COMBINED PHOTO-BIOCHEMICAL REACTOR FOR THE DESTRUCTION OF ORGANIC POLLUTANTS IN WATER

OLGA COVALIOVA

Department of Industrial and Ecological Chemistry, State University of Moldova,
60 Mateevici Street, 2009 Chisinau, Moldova, olga196cov@yahoo.com

Abstract. A new type of a hybrid photocatalytic reactor, working under the combined natural solar and artificial UV-irradiation, and a biochemical aerobic reactor with floating package with fixed microflora are described. The destruction process can be performed either under homogeneous conditions when Fenton's reagent based on iron trioxalate and hydrogen peroxide was used as catalyst, or under heterogeneous conditions, when dispersed TiO_2 with an anatase structure was applied. It was synthesized by electrochemical dissolving of Ti anodes in alkaline medium under application of periodic current with regulated impulse. Titanium hydroxide thus formed was annealed under the special regimes so as to reduce the probability of ruthil and brukite formation. The two-stage photocatalytic and biochemical treatments of benzothiazoles-containing solutions were studied, dependent on the oxidant and dispersed TiO_2 concentration. Theoretical aspects of this problem are discussed.

Keywords: photocatalytic reactor, benzothiazoles, dispersed TiO_2, heterogeneous catalysis.

1. Introduction

Benzothiazoles (BTs) are broadly used in the industry, mainly due to their high chemical stability. They make parts of synthetic colorants, pesticides, herbicides, vulcanization accelerators and are applied in many technological processes. Their estimated worldwide production reaches thousands of tons, although they were confirmed to possess toxic and carcinogenic properties. That is why their distribution in the environment is a matter of serious concern. These substances cannot be easily destroyed using the conventional chemical and microbiological methods, so new approaches for their de-toxication are needed. Earlier research [1] have evidenced the efficiency of photocatalytical methods for their destruction. In a

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number of investigations, a combination of photocatalytical and biochemical processes in special reactors have been applied [2–3]. The processes of water treatment systems in integrated photocatalytical reactors have been studied, with the removal of colorants, polyphenols, pesticides, and other persistent compounds [4]. As catalysts, Fenton systems are used based on hydrogen peroxide, or other oxidizing agents in homogeneous medium. To conduct the heterogeneous catalytic processes, metal oxides (of Ti, Fe, Zn, Al, Ru, etc.) are used, being introduced into the reactor as suspensions. Among them TiO_2 has the highest stability in photochemical processes, is non-toxic and is most photo-active.

2. Integrated bench-scale reactors

The study of the primary photocatalytical destructive treatment of biochemically hardly degrading organics was performed in an integrated flow-through reactor, with the alternative application of solar energy and UV-lamps. Such reactor (Fig. 2.1) is combined with the aerobic biochemical reactor, in which the microbial treatment of water is provided.

Photo-biocatalytical reactor [5–7] involves quartz glass tube canals with reflectors, fixed on the inclined framework in order to ensure the solar and artificial irradiation of the treated liquid. The hydro-mechanical unit is designed for the cleaning of their interior surfaces. This unit is equipped with a rotable brush and a motor, which at the same time acts as a transportation pump for the permanent recirculation of the liquid from the reception reservoir through the photocatalytic system. Due to this design, the liquid is moved upstream the pipes, with the overflow through the upper collector into the reception reservoir recirculating thereby. The DRP-400 UV-lamps used had the power capacity of 15–20 W/m^2.

The treated solution and photocatalytic activators (TiO_2) are pumped with the dosing pump. Switching from solar to artificial irradiation is provided with the programmer with a photoelectric sensor, which also ensures the rotation of inclined framework following the sun movements within the daytime.

After the photocatalytic destruction cycle is ended, the treated liquid will flow through the vertical tube into the biochemical compartment of the reactor, filling up its volume. The particles of floating solid substrate with fixed microflora reach the level of limiting grid, which prevents their removal from the reaction zone, thus stabilizing the microbiological destruction processes.

Then the air blowing device is switched on, and air partly flows through the pipe, enters the aerolift system, ensuring the permanent upward movement of the treated solution. This intensifies the mass-exchange and mass-transfer processes, and provides the enrichment of the treated circulating liquid with air, thus promoting the biochemical processes. At the same time, a part of air from the air blower is transported into the aeration system.

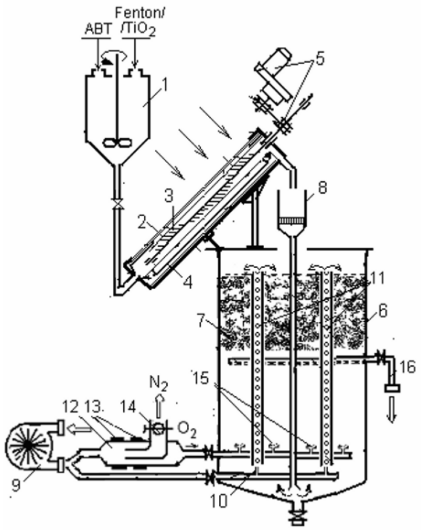

Fig. 2.1. The scheme of the combined photocatalytic and biochemical reactors for the destruction treatment of water, containing persistent organic compounds: 1 – inclined framework; 2 – quartz tubes; 3 – brush; 4 – UV-lamps; 5 – motor; 6 – bioreactor's case; 7 – substrate for microflora fixation; 8 – filter; 9 – air blower; 10 – air inlet; 11 – aerolift; 12 – oxygen enrichment; 13 – magnets; 14 – regulating choker; 15 – bubbling; 16 – outlet for treated water.

The air is enriched with oxygen in the magnetic field. The enrichment principle is based on that the oxygen is the only magnetic-susceptible air constituent; therefore, it is attracted from the air flow to the inferior walls of the cylinder and is moving along the walls. Then the oxygen-enriched air enters the aeration system. The low-oxygen part of air, from the middle part of air flow, enters the curved air pipe and flows away through the outlet, with the help of regulating choker.

Thus, the oxygen content in the air, used for the biochemical process, is increased by 3–5%, compared to the conventional value, which is beneficial for the development of aerobic microorganisms. Under these conditions, the organic molecules are further subjected to the microbial destruction, forming non-toxic metabolites up to their complete mineralization.

3. Experimental

The subject of the research was a 0.5 mM water solution of benzothiazole (BT). BT concentration was determined by HPLC. (Agilent Technologies, RP 18 column 15 × 3 mm, acetonitrile:water (20:80), flow rate 1 ml/min, UV detector 265 nm.)

The tests of integrated photo-biochemical reactor were based on the estimation of the BT photocatalytic destruction under heterogeneous conditions. Using photocatalytically active Fenton's reagent based on hydrogen peroxide and iron (III) salts, present as the hydrocomplex $Fe(OH)^{2+}$ as the source of active oxidizing $^{\bullet}OH$ radicals, is impossible in acid medium, as it provokes the inactivation of microorganisms under the low pH regime. At the same time, at neutral pH favourable for the biochemical processes, the formation of $Fe(OH)_3$ precipitates proceeds, which reduces its catalytic activity.

As the neutral pH is needed for microorganisms, our photo- and biochemical experiments were carried out pH 7.5, and titanium dioxide was used as photoinducer for BT degradation. This reagent is known to be photocatalytically active and does not inhibite the biochemical processes. However, its particles were used in the photo-chemical reactor only and they did not reach the biochemical reactor due to filtration effects.

There are three crystalline modifications of TiO_2 known: anatase, ruthyl and brukite, from which mainly anatase exert the photocatalytic activity [8]. This activity is explained with the processes running under UV-irradiation with the formation of electron holes (h^+) and free electron (e^-) following the reaction: $TiO_2 + h\nu \rightarrow e^- + h^+$, which in their turn promote the formation of $^{\bullet}O^{2-}$ radical: $e^- + O_2 \rightarrow {}^{\bullet}O^{2-}$, and $TiO_2(h^+) + H_2O_{ads} \rightarrow TiO_2 + {}^{\bullet}OH_{ads.} + H^+$. Apart from this, the formation of other reactive radicals is possible, which contribute to the destruction of persistent organic pollutants.

Meanwhile, commercial TiO_2 as a rule consists of the mixture of three crystallic modificatios, which makes it necessary to develop a method of preparation of the anatase structure. In order to obtain the titanium dioxide of atanase structure, the cryochemical method was used. For this purpose, the ammonium complex of titanium chloride with the general formula $TiCl_4{\cdot}nNH_3$ was squeezed through the system of micro-inlets, with the jet break into the super-cooled liquid (liquid nitrogen) for the formation of spherical particles of cryo-hydrate. Then the cryohydrated salt particles were exposed to sublimation, hydrolytic decomposition and low-temperature oxidation under heating up to 500–550°C [9]. As a result, TiO_2 fine particles are nanostructurized, possess' high specific surface and improved photocatalytic properties. Also, another method for obtaining TiO_2 was tested, when metallic Ti was electrochemically dissolved using alternating current [10], and Ti hydroxide was subsequently annealed under the same temperature as before. The TiO_2 particles formed have mainly atanase crystalline structure with the following crystalline lattice parameters, Å: a = 3,782, c = 9,509. The mean particle size, estimated on the base of the scanning electron microscopy data, was within the limits 10-25 nm, while the specific surface determined by the BET method, made 24.7 m^3/g.

Titanuim dioxide thus synthesized was introduced into the solutions to be treated in concentrations of 0.5–2.0 g/l.

As microflora, the aerobic culture *Rodococcus rhodochrous* was used, which was found to be the most efficient for the microbiological destruction of this class of compounds especially. As a floating hard carrier for microflora fixation the suspended micro- and micro-porous perlit can be used, which possess a low bulk density and floating properties.

4. Results and discussion

BT is stable in water and its degradation in water solution is not observed in the absence of light at 25–35°C. Moreover, it does not absorb wavelengths above 300 nm, and no degradation is observed in the reactor in this case. BT is characterized with three absorbtion maxima at 215, 251 and 284 nm with the molecular absorbtion coefficients of 21,379, 7,018 and 2,441 M^{-1} sm^{-1}, accordingly.

HPLC chromatograms of BT solutions in water are characterized with an R_T of 10.0 min. However, after the treatment the intensity of this peak decreases from 125 to 20 mV, which testifies the destruction processes occurred. Measuring of these peaks area makes it possible to assess the decrease of BT concentration and its destruction degree. Small peaks appeared on chromatograms have not been unambiguously identified.

The tests in photocatalytic reactor have shown (Fig. 4.1) that in the absence of light no BT destruction was observed. Under the photocatalytical treatment the destruction increases with the increase of the amount of introduced TiO_2, reaching 44%, 60% and 84%, which might be associated with the photocatalytic properties of TiO_2, which can be explained on the base of zonal structure of its electronic levels.

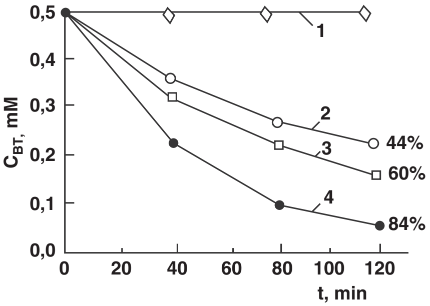

Fig. 4.1. Efficiency of BT photocatalytic destruction (0.5 mM) at pH 7,5 and combined solar and artificial irradiation, dependent on TiO_2 concentration, g/l :1 – 0; 2 – 0.5; 3 – 1; 4 – 2.0.

It is known that out of the three known crystalline structure types of TiO_2 – atanase, rutyl and brukite, only atanase possess the high photocatalytic activity. The UV light with the wavelength $l < 385$ nm excites the electron from the valence zone to conductivity zone, forming the pair electron-hole. Two reagents may be absorbed at the same time during the photocatalysis, which can be reduced and oxdized under an efficient light absorbance ($h\nu \geq$ Eg). The electron transfer capacity from the conductivity zone to the absorbed particle (acceptor) depends on the position of energy zone (energy band) of semiconductor and the redox-potential of the absorbant. If the absorbed pairs consist of water and dissolved oxygen (H_2O/O_2), then water will be oxidized with the positive holes and will be disintegrated forming $^{\bullet}OH$ and H^+. As oxygen is an easily reducible substance, its reduction with photoelectron within the conductivity zone provokes the generation of superoxide-radical anions ($^{\bullet}O_2^-$), which in their turn react with H^+, generating the hydrogen dioxide radical ($^{\bullet}HO_2$). As a result of the further collisions with electron, hydrogen dioxide radical HO_2^- is formed, and then the formation of hydrogen ion and H_2O_2 molecule is possible. Therefore, the above-described reaction chain result in the formation of a series of reactive oxygen-containing particles such as H_2O_2, $^{\bullet}O_2^-$, $^{\bullet}OH$, etc. [8].

Thus, the main heterogeneous reactions causing the formation of active radicals on TiO_2 particles under UV-irradiation, within the conductivity zones (e^-) might be represented as follows:

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + {}^{\bullet}O_2^-$$

$$TiO_2\,(e^-) + {}^{\bullet}O_2^- + 2H^+ \rightarrow TiO_2 + H_2O_2$$

$$TiO_2\,(e^-) + H_2O_2 \rightarrow TiO_2 + {}^{\bullet}OH + OH^-$$

$${}^{\bullet}O2^- + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + O_2; {}^{\bullet}O2^- + H^+ \rightarrow {}^{\bullet}HO_2$$

$$TiO_2\,(e^-) + {}^{\bullet}HO_2 \rightarrow TiO_2 + HO_2^-.$$

The main photocatalytic reactions within the valence zones (h^+) on the activated surface of microparticles, are:

$$TiO_2(h^+) + H_2O_{ads} \rightarrow TiO_2 + {}^{\bullet}OH_{ads} + H^+$$

$$TiO_2\,(h^+) + 2H2O_{ads} \rightarrow TiO_2 + 2H^+ + H_2O_2$$

$$TiO_2\,(h^+) + OH^-_{ads} \rightarrow TiO_2 + {}^{\bullet}OH_{ads}.$$

Hydroxyl-radical $^{\bullet}OH$ is a highly reactive but a short-living species. Superoxide radical-anion $^{\bullet}O_2^-$ is a longer-living radical having a negative charge, which is like hydrogen peroxide a precursor of hydroxyl-radical, providing the photocatalytic destruction of complex organic molecules.

Therefore, during the photo-irradiation in the presence of TiO_2 under the studied conditions, the BT destruction is provided, which might be connected with the opening of the aromatic ring, resulting in the formation of photoproducts which could not identified with an HPLC with UV-detector. The accumulation of intermediates was not observes.

At the biochemical stage of the treatment in the combined photo-bioreactor, the destruction cycle of BT molecules is finalized with their complete mineralization. According to the research findings presented in [11], the main products identified in the biochemical process formed by the *Rodococcus rhodochrous* bacteria, are the intermediate metabolites – 2-hydroxybenzothiazol (OBT) and 2,6-dihydroxy-benzothiazol (di-OBT) (Fig. 4.2). Their subsequent complete mineralization proceeds according to the following proposed scheme.

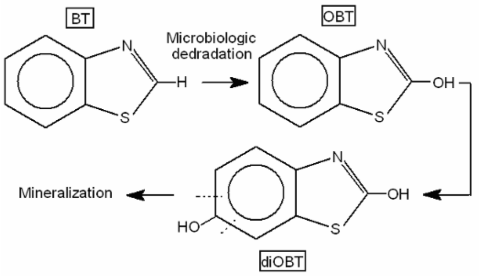

Fig. 4.2. Microbial BT degradation with *Rodococcus rhodochrous* bacteria [11].

UV-visible light spectra of OBT are characterized with the absorbtion maxima at 211; 243; 279 and 286 nm, while those for di-OBT – at 212; 252 and 297 nm.

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