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PHOTOCATALYSIS IN THE TREATMENT AND DISINFECTION OF WATER. PART I. THEORETICAL BACKGROUNDS

FOTOKATALIZA W OCZYSZCZANIU I DEZYNFEKCJI WODY CZĘŚĆ I. PODSTAWY TEORETYCZNE

Abstract: Photocatalysis process belongs to an advanced oxidation technology for the removal of persistent organic compounds and microorganisms from water. It is the technology with a great potential, a low-cost, environmental friendly and sustainable treatment technology to align with the "zero" waste scheme in the water/wastewater industry. At present, the main technical barriers that impede its full commercialization remained on the post-recovery of the catalyst particles after water treatment. This paper reviews the background of the process and photooxidation mechanisms of the organic pollutants and microorganisms. The review of the latest progresses of engineered-photocatalysts, photo-reactor systems, and the kinetics and modeling associated with the photocatalytic and photodisinfection water and wastewater treatment process, has been presented. A number of potential and commercial photocatalytic reactor configurations are discussed, in particular the photocatalytic membrane reactors. The effects of key photo-reactor operation parameters and water quality on the photoprocess performances in terms of the mineralization and disinfection are assessed.

Keywords: photocatalysis, TiO_2, water and wastewater treatment, photocatalitic reactors, kinetic of photocatalysis, disinfection

Introduction

The increasing demand for clean water together with its decreasing resources caused by the expansion of industries, human population swelling and long-term droughts have become the serious problem all over the world. It results in the demand of development of new, practically and economically attractive technologies enabling reasonable water use. It is estimated that over 4 billions of people have a very limited access to clean water and millions of people die every year because of diseases caused by bacteriologically damaged water [1]. It should be expected that in future those numbers will increase according to rising environment pollution caused by deposition of hazardous substances to natural water cycle [2]. According to the poor quality of natural water and clean water deficiency the

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development of cheap and effective water and wastewater treatment technologies are required.

Classical water treatment methods (coagulation/flocculation/sedimentation, filtration, activated carbon adsorption and chlorination) applied as single or integrated processes are not able to eliminate microorganisms and toxic inorganic and organic compounds from drinking water sources. Thus, the development of novel water and wastewater treatment processes *ie* membrane technologies, UV disinfection and "*Advanced Oxidation Processes*" is observed [3, 4]. However, those methods enable only the concentration or transportation of impurities to another phase, while their total elimination or neutralization is not obtained. Chlorination is generally applied to disinfection process, but it may result in formation of mutagenic and cancerogenic by-products [5]. Chemical and membrane methods (*ie* microfiltration, ultrafiltration, nanofiltration and reverse osmosis) characterize with high operational costs and can generate toxic secondary contaminants which are introduced to ecosystems. Despite that membrane technologies have become an alternative for classical treatment methods [6] they are significantly limited. Firstly, those processes assure only physical separation of microorganisms, organic and inorganic compounds. Hence, the concentrated stream (*ie* ca 10% volume of treated water) contains active pathogenic microorganisms and may cause a significant damage in feed stream or deposition place [6]. Secondly, the exploitation of membrane processes is always limited by fouling, which is especially characteristic for polymeric membranes [3]. Several fouling mechanisms have been distinguished among which (a) crystals formation caused by the excess over the solubility equilibrium of salts in concentrated stream (membrane scaling), (b) deposition of natural organic matter (organic fouling), (c) deposition of flocks and colloids (colloidal fouling) and (d) adhesion of polymeric extracellular substances and microorganisms (biofouling) are of the greatest importance. A-c types of fouling also known as physical fouling, which can be removed using hydraulic or chemical methods. Biofouling, on the other hand, is very problematic as it is initiated by microorganisms, extracellular polymeric compounds and even DNA [7], which are very strictly connected to membrane surface and cause changes in its selectivity and hydraulic permeability. Chemical cleaning and hydraulic actions are usually applied to keep membrane flux stable. However, they generate additional costs, which can reach up to 30% of total treatment costs [7]. Additionally, biofouling often appear in the irreversible form, thus it is not always possible to recover initial membrane capacity *via* cleaning.

Difficulties observed in the discussed treatment methods have resulted in fast development of *Advanced Oxidation Processes* (AOP) as a novel technology for water and wastewater treatment. AOP are based on transient *in situ* generation of highly reactive oxidants and radicals (mainly $OH^{\bullet}$, $O_2^{\bullet-}$, H_2O_2, O_3) which cause mineralization of organic compounds, water pathogens and disinfection by-products [2]. Among heterogenic photocatalysts applied in AOP semiconductive materials (TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS) are very popular. Those catalysts characterize with highly effective organic matter decomposition which results in formation of more biodegradable compounds or their total mineralization to carbon dioxide and water. Titanium dioxide (TiO_2) is semiconductive material usually applied in photocatalysis technology. TiO_2 is the most active photocatalysts of photon energy 300 nm $< l <$ 390 nm which remains stable during repetition catalytic cycles [1]. It also characterizes with high chemical, physical and thermal stability what guarantees it successful and wide application in water and wastewater treatment [1, 2, 4, 7].
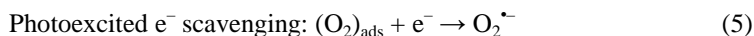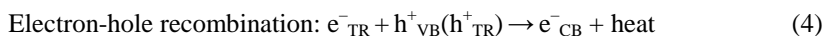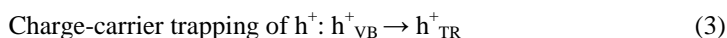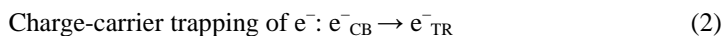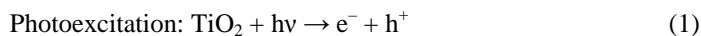
Introduction of heterogenic photocatalysis to water and wastewater technology processes has many advantages *eg* exploitation in the ambient temperature and normal pressure, complete mineralization of chemical substances and low operational costs [2]. It has been already reported that highly reactive oxygen forms generated during photo-induction on TiO_2 surface lead to microbiological inactivation and mineralization of organic compounds without the risk of formation of secondary contaminants [2, 8]. The main limitation of global scale application of the process is the final separation of semiconductive catalyst TiO_2 from the treated stream. Small size of TiO_2 particles and its high specific surface and surface energy result in the catalyst agglomeration during the reaction. It causes the reduction of specific surface and limits the multiple application of TiO_2. Moreover, the process should be improved in the field of catalysts photo-activity range or the possibility of integration into photocatalytic reactors [2, 7, 9].

The paper discusses the possibility of application of photocatalysis to the treatment of water and wastewater and is focused on mineralization of harmful and chemically and biologically stable contaminants and microorganisms inactivation.

Photocatalysis definition and mechanism

During photocatalysis solid, semiconductive catalysts generates active oxygen forms on its surface at radiation of light of proper wavelength. These oxygen forms are responsible for oxidation and reduction of compounds adsorbed on catalyst surface [1, 2, 7-9]. By definition, catalysts takes part in the reaction and speeds transformation of organic compounds, but remains in unchanged form at the end of the catalytic cycle [8].

The aim of the heterogenic photocatalysis with the use of semiconductive catalyst TiO_2 is to perform series of redox reactions on the catalyst surface [1, 2, 7-9]. It is exclusively connected with properties of electrons located on the outer molecular orbital. When photon energy (hν) of greater than or equal to valence to the *band gap energy* (TR) of TiO_2 is illuminated onto the catalyst surface (usually 3.2 eV - anatase or 3.0 eV - rutile), free electrons are transferred from TR to empty *conductive band* (CB) within few femtoseconds (1 quadrillionth - 10^{-15} of second). Hence, "electron gap - electron" pairs are formed (e^- - h^+) [2]. In case of TiO_2 the energy gap between bands can be balanced by delivering photon energy from near-UV, what usually corresponds to the wavelength $\lambda < 400$ nm. Energy consumption and next generation of "electron gap - electron" pairs are stages that initiate photolycatalysis process. Chain redox reactions which occur on the photocatalyst surface are described by equations (1)-(11) [2, 9, 10]:
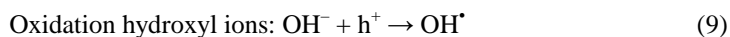
$$\text{Photoexcitation: } TiO_2 + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$\text{Charge-carrier trapping of } e^-: e^-_{CB} \rightarrow e^-_{TR} \tag{2}$$

$$\text{Charge-carrier trapping of } h^+: h^+_{VB} \rightarrow h^+_{TR} \tag{3}$$

$$\text{Electron-hole recombination: } e^-_{TR} + h^+_{VB}(h^+_{TR}) \rightarrow e^-_{CB} + \text{heat} \tag{4}$$

$$\text{Photoexcited } e^- \text{ scavenging: } (O_2)_{ads} + e^- \rightarrow O_2^{\bullet -} \tag{5}$$

The e^-_{TR} and h^+_{TR} in equations (1)-(4) correspond to electrons in valence band and electron gaps in conductive band, respectively. Those electron gaps are carriers of trapped electrons and do not recombine immediately after their excitation with photons [2]. In the absence of electron scavengers, the photo-excited electron is recombined with the valence band within few nanosecond with simultaneous heat dispersion (equation (4)). Thus, the

presence of electrons scavengers (acceptors) *eg* oxygen is crucial for recombination elongation and successful photocatalysis performance. The action of oxygen avoiding electron recombination and enabling formation of peroxide ($O_2^{\bullet-}$) free radicals is shown in equation (5). Those radicals can again undergo protonation forming hydroperoxide radicals ($HO_2^{\bullet}$) and, finally, hydrogen peroxide, what is shown in the equations [9]:

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \tag{6}$$

$$O_2^{\bullet-} + O_2^{\bullet-} \rightarrow H_2O_2 + O_2 \tag{7}$$
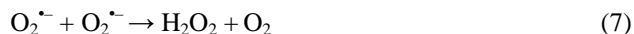
The $HO_2^{\bullet}$ radicals also act as electrons scavenger and thus, according to their coexistence, the recombination time of h^+_{TR} in the entire photocatalysis reaction, can be doubled. Interaction of electron gaps with water particles and hydroxyl ions results in formation of highly reactive hydroxyl radicals:

$$\text{Oxidation of water: } H_2O + h^+ \rightarrow OH^{\bullet} + H^+ \tag{8}$$

$$\text{Oxidation hydroxyl ions: } OH^- + h^+ \rightarrow OH^{\bullet} \tag{9}$$

Those radicals are bonded to the surface of hydrated metal oxide and act as a basic oxidant in photocatalytic system [2, 8, 9]:

$$\text{Photodegradation caused with } OH^{\bullet} \text{ radicals: } Re\text{-}H + OH^{\bullet} \rightarrow R^{\bullet\bullet} + H_2O \tag{10}$$

$$\text{Direct contribution of electron hole:}$$
$$R + h^+ \rightarrow R^{+\bullet} \rightarrow \text{Intermediate(s) - final degradation products} \tag{11}$$
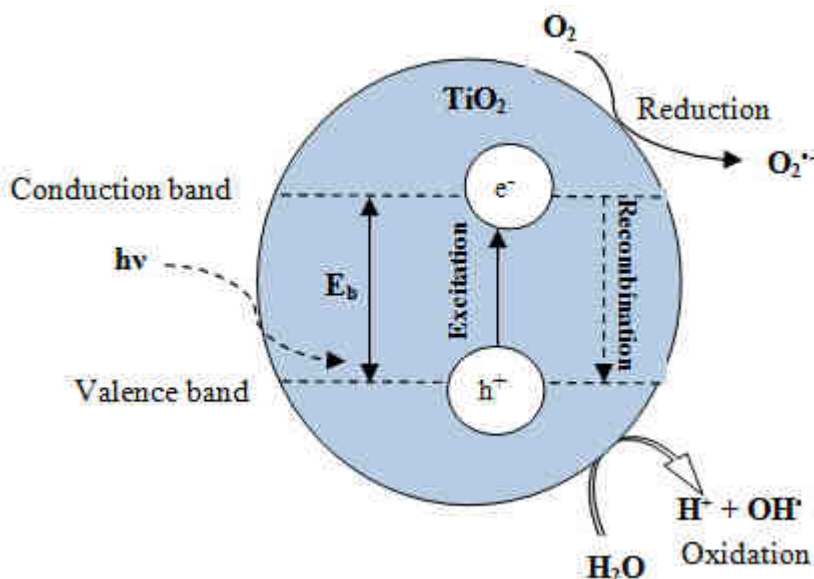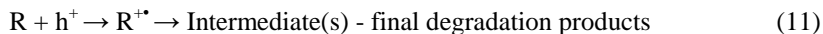

Fig. 1. Photo-induced formation of electron - hole pair in a semiconductor TiO_2 particle

One must notice that all discussed photocatalytic processes occur only in the presence of dissolved oxygen and water molecules. At the absence of water the formation of highly reactive hydroxyl radicals ($OH^{\bullet}$) could not be formed and photodegradation of organic

substances present in the liquid phase is not possible. Some simple organic compounds (*eg* oxalate and formic acid) can be mineralized *via* direct electrochemical oxidation, during which the e^-_{TR} is scavenged by metal ions in the absence of water [2]. Even though it is supposed that the h^+_{TR} posses the ability of direct oxidation of organic compounds, however this ability is inconsistent.

In Figure 1 the electron gap formation mechanism in valence band - electron in conductive band pairs while TiO_2 particles are already radiated is shown [2, 9]. In Figure 2 the influence of light wavelength on photocatalytic reaction is presented [7].

The photoexcitation of TiO_2 that causes generation of „electron - hole" pairs and next $OH^\bullet$ free radicals requires greater energy than the gap between valence and conductive band (E_b). It corresponds to the radiation wavelength less than 380 nm for anatase (the most often used polymorphic TiO_2 form) and below 400 nm for rutile (crystalline TiO_2). Those wavelengths are covered by near-UV range (300÷400 nm) and must be provided by commercial UV lamps or UV part of solar light (Fig. 2). However, sun radiation characterizes with only 5% of UV range. Thus, photocatalytic systems based on sun radiation and TiO_2 characterize with significant surface area, which result in high operational costs [11]. Many successful studies show the possibility of addition of several metals to TiO_2 in order to change the wavelength range to visible one. However, final catalysts characterize with decreased photo-activity as recombination process is enhanced by metal ions [12]. Experiments with NH_4OH addition to colloidal TiO_2 also has been performed. They have resulted in absorption of visible light by the material as the energy of electron transfer from valence to the conductive band has decreased [7]. Those studies caused the increase of the interest in detailed description of TiO_2 properties in the mixture with anions [13]. It has been shown that TiO_2 containing carbon atoms is a very promising alternative for nitrogen-based materials [14].
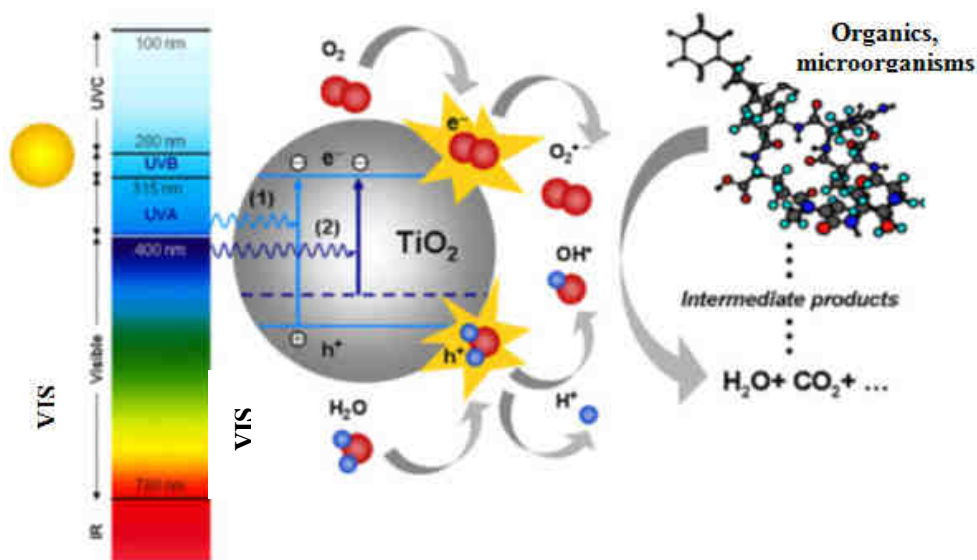

Fig. 2. Scheme of the photocatalytic action of TiO_2 under UV (1) and visible (2) irradiation

Organic compounds photodegradation mechanism

Many basic studies of photochemical degradation of various chemical compounds on TiO$_2$ surface (*ie* phenols, chlorophenols, dyes, pesticides, herbicides, humic and fulvic acids, pharmaceuticals, endocrine disruptors, heavy metals and other inorganic compounds) have already been performed [2, 4, 7, 10, 15-17]. In fact, every group of chemical compounds can undergo photodegradation according to different mechanism, which depends on chemical structure and character of functional groups. For example, aromatic compounds can be hydroxylated by reactive OH$^•$ radicals and undergo oxidation/addition which is finished with the ring opening. Obtained by-products, aldehydes and carboxylic acids, are next oxidized to carbon dioxide and water. As photocatalytic reaction takes place on TiO$_2$ surface activated by photons, it is crucial to understand stages of organic compounds photodegradation in order to develop kinetic equations. In case of heterogenic photocatalysis organic compounds present in aqueous phase are transformed into by-product and finally mineralized to carbon dioxide and water at proper radiation:

$$\text{Organic contaminants Intermediate(s)} \xrightarrow{\text{TiO}_2/\text{h}\upsilon} CO_2 + H_2O \qquad (12)$$
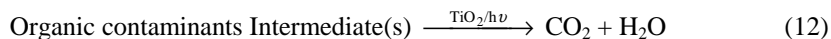
Generally, photocatalytic reaction defined by equation (12) can be divided into 6 independent steps [2, 9]:

1. Diffusion of organic compounds (*eg* A) from aqueous phase to TiO$_2$ surface - external mass transport.
2. Diffusion of substrates between and/or inside particles to the active catalyst surface - internal mass transport.
3. Adsorption of organic compounds on TiO$_2$ surface activated by photons (the activation of catalyst surface by photon energy also occurs).
4. Photocatalysis of phase adsorbed on TiO$_2$ (*eg* A→B).
5. Desorption of by-products (*eg* B) from TiO$_2$ surface.
6. Transport of by-products (*eg* B) from interfacial surface to aqueous phase.

Photodisinfection mechanism

As photocatalysis can be effectively applied to degradation of organic and inorganic compounds, it should be possible to use it for destruction of microorganisms. All microorganisms, such as bacteria cell, consist of water (70÷90%) and major cell compounds *ie* polysaccharides, lipids, lipopolysaccharides, proteins and nucleic acids. Thus, their cell can be attacked by oxygen containing radicals and completely destroyed [8]. Matsunaga et al [18] were frontiers that prove bactericidal properties of TiO$_2$. TiO$_2$ can cause significant damage in amino acids [19] and DNA molecules [20], when they are oxidized separately. However, many of these molecules are very complex, and collectively, posses different chemical and physical resistances to possibility of total cell degradation. There are several phospholipids groups of various types which differ in composition of fatty acids. Thus, many genetic differences and various growth conditions can be observed [21]. Moreover, except of differences in particular components the specific structure (*eg* double-layer lipids or cross-linked peptides chains) also increases their resistance to inactivation.

Nevertheless, photocatalysis can be used for destruction of bacteria and viruses. Nowadays, the application of the process to water and wastewater disinfection is of a great

interest. The possibility of using sunlight as the radiation source is very attractive. Several pilot scale studies revealed the occurrence of photocatalytic disinfection at sunlight radiation [22, 23]. *Streptococcus natuss, Streptococcus cricetus, faecalis* and *aureus, Escherichia coli* and total *Coli, Scaccharomyces cerevisisas, Lactobacillus acidophilus, Enterobacter cloacae Chlorella vulgaris, Candida albicans, Fusarium solami, Aspergillus niger,* Polio 1 virus have been successfully inactivated using heterogenic photocatalysis [2, 10]. The expanding algal blooms observed in fresh water sources results in possibility of its contamination with *Microcystin toxins*, which can be eliminated by application of TiO_2 to their degradation [7, 10, 24]. Photodisinfection with TiO_2 has also resulted in partial degradation of *Chlorella vulgaris* (Green algae) which cells has significant wall thickness [10].

Several mechanisms of photocatalytic inactivation have been proposed. However, as a simplification, they can be divided into extracellular and intracellular mechanisms [8]. Cell membrane and wall are classified as extracellular elements. Surface interaction of microorganisms with photocatalyst is crucial for inactivation process. External cellular layers (*ie* wall and membrane) are very complex, however there are many places which can be affected by free radicals and highly active oxidants action. In case of bacteria 3 types of structures are taken into consideration [8]:

- peptidoglycan layer, present in Gram-positive and Gram-negative bacteria, is a component of bacteria cell wall composed of polysaccharide and peptide chains in a strong molecular network. Chemically it is a biopolymer of muramic acid and *N*-acetylglucosoamine with tripeptide: D-alanine, D-glutamic acid and mesodiaminpimelinic acid;
- *lipopolysaccharide layer* (LPS), peripheral layer characteristic only for Gram-negative bacteria;
- phospholipids double layer - 2 layers in Gram-negative and one in Gram-positive bacteria.

Peptidoglycan layer can be affected by free radicals only in a limited extent according to its porous nature (it enables transport of molecules of diameter ca 2 nm) [8]. While the size of pores can be suitable for transport of hydroxyl or peroxyl radicals, it may still be difficult for such molecules to permeate to the inner cell structure due to their reactivity in the external environment.

During the direct contact of free radicals and strong oxidants with microorganisms results firstly in the action on lipopolysaccharide layer *ie* external layer of the cell wall [2, 8], especially polyunsaturated fatty acids. The formation of perhydroxyl groups takes place and leads to oxidation of cell membrane proteins. In photocatalytic lipids reaction peroxidation step is very important as LPS layer and phospholipids double layer are composed from fatty acids which are susceptible to peroxidation. Peroxidation of lipids is based on biological oxidation of lipids *via* chain and free radical reaction during which peroxides of those lipids are formed in cells (Fig. 3). It has been shown that the process takes place in both, photocatalytic experiments [25, 26] and also other reactions with free radicals [27, 28]. Poly-unsaturated fatty acids present in lipids are usually oxygen-sensitive compounds. The reaction of unsaturated fatty acids with radicals at the presence of oxygen results in formation of peroxyl radicals, which can react with other nearby lipid molecules generating additional lipid radicals [8]. The propagation of the process takes place as formed lipid radicals react with other unsaturated lipids (Fig. 3). All those actions result in

leakage of potassium from bacteria cell, what significantly affects cell life. The limitation of cell vitality usually results of peroxyl groups formation from unsaturated phospholipids - components of cell membranes (*ie* the loss of basic cell functions) what finally leads to the cell death.
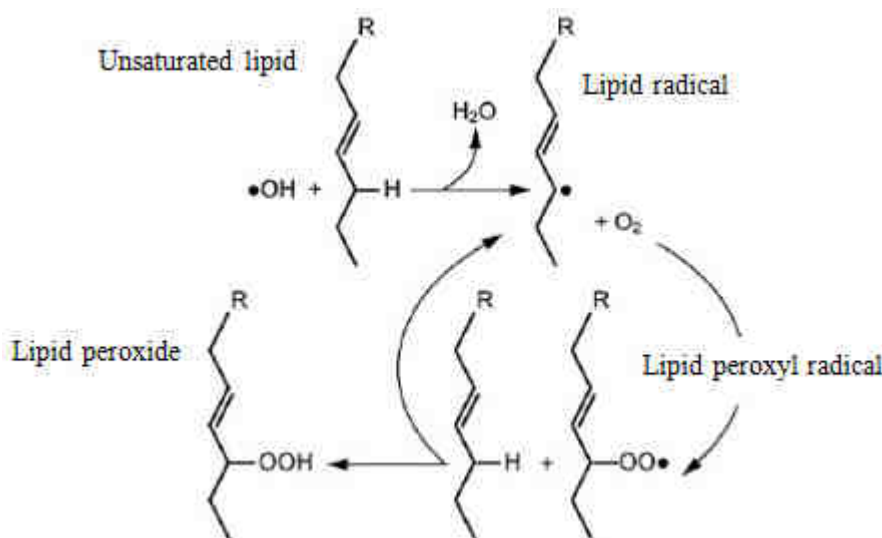

Fig. 3. Scheme of lipid peroxidation

Other intracellular substances (*ie* cytoplasm) can also be the target of oxidants action during photocatalysis. DNA, RNS and ribosome present in cytoplasm together with other dissolved or suspended substances are crucial for proper functionality of the cell. However, cytoplasm is protected by cell membrane, which is impermeable for most of compounds except of water, oxygen, carbon dioxide and few other neutral substances. Thus, the access to intracellular structures is highly limited [18, 29-31]. The inactivation of intracellular components must be preceded by generation of other oxidants *ie* lipid radicals, hydrogen peroxide, peroxides or surface bonded radicals, which can reach cytoplasm after a serious damage of membrane cell [32, 33]. Despite direct attack, peroxides and hydrogen peroxide are able to form perhydroxyl radicals *via* Fenton reaction in intracellular environment as many cells contain iron [34-36].

Influence of process parameters on photocatalysis effectiveness

Photocatalytic oxidation effectiveness is depended on series of operational parameters, which impact on the process is discussed below [2, 9, 37-39].

Catalyst dose

The increase of catalyst dose results in increase of active surface available for adsorption and degradation processes. On the other hand, the turbidity of the solution increases, thus the penetration of stream by photons is limited [40]. Moreover, the surface

decrease can be also observed as at high solid concentration TiO_2 particles form agglomerates [41]. Hence, the initial rate of photoreaction and its effectiveness are directly proportional to catalyst mass. However, when the critical dose is exceeded, the reaction rate is independent from it and remains constant or even decreases with the catalyst dose increase. Thus, the proper estimation of optimal catalyst dose must be done for a given application (*ie* reactor configuration, source of radiation, contaminants concentration, etc).

pH

The influence of pH on photocatalytic degradation of organic compounds in water is mainly related to the rate of ionization of TiO_2 surface, position of valence and conductive bands of photocatalyst, the degree of TiO_2 agglomeration and formation of hydroxyl radicals [9, 42]. The isoelectric point of TiO_2 (*zero charge point* - ZCP) changes within pH range 6-7 depending on the catalyst applied [2, 9, 43]. For commercial TiO_2 (*eg* Degussa P25, ZCP is obtained at pH = 6.8) at pH < ZCP(TiO_2) the surface charge of the catalyst becomes positive and step wisely increases the electrostatic attraction of negatively charged compounds. Such a polar interaction between TiO_2 and charged anionic organic compounds can intensify the adsorption on the TiO_2 surface, which is activated with photons for next photocatalytic reactions [2, 44]. It is especially important in case of low concentration of anionic organic compounds. At pH > ZCP(TiO_2) the catalyst surface becomes negatively charged and repulses anionic compounds present in water; pH changes can affect surface charge density of TiO_2 catalyst [25, 26] according to the presented equations of chemical equilibrium in water:

$$\text{at pH < PZC: TiOH} + H^+ \leftrightarrow TiOH_2^+ \tag{13}$$

$$\text{at pH > PZC: TiOH} + OH^- \leftrightarrow TiO^- + H_2O \tag{14}$$

The distribution of surface charge density of TiO_2 catalyst depends on the reaction environment pH. It has been found that the content of TiOH may exceed 80% at $3 < pH < 10$, while $TiO^- \geq 20\%$ at pH > 10 and $TiOH_2^+ \geq 20\%$ at pH < 3. The equilibrium constants of those reactions at various pH are equal to $pK_{TiOH2+} = 2.4$ and $pK_{TiOH} = 8.0$ [2].

Similar electrostatic interactions have been observed also in photo-disinfection process [44]. During photodisinfection the destruction of external cellular walls layers containing liposaccharides and peptidoglycans firstly takes place. It results in peroxidation of the lipid membrane and next, the oxidation of the membrane proteins and polysaccharides occurs. The increase of $TiOH^{2+}$ density (at low pH) may form an electrostatic bond between the bacteria cell and negatively charged surface speeding the disinfection up. One must concern that the improved bactericidal action of TiO_2 at low pH is caused only by TiO_2 photoeffect, not by the cell acidification. The confirmation of such a behavior can be found in Rincon and Pulgari studies [45, 46], during which no pH effect (in the range 4-9) on *Escherichia coli* cells inactivation was observed.

Except of discussed phenomena also pH depended interactions between catalyst particles are observed. The size of catalyst particles may vary from 300 nm up to 4 mm depending on the difference between ZCP TiO_2 and reaction pH [1]. At pH = ZCP the neutral charge of the catalyst surface is not able to hold solid particles in the liquid. Thus, the aggregation of catalyst particles and their sedimentation takes place [47, 48]. The phenomenon is usually used in membrane photoreactor systems, in which wastewater after the phototreatment is neutralized to pH = 7 in order to recover catalyst particles. The

efficiency of the catalyst recovery by means of neutralization can reach up to 97%. The rest of the catalyst can be recovered for example by means of microfiltration. Nevertheless, the proper design of the pH control of the photoreaction is crucial for every photocatalytic water treatment process.

Temperature

Many studies have revealed the dependence of the effectiveness and rate of the photocatalysis on the temperature [2, 8, 9]. Generally, the process should be carried out at the temperature range of 20÷80°C [8, 37, 38]. At very low temperature (*ie* below 0°C) the activity of the catalyst decreases and the desorption of the final product from the catalyst surface becomes the limiting step of the reaction rate. On the other hand, at temperature above 80°C, the adsorption of contaminants is ineffective and thus the photoreaction performance is limited [38, 39]. At the temperature range 20÷60°C the increase of the photoreaction rate with the increase of the temperature is observed [49-51]. The activation of TiO_2 surface and the proper understanding of the reaction rate dependence on the temperature is very important when the process is carried out under natural sunlight conditions.

In case of photodisinfection performance using TiO_2 catalyst the increase of the temperature results in the more effective inactivation of microorganisms [46]. Such a dependence is described by Van't Hoff-Arrhenius equation, in which k constant is linearly proportional to $\exp(-1/T)$:

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ (15)

where k_1 and k_2 are the constants for temperature T_1 and T_2, E_a is the energy of activation and R is the universal gas constant. The vitality of microorganisms with respect to the catalyst activity depends on the incubation temperature and type and resistance to temperature change. Generally, the order of resistance of microorganisms to conventional disinfection systems is of: non-spore forming bacteria < viruses < spore forming bacteria < parasites < protozoa (oocytes) [8]. Nevertheless, any complex studies of the impact of the photodisinfection with TiO_2 at various temperature conditions on microorganisms have been performed. Thus, usually the photodisinfection is carried out at the temperature below 80°C in order to reduce operational costs connected with water heating (high water heat capacity) [8].

Dissolved oxygen

The concentration of the dissolved oxygen in the photocatalytic system with TiO_2 is very important as it provides the efficient electron scavenging in the conductive band and prevents their recombination [2, 52]. The presence of the dissolved oxygen also influences the formation of oxygen-containing radicals other than hydroxyl ones and guarantees the stability of semi-radicals, mineralization and photocatalytic reaction itself. The dissolved oxygen also allows to hold TiO_2 particles in the suspension. However, the operation of photoreactor equipped with the pure oxygen supply is very expensive. Thus, it can be replaced with air as any significant differences in the process performance have been observed.

The influence of the dissolved oxygen concentration on the photodisinfection efficiency has not been investigated in detail. It has been assumed that the formation of various oxygen-containing radicals which take part in redox reactions on the photocatalyst surface is similar for both, photomineralization and photodisinfection [2]. If the amount of nutrients in the system is sufficient, the constant oxygen supply will promote the microbiological growth and may affect photodisinfection effectiveness. It results in the elongation of the radiation time required for the desired microorganisms inactivation. Thus, it is recommended to investigate in detail the impact of the dissolved oxygen content on particular steps of the photodisinfection in order to design the proper strategy of the oxygen introduction to the system.

Initial concentration of reagents

In general, the rate of organic contaminants degradation increases with the increase of substrates initial concentration. However, this increase is observed only to a given point, exceeding of which results in the decrease of the degradation rate [2, 9, 42].

The study confirmed that at the similar process conditions the change of the initial water contaminants concentration causes the change of necessary radiation time required for total disinfection or mineralization. In respect to the photonic character of the photocatalytic reaction the excessive concentration of organic substrates causes both, the saturation of TiO_2 surface and the reduction of photocatalysis efficiency, what results in the inactivation of the photocatalyst [53]. Moreover, the time of radiation strongly depends on the chemical character of organic substrates. More complex compounds generally undergo through series of degradation reactions and many various by-products is formed, while simple compounds (*eg* oxalic acid) are directly decomposed to carbon dioxide and water [2]. Such an evolution through by-products formation results in the elongation of the radiation time necessary for complete mineralization according to the direct competition of compounds to TiO_2 active site.

Recently, the heterogenic photocatalysis has been combined with biological wastewater treatment in order to improve its industrial application [54]. Such a combination allow to reduce the retention time of biological treatment as refractive compounds present in wastewater can be transformed to biodegradable ones during photocatalytic oxidation. Additionally, the evaluation of photodisinfection of various microorganisms has been performed to check the possibility of the replacement of chemical disinfection methods by the photocatalytic technology. In general, the mechanism of microbiological disinfection is based on the destruction of protein structures and the inhibition of enzymatic activity [54]. Among all investigated microorganisms the highest immunity has been revealed by *Coccidia* parasites (*Cryptosporidium*), next by Endospores bacteria (*Bacillus*), *Mycobacterium tuberculosis* (MTB), viruses *(Polio)*, fungi (*Aspergillus*), Gram-negative bacteria (*Pseudomonas*) and eventually Gram-positive bacteria (*Enterococcus*) [1].

Feed water quality

In practical application photocatalysis can be used for treatment of water of various quality. Treated water parameters have a great impact on the performance of advanced photocatalytic processes with TiO_2 [2].

Turbidity, which is caused by insoluble solid particles present in the raw water, is a significant disruptor of photocatalytic process based on TiO_2. Suspended or dispersed

particles have a huge influence on optical water properties and further impede the transmission of UV light by strong dispersion and adsorption of the rays [55, 56]. It causes changes in expected TiO_2 charge and affects pathway and intensity of UV light. Moreover, a significant turbidity may cause shielding effect, which decreases light transmission, protects contaminants from UV rays action and limits the performance of both, photocatalysis and photodisinfection [25, 55, 56]. Finally, the action of all those factors causes the ineffective photocatalytic water treatment. In order to ensure the proper rate of photocatalytic reaction the water turbidity should not exceed 5 NTU what enables the optimal use of UV light [57, 58]. Rincon and Pulgarin [45] observed that the increase of the turbidity above 30 NTU had a negative effect on photocatalytic disinfection rate. 5 NTU limit is arbitrary and depends on water source and desired treatment level [2]. As photocatalytic processes with TiO_2 are used at the advanced stage of water treatment the decrease of the turbidity may be obtained during convectional treatment *ie* sieving, filtration, sedimentation, coagulation and flocculation.

Water and wastewater used to photocatalytic treatment with TiO_2 usually contain **inorganic ions.** Thus, the understanding of their influence on the photocatalysis performance is very important. It has been found, that during the application of suspended or fixed-bed catalyst configurations in treatment of water containing various inorganic ions, the inactivation of the photocatalyst surface is observed [2]. Thus, the impact of inorganic cations (Na^+, K^+, Ca^{2+}, Cu^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Al^{3+}) and anions (Cl^-, NO_3^-, HCO_3^-, ClO_4^-, SO_4^{2-}, HPO_4^{2-}, PO_4^{3-}) on photocatalytic water treatment has been investigated [2]. The study showed that at certain concentration Cu^{2+}, Fe^{2+}, Al^{3+}, Cl^-, PO_4^{3-} ions caused the decrease of photocatalytic reaction efficiency, while Ca^{2+}, Mg^{2+}, Zn^{2+} ions had no influence on the process, probably because they reached their maximum oxidation state. If Fe^{2+} ions are present in water they can catalyze both, Fenton and photo-Fenton reactions. Moreover, Choi et al [59] observed that Fe^{2+} ions cause fouling of photocatalysts surface by the formation of $Fe(OH)_3$ which changes the color of the photocatalyst to reddish-orange, while PO_4^{3-} ions at nomina pH range are strongly adsorbed on the catalyst surface and inhibit its photoactivity [2, 60]. It has been also found that NO_3^-, SO_4^{2-}, ClO_4^- and HCO_3^- ions limited activity of photocatalysts surface during both, mineralization and disinfection [61]. Cu^{2+} ions may improve the activity of photocatalysts but only at concentration below 0.01 mM, while above this level the decrease of the reaction rate is observed [62]. The inhibition character has been also defined for nitrogen containing molecules, which are mineralized mainly to NO_3^- and NH_4^+, while sulfur present in compounds is transformed directly to sulfate ions [2].

The influence of catalyst surface fouling with inorganic ions on photoactivity of TiO_2 has been described by several mechanisms [63, 64]. They include screening effect of UV rays, adsorption competition of active sites and photons on particles surface, radicals and electron gaps scavenging and direct interaction with photocatalyst. Such properties are mainly exhibited by NO_3^-, Cl^-, SO_4^{2-}, HCO_3^- and PO_4^{3-} ions. The mechanism of the photocatalysis inhibition by Cl^- and HCO_3^- anions by scavenging of radicals and electron gaps can be described by following reactions [22, 65]:

$$Cl^- + OH^\bullet \rightarrow Cl^\bullet + OH^- \tag{16}$$

$$Cl^- + h^+ \rightarrow Cl^\bullet \tag{17}$$

The Cl^- ions also cause inhibition of photocatalysis with TiO_2 described by the mechanism of preferential adsorption towards OH^- ions bonded with the surface. It decreases the amount of available OH^- ions on TiO_2 surface, while substitute Cl^- ions increase the recombination of electron-electron gap pairs [2].

In order to avoid TiO_2 photocatalyst fouling prevention or regeneration strategies are applied in regard to inactivation character in water matrix. The prevention strategies based on water pretreatment *eg* complexation of fouling substances and modification of the catalyst surface, while washing of TiO_2 with various chemicals is regarded as the regeneration strategy [2].

The strong toxic effect on the photocatalysis has also been revealed by **heavy metals** at certain oxidation states which were present in treated stream in trace amounts [66].

Parameters of light source

The applied light with different wavelength emitting ranges will have a great impact on the photocatalytic reaction rate, depending on type and crystalline form of catalyst used. In case of commercial TiO_2 P-25 Degussa catalyst which characterizes with crystalline ratio of anatase to rutile 70/80:20/30 the wavelength of $\lambda < 380$ nm is sufficient for photonic activation [2, 67]. Crystalline phase of rutile TiO_2 have lower energy for conductive band formation comparing with anatase TiO_2 [68]. Hence, rutile can be activated at the wavelength up to 400 nm. It shows that in order to perform photocatalytic decomposition reaction the applied light spectrum should be at least at near-UV range. Both light sources can be used *ie* artificial light or sun light [69]. However, the artificial UV light source immersed or placed outside of the reactor and emits UV-A ($\lambda_{max} = 355 \div 365$ nm) or UV-C (germicidal lamps, $\lambda_{max} = 254$ nm) light, is most frequently applied. The wider application of artificial light is caused by the fact that the higher photon streams are obtained. The study show that UV-A and UV-B light posses photons which are able to activate catalyst [55, 70, 71]. However, the mechanism of photolysis of UV-A and UV-B radiation and microorganisms cells inactivation differs from the mechanism of UV-C radiation. In case of sun light, UV-C radiation is usually absorbed by the atmosphere and does not reach to the Earth surface. Thus, the photocatalytic disinfection is performed in systems of photoreactors, which use artificial UV-C radiation for catalytic activation. Longer sunlight wavelengths ($\lambda < 400$ nm) have also been investigated for sunlight disinfection [2]. However, the mechanism of photodisinfection of combined UV-A radiation and sunlight spectrum is not clear yet. It has been shown that during sunlight disinfection pathogens present in drinking water placed in PET bottles became inactivated within 6 hours exposure to sunlight [2].

The typical UV light stream measure near earth is equal to $20 \div 30$ W/m^2. It corresponds to $0.2 \div 0.3$ mol of photons/m^{2}h in the range of $300 \div 400$ nm delivered by the Sun. Nevertheless, only 5% of total sun radiation posses energy sufficient for photoexcitation [68]. Those photons can be used for photocatalytic decomposition of contaminants present in water. It has been proved during series of experiments which were carried out in sun photoreactors designed and tented within last twenty years [67]. One must know that during clouded days the application of sunlight is significantly limited. Thus, latest experiments are focused on the development and application of new catalysts which are able to use visible light spectrum [72].

In order to characterize the influence of the **light intensity** on the photocatalytic reaction rate it can be said that [2, 73, 74]:

- at low irradiance (0÷20 mW/cm^2) the increase of the reaction rate with the increase of the light intensity is linear (first order reaction) as electron gaps formation is dominant, their recombination is absent,
- at medium irradiance (ca 25 mW/cm^2) the reaction rate depends on the square root of irradiance (0.5 order reaction) as electron gaps formation competes with recombination and thus limits its influence on the total reaction rate,
- at high irradiance the reaction rate is independent from the light intensity.

The increase of light intensity results in the increase of the reaction rate until the mass transport in the reaction becomes limited (*ie* at high light intensity) [74]. The higher irradiance causes the move of the electron from catalyst to oxygen present in the solution, what results in the formation of $O_2^{\bullet-}$ radicals which limit reaction rate especially in case when photocatalyst particles are agglomerated [75].

The effectiveness of photocatalytic disinfection also significantly depends on the time of radiation at given irradiance. Rincon and Pulgarin [45] investigated the influence of light intensity at the range of 400 and 1000 W/m^2 lethality and regrowth of bacteria and showed that the higher constant irradiance caused irreversible damage of *E. coli* bacteria cells. In case of irregular radiation bacteria had a tendency to regrowth within 24 to 48 hours. Several study suggest that the bacteria regrowth is caused by the recovery of cell fragments at the present of nutrients [76]. Other studies suggest that partially damaged but not completely inactivated cell can recover the vitality at 300-500 nm radiation or the re-synthesis and replication of cells takes place [45, 77]. The results of disinfection at irradiance 400 W/m^2 carried out for 2.5 h are different from once obtained for processes at irradiance 1000 W/m^2 run for 1h. Thus, in order to predict the minimal exposure time at constant irradiance the preliminary studies discussing photoreactor characteristic and microbiological resistance of microorganisms should be performed [2].

Kinetics and modeling

Kinetics and mechanistic studies of water pollutants photomineralization and photodisinfection are very useful tool considering the process scale-up. The proper use of kinetic models to interpretation of experimental data enables design and optimization of photoreactor system with the sufficient accuracy and size [2, 4, 8, 9].

Photomineralization kinetics

In most of the studies of photocatalysis kinetics or mechanistic modeling usually single representative organic compound is used. Thus, the series of papers discussing the kinetic of photodecomposition of various organic compounds, mainly dyes, pesticides, herbicides, phenols, halogenated phenols, alkanes, halogenated alkanes, aliphatic alcohols, carboxylic acids and series of others can be found in the literature [1, 39, 67, 68]. Non-selective character of OH$^{\bullet}$ radicals suggests that the rate of decomposition and time of exposure should not be only parameters considered during reactor design. It is caused by the formation of many mineralization by-products which is usually omitted in kinetic model of photomineralization. Thus, the concentration of organic compounds should be commonly marked as COD or TOC to enable the deeper understanding of photomineralization kinetics.

It is sometimes said that simple first-order or zero order reaction kinetics is sufficient enough to model photomineralization of organic compounds. However, it can only be applied in limited cases, generally when compounds concentration is sufficiently low [2].

In general, the non-linear kinetic profile is obtained as the rate of oxidation increases with radiation time until zero rate is reached [78, 79]. Such a kinetic run usually corresponds to Langmuir-Hinshelwood (LH) model [37, 80, 81]. As LH model depends on catalyst surface, the reaction rate increase with the radiation time is expected, as during radiation concentration of organic substrate decreases while the access to catalyst surface increases. The zero degradation rate is connected with achievement of the total degradation point. There are several assumptions of LH kinetics and possibilities of its application to photomineralization effectiveness calculations, while the reaction can occur between: (1) two adsorbed components *ie* radicals and organic compounds; (2) aqueous phase radical and adsorbed organic compound; (3) radical on the catalyst surface and organic compound in the aqueous phase; (4) both, radical and organic compound in the aqueous phase [2]. Hence, according to LH model the *rate of photocatalytic reaction* (r) is directly proportional to the part of the surface covered with organic substrate (Θ_x) [2, 9]:

$$r = \frac{dC}{dt} = k_r \Theta_x = \frac{k_r KC}{1 + KC} \tag{18}$$

where: k_r - reaction rate constant, C - concentration of organics, K - Langmuir adsorption constant.

The applicability of equation (18) depends on several assumptions *ie* (1) the reaction system is in the dynamic equilibrium; (2) the reaction occurs on the surface; (3) the competition of by-products adsorption on the active TiO_2 surface takes place and other types of oxygen reactive forms are unlimited [52]. Thus, it is assumed that the photocatalyst is only composed of active adsorption sites, organic molecules and their by-products, electron gap-electron pairs and several reactive oxygen forms. The reaction rate constant (k_r) is equal to $10^6 \div 10^9$ M/s for most of photocatalytic reactions taking place in water. Such k_r values indicate that the photocatalysis effectiveness is directly proportional to substance concentration. The K parameter is the Langmuir dynamic adsorption constant (M) which represents the capability of catalysts to adsorption (equation (19)), which is the solution of equation (18) at boundary conditions from $t = 0$ $C = C_0$ (initial concentration) to any time t at which concentration is equal to C:

$$\ln \frac{C}{C_0} + K(C - C_0) = -k_r Kt \tag{19}$$

The value of K can be also calculated from equation (18) after linearization from the plot $1/r$ as a function of $1/C$:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r KC_0} \tag{20}$$

It has been found that K values obtained from above equations are practically much lower [1]. It has been explained by differences in adsorption-desorption processes performed without and with catalyst exposure. If the concentration of organic substances is low (mM) the first order reaction rate constant can be expressed as k' ($\min^{-1}$) = $k_r K$:

$$r = \frac{dC}{dt} = k_r KC = k'C \tag{21}$$

The transformation and integration of equation (21) give the typical model of pseudo-first order reaction show by equations:

$$C = C_0 e^{-k't} \tag{22}$$

$$\ln \frac{C}{C_0} = -k_r Kt = k't \tag{23}$$

However, the apparent reaction rate constant is only used as a comparison of photocatalytic reaction rate description. In Figure 4 a common kinetic plot of saturation for degradation of organic dye in the annular photoreactor system is shown. The reaction rate increases to the point where the flat surface of the curve course is observed [2]. In order to interpret maximum photomineralization reaction rate tailing (deviation) of LH saturation profile should be omitted. Only the tangent slope to inflexion point should be used to obtain maximum photomineralization rate. In this case the unit of the slop is of the same chemical reaction order as the zero order reaction rate constant.
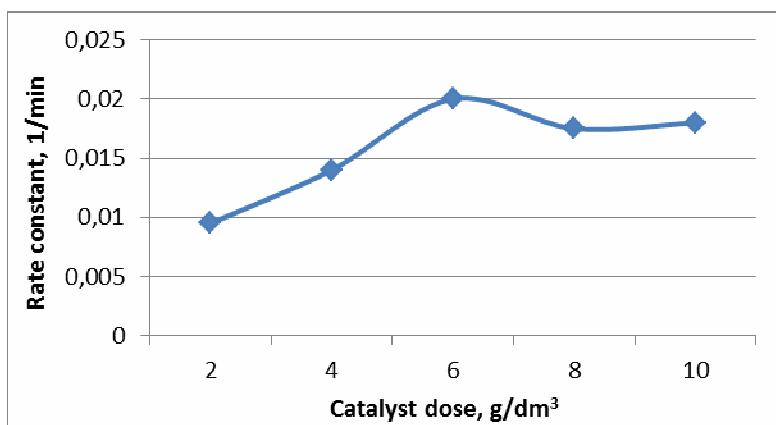

Fig. 4. Typical saturation kinetics plot for the degradation of organic dye molecules in an annular photoreactor system

LH saturation kinetic profile has also been used to approximate particular systems of photocatalytic reactor in practical application [82]. In such an empirical LH approximation the mineralization rate of organic substances is actually expressed as TOC:

$$r_{TOC,o} = \frac{\beta_1[TOC]}{\beta_2 + \beta_3[TOC]} \tag{24}$$

Equation (24) allows to predict the rate of TOC degradation as a function of exposure time. As it is shown, the plot of $1/r$ vs $1/[TOC]$ enables the determination of empirical parameters β_1, β_2 and β_3 in equation (24). The times of exposure necessary for partial decomposition of TOC can also be approximated when equation (23) is introduced to

reaction (19). Such an empirical LH model enables precise determination of kinetics and accurate approximation of every photoreactor system.

Photodisinfection kinetics and modeling

Chick model is based on a classical chemical disinfection, at which disinfection rate (*r*) is a first order reaction defined by the equation [8]:

$$r = -kN \qquad (25)$$

where *k* is rate constant and *N* microorganism concentration.

The model is regarded as a diparticle chemical reaction at which microorganisms act as particles of chemical substances. Chick model is very simplified, nevertheless it is widely applied to disinfection processes with chlorine, ozone, hydrogen peroxide and chloramines [8]. Watts et al [83] have applied Chick model to calculations of reaction rate of disinfection performed via photocatalytic inactivation of viruses and *E. coli* bacteria present in secondary sediment tank at real wastewater treatment plant.

However, the most popular model applied to photodisinfection studies is Chick-Watson mechanistic model [2, 8, 84, 85]:

$$N/N_0 = e^{-k't} \qquad (26)$$

where: *N* - microorganism number survivors at irradiation time *t*, N_0 - initial microorganism number, *k'* - pseudo-kinetic constants expressed by equation [8]:

$$k' = -k[c]^n \qquad (27)$$

where *c* and *n* are constants.

In Chick-Watson model the rate of photodisinfection is a linear function of microorganisms number and catalyst charge, thus it assumes first order reaction kinetics. Moreover, introduced constant parameters (*c* and *n*) does not have a physical meaning. Hence, Chick-Watson model is not always used as in many studies linear dependence of photodisinfection derived from the model is not obtained. The modified Chick-Watson model [2] introduces "delay" parameter for initial disinfection phase and enables the approximation of kinetic parameter, which defines the dependence between catalyst concentration and time of exposure necessary (CT parameter) for total inactivation. The parameter is widely applied as a reference point for designing of photoreactors.

Hom [86] derived a very useful empirical modification of Chick-Watson model for disinfection of algae bacteria systems which revealed power dependence of concentration change in time:

$$\log \frac{N}{N_0} = -kC^n T^m \qquad (28)$$

In the Hom model the predicted level of bacteria inactivation is not a linear function of *C* and *T*, but the dependence has a power character compatible with n and m constants. As Hom model is two-parameter model it can be applied only to photodisinfection profile with maximum two non-linear areas. For m values higher than 1, the inactivation curve firstly shows the deviation to higher values, while for m below 1 the curve "tailing" to lower values can be observed. Thus, the model includes initial and final deviation depending on the curve.

Power kinetic model is also often applied. In the model the inactivation rate assumes the power dependence on microorganisms concentration [8]. It can be expressed as:

$$\frac{dN}{dt} = -N^x C^n \tag{29}$$

The integration of equation (29) results in the model expressed by the equation:

$$\log \frac{N}{N_0} = -\frac{\log[1 + N_0^{x-1}(x-1)K^n T]}{(x-1)} \tag{30}$$

Model expressed by equation (30) also describes initial deviations and "tailing" of kinetic curves what is characteristic for x values greater or smaller than 1, respectively.

Configuration of photocatalytic reactors

Considering the form of the catalyst, photocatalytic water and wastewater treatment reactors can be designed in configurations *ie*:
-    reactors with suspended catalyst,
-    reactors with catalyst immobilized on the neutral support.

The main difference between those systems is the need of separate catalyst separation system in case of suspended reactor, while the second system can be operated in the continuous mode. If the construction of the reactor is considered, annular suspended (slurry) photoreactors [52], cascade photoreactors [87], contact photoreactors [71], but also other design solutions can be distinguished.

Pareek et al [88] showed in their studies that the most important in choosing the photoreactor configuration are the total irradiated rate surface area of the catalyst per volume unit and the proper light distribution within the reactor. Suspended photocatalytic reactors characterize with high ratio of the catalyst surface per volume unit while immobilized reactors have limited mass transfer performance over the immobilized layer of the photocatalyst. The radiation of the reactor can be made using direct or dispersed light [89]. In the first type the catalyst is directly activated by photons light and parabolic light deflectors (baffles) are used. The proper location of the light source is crucial in order to obtain uniform photon stream dispersion in the reactor and maximum and symmetric light transmittance and distribution. Quite recently, suspended photocatalytic reactor used to be a preferable configuration according to significant ratio of total photocatalyst surface on unit volume as well as to easy reusing of the catalyst. Catalyst particles can be separated in sedimentation tank or external filtration systems operated in the cross flow mode enabling constant reactor performance. The separation of photocatalyst particles after the end of photoreaction using hybrid membrane photoreactors is promising technical solution [9, 90]. The application of such a hybrid system eliminates the necessity of coagulation and flocculation or sedimentation for particle separation from treated water stream. Other advantages are the lower energy consumption and lower installation size according to its cube capacity and surface [2].

Photocatalytic membrane reactors

The hybrid systems comprised of photocatalytic reactor and membrane process are known as membrane photocatalytic reactors [9, 90]. The membrane module can be placed outside (Fig. 5) or inside (Fig. 6) the photocatalytic reactor.
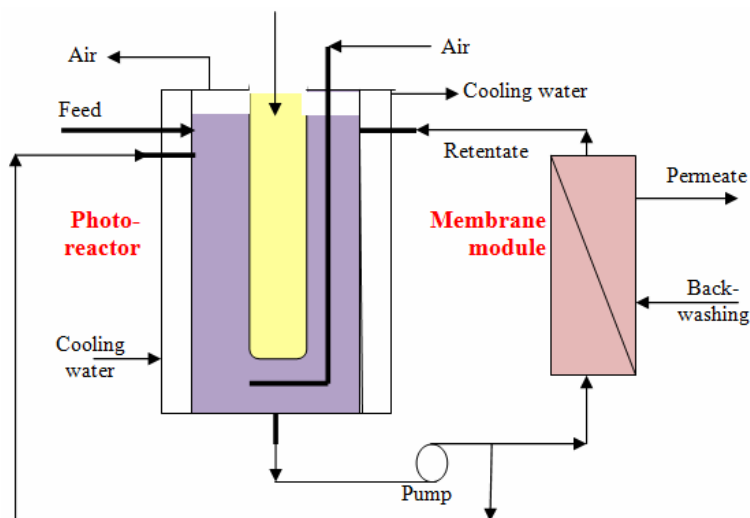

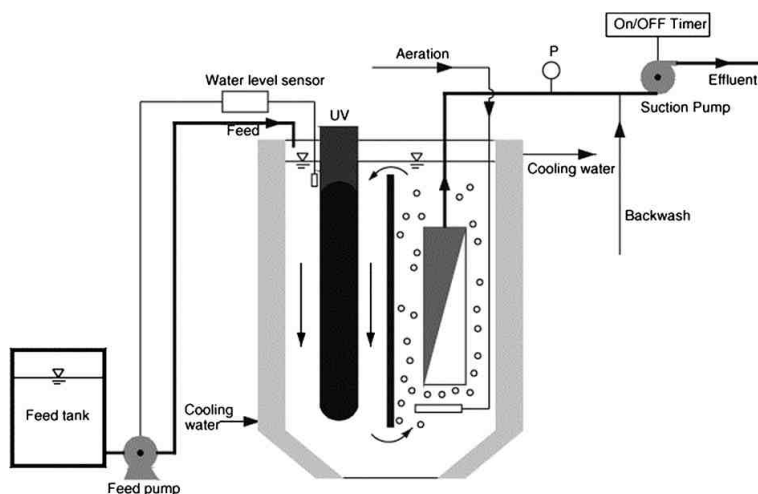Fig. 5. Photoreactor with outside membrane module

Fig. 6. Schematic of submerged membrane photocatalytic reactor

In case when the membrane module is placed outside the reactor three different configurations can be distinguish *ie* the source of light is located over the feed tank, over the membrane module or over the additional tank (photoreactor) which is situated between feed

tank and membrane module [9]. In some cases the source of light can be placed over both, membrane module and feed tank (or inside feed tank in case of immersed UV lamps).

Immersed membrane reactor consists of reaction zone, in which TiO_2 suspension radiated with UV rays is separated from membrane module by moveable baffle (Fig. 6) [91].

Generally, such reactors can be designed with irradiation of membrane module or suspended catalyst feed tank [92, 93]. In suspended reactors the membrane acts as physical barrier for both, photocatalyst particles and/or organic molecules and reaction by-products. In the first configuration the photocatalyst can be either suspended in water phase or immobilized on the membrane.

In membrane reactor with immobilized catalyst membrane module is used as a support for photocatalyst particles (photocatalytic membranes) and acts as a barrier for organic molecules or microorganisms present in the treated mixture. The application of photocatalytic membranes is well-found as photocatalytic reaction runs on the surface or inside membrane pores and cleaned water (wastewater) can be continuously removed from the reactor without catalyst loss. Photocatalytic membranes can be formed using various materials and methods. It includes composite ceramic membranes TiO_2/Al_2O_3 [94-98], polymeric and metallic membranes with immobilized TiO_2 [99-101] or polymeric membranes with TiO_2 particles trapped in their structures during the production process [102-104]. Nevertheless, studies with polymeric and inorganic membranes containing TiO_2 have already been performed [99, 105, 106]. However, the application of photocatalytic membranes is limited by many technical problems *ie* the change of membrane structure, low photocatalytic activity and decrease of immobilized TiO_2 amount in time.

Considering the size of contaminants molecules and required quality of treated water, *microfiltration* (MF) [107-112], *ultrafiltration* (UF) [93, 113, 114] and *nanofiltration* (NF) [92, 93, 104, 106, 115] membrane modules can be used. MF membranes are useful in case of contaminants particles size of 0.1÷5 µm, while UF and NF modules must be applied in case of smaller compounds removal. The effectiveness of photooxidation is higher for suspended reactors than for ones with immobilized catalyst [104]. It has been shown that photocatalyst immobilization results in serious damage of membrane structure according to its direct contact with UV photons and hydroxyl radicals [116]. Thus, hybrid configurations of membrane processes with suspended reactors seem to be more advantageous solution. The application of various photocatalytic membrane reactors set-ups for treatment of water containing of humic acids [107, 110, 113, 114], fulvic acids [91, 117-119], bisphenol A [116], phenol [93], 4-nitrophenol [92], 4-chlorophenol [107], dyes [93, 94, 107, 120-124], greywater [108, 109] and many other contaminants has been already investigated. In recent studies, dialysis [125], pervaporation [126] and contact *membrane distillation* (MD) [9, 90, 122] are used as a part of hybrid membrane photoreactor (Fig. 7).

Considering operation of membrane photoreactors in which pressure-driven membrane processes are used (especially MF and UF) membrane fouling which causes the decrease of permeate flux must be taken into account. It is known that cost of water and wastewater treatment in membrane photoreactors increases when photocatalysts of small particles and colloidal sizes are used. Fu et al [91] used TiO_2 particles of spherical shape which did not cause membrane pores blocking. Moreover, properties of photocatalyst particles surface can be specially modified to prevent membrane blocking. In order to avoid problems connected

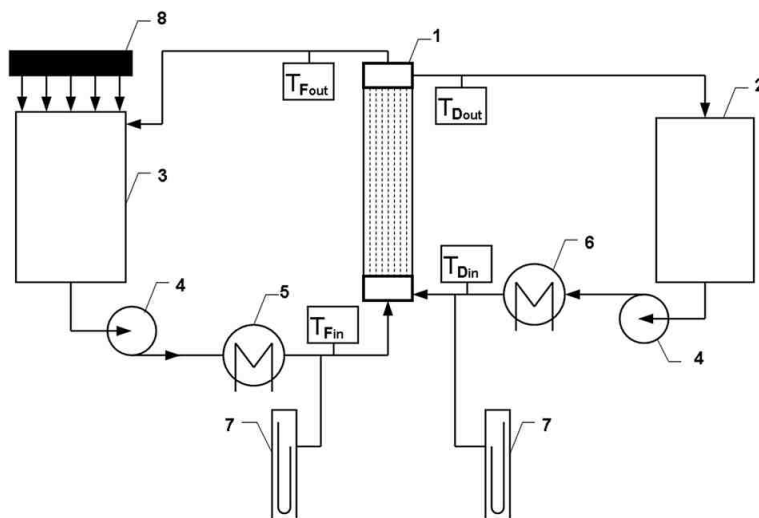with membrane coating with TiO_2 special hybrid suspension-membrane systems are configured.

Fig. 7. Schematic diagram of the hybrid photocatalytic process with membrane distillation: 1 - membrane module; 2 - distillate tank; 3 - feed tank ($V = 2.9$ dm^3); 4 - pump; 5 - and 6 - heat exchangers; 7 - manometers; 8 - UV lamp; T_{Fin}, T_{Din}, T_{Fout}, T_{Dout} - inlet and outlet temperatures of feed and distillate, respectively

Membrane photoreactors enable both, continuous process operation without any and independent control of reaction time. It results in obtaining a proper water and wastewater treatment performance before introduction to membrane filtration.

Summary

Semiconductive photocatalysis with the use of UV or sun radiation has become the usable method for both, organic compounds mineralization and disinfection. It is very important considering refractive organic substances, which are not transported to different phase, but also completely mineralized. The integration of the process with other treatment techniques creates a serious alternative for other methods applied in water and wastewater treatment.

In order to spread the application of photocatalytic process for water and wastewater technology number of operational improvements should be made *ie* (1) the development of catalytic material of high photoeffectiveness which can be used in wider radiation range (visible light radiation), (2) immobilization of catalyst to assure economically attractive solid-liquid separation, (3) the expansion of operational pH range and minimization of additional oxidants dosing, (4) development of new systems improving photo-mineralization and photo-disinfection kinetics, (5) effective design of photocatalytic reactors or parabolic sun collectors to increase the share of sun energy and decrease energy costs.

Acknowledgements

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FOTOKATALIZA W OCZYSZCZANIU I DEZYNFEKCJI WODY
CZĘŚĆ I. PODSTAWY TEORETYCZNE

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Abstrakt: Proces fotokatalizy należy do wysoko zaawansowanych technik utleniania o możliwościach usuwania trwałych związków organicznych i mikroorganizmów z wody. Jest to technologia o dużym potencjale, niskich kosztach, przyjazna dla środowiska oraz o cechach zrównoważonego rozwoju i "zerowym" odprowadzaniu odpadów w przemysłowych systemach wodno-ściekowych. Obecnie, główne bariery techniczne, które ograniczają pełną komercjalizację metody, są związane z zagospodarowaniem cząstek katalizatora po uzdatnianiu wody (ścieków). W pracy przedstawiono podstawy teoretyczne procesu oraz mechanizmy fotoutlenienia zanieczyszczeń organicznych i mikrobiologicznych. Dokonano również przeglądu ostatnich postępów w badaniach inżynierii fotokatalizatorów, systemów fotoreaktorów oraz kinetykę fotomineralizacji i fotodezynfekcji i ich modelowanie związane z procesami fotokatalitycznego oczyszczania wody (ścieków). Omówiono wiele potencjalnych i komercyjnych konfiguracji reaktorów fotokatalitycznych, w szczególności membranowych reaktorów fotokatalitycznych oraz wpływ parametrów operacyjnych i jakości wody na efektywność mineralizacji i dezynfekcji.

Słowa kluczowe: fotokataliza, TiO_2, oczyszczanie wody i ścieków, reaktory fotokatalityczne, kinetyka fotokatalizy, dezynfekcja