3$  (3) a composite system based on in water (pH 4.5) (a); photo generation of  $\text{H}_2\text{O}_2$  in aqueous suspension  $\text{Fe}_2\text{O}_3$  (1 wt%)— $\text{TiO}_2$ , ( $1 \text{ g } \mu\text{M}^{-3}$ ) in an oxygen atmosphere under UV light (high-pressure mercury UV lamp SVD-120, 380–400 nm) at pH: 1–6.0; 2–3.0; 3–9.0 (b).

photocatalytic activity, which allows intensifying photodestruction of dichloroethane in water and dichloromethane.

Composite based on the system  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  has increased process ability as compared to the initial  $\text{TiO}_2$  (Figure 5(a)). In this case, there is a symbiotic relationship between sorption and photocatalytic properties of PC. These

photocatalytic processes also involve generation of hydrogen peroxide by oxidation of water holes (Figure 5(b)).

#### 4. Conclusions

The results of these studies and the literature data indicate a high efficiency of photocatalytic methods in the oxidative degradation of organic pollutants in aquatic environments. The paper discusses the basic laws of the oxidative degradation of organic compounds of different classes with the use of homogeneous and heterogeneous photocatalytic systems with a view of their complete mineralization.

The comparative evaluation of different methods of chemical modification of semiconductor catalysts in terms of improving the efficiency of their use in industrial water treatment schemes and ways to improve the efficiency of oxidative destructive process by establishing composite photocatalytic materials are submitted.

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