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PRODUCTION, STRUCTURE AND PHOTOCATALYTIC PROPERTIES OF NANOTUBULAR TiO_2

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Abstract

Photocatalytic processes are among the most efficient treatment methods of waters polluted with recalcitrant organic substances. Nanotubular TiO_2 arrays with photocatalytic properties were obtained in the process of titanium anodic oxidation in the fluoride-containing electrolyte. Under the proposed conditions of electrolysis, a coherent system of tightly adjoining nanotubes was formed with the internal diameter of 60-80 nm and walls thickness up to 60-65 nm, the tubes height being dependent on process duration, reaching over 200 mkm. It was shown that it is the specifics of the formation, destruction and renewal of the barrier layer that determines the tubular structure of anodic titanium coatings formed. Various anodizing regimes were proposed to obtain the different TiO_2-containing structures – nanotubular and fine dispersed ones. Subsequent annealing of nanotubular titanium dioxide provokes the series of structural-phase transformations, modifying its photocatalytic properties. The nanotubular systems thus obtained were tested as photo-catalysts, both as compact coatings and as fine dispersed particles, in the especially developed integrated photoreactor. It was shown that using the proposed equipment and photocatalysts produced, the efficient photodestruction of the persistent organic pollutants such as benozhiazol (BT) can be reached due to the combination of chemical and physical effects.

Keywords: active radicals, nanotubes, photocatalytic process, titanium dioxide

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1. Introduction

Photocatalytic processes are among the most efficient treatment methods of wastewaters containing the organic pollutants (Chang et al., 2016; Duca, 2012a, Khalik et al., 2018; Khamdahsag et al., 2018).

These methods involve various redox-processes with participation of metal ions and complexes (Covaliov et al., 2004; Delort et al., 2008; Duca et al., 2002; Duca, 2012b), the most well studied of them being photo-Fenton systems (Fe^{3+}-$Fe^{2+}/H_2O_2/UV$) (Catrinescu et al., 2017; Iboukhoulef et al., 2018; Kwan and Voelker, 2003; Li et al., 2010; Sarasa et al., 2006; Walling, 1975), as well as the other peroxide systems including the transition metal ions, such as Cu, Mn, etc. (Kwan and Voelker, 2002; Lodha et al.; 2008; Mailhot et al., 1995; Sychev and Isac, 1990). A common point of these methods is the formation, under the artificial or natural solar UV-irradiation within the wavelength 280-400 nm, of active radicals with high oxidizing capacity which decompose the organic matter in water with the rate constant close to that of the diffusion-controlled processes (Buxton et al., 1988; Lanzafame et al., 2017; Palma et al., 2018). The most active radicals are $^{\bullet}OH$ and system $HO_2^{\bullet}/O_2^{\bullet}$, which provoke the bonds breakage in the organic compounds and their transformation to various intermediates, up to mineralization with the formation of simple inorganic forms like CO_2, H_2O, mineral salts.

Using of titanium dioxide TiO_2 as a photoinductor in photocatalytic heterogeneous technologies represents a certain interest, due to its specific photocatalytic properties (Bellobono et al.,

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1994, Lutic et al., 2017; Saien et al., 2018), chemical inertness, lack of toxicity and low cost. Photocatalytic activity of TiO_2 is manifested due to the unique properties of the "electron-hole" pair, capable to generate the active radicals, which makes it possible to initiate the oxidation-reduction reactions with the adsorbed molecules, providing purification of water and air, hydrogen formation during the water photolysis, reducing the CO_2 emissions and generating methane and its homologues, so as to broaden the energy resource base.

At the same time, one of the TiO_2 specific properties is rather narrow adsorption spectrum limited to UV-field. Out of its three crystal modifications, the best photocatalytic properties are manifested by anatase under the UV-irradiation within the waverange 260-400 nm, however, this area of solar spectrum does not exceed 7% (Asahi et al., 2000; Kandiel et al., 2013; Landmann et al., 2012; Linsebigler et al., 1995). Thus, the overall range of solar light energy cannot be efficiently used.

Therefore, the elaboration of photocatalycally active coatings with highly-developed surface on the base of TiO_2 remains to be an actual objective. At the same time, the development of novel methods of nanoscale TiO_2 particles production, along with the modification of the obtained material in view to ensure the spatial charge separation within its particles and shift the absorption spectrum towards the lower energies area are important directions in the creation of highly active photocatalyst.

To improve the photocatalytic activity of nanoscale TiO_2 particles within the visible light area, the coating and doping with various metals and non-metals can be applied (Behnajady et al., 2018; Chen and Mao, 2007; Duduman et al., 2018; Gholami et al., 2018; Kwoka et al., 2017; Nah et al., 2010). Titamium nanofilms can also be used as photocatalysts (Serio et al., 2018).

Another way to achieve the higher photocatalytically active surface of titanium dioxide is the production of nano-tubular structure (Arenas et al., 2018; Paramasivam et al., 2012; Roy et al., 2011; Wanga et al., 2009), which allows to improve the efficiency of photocatalytic processes due to the broadening of the adsorbtion spectrum and separation of electron-hole pair. The nano-structured materials based on TiO_2 can be obtained using the different approaches (Covaliova and Enachi, 2010a; Gong et al., 2001; Palouse et al., 2006; Wu, 2004; Wu et al., 2005), however, the most of these methods allow to obtain the powdery catalyst, which, regardless of certain advantages (high specific surface, possibility to assure the high mass-transfer and mass-exchange in the reactors), possesses the non-ordered amorphous or crystal structure. Development of nano-structured tubular coatings of titanium oxides on the plain surface by the electrochemical oxidation method makes it possible to obtain more ordered structures with targeted properties, which parameters can be managed, varying the oxidation conditions (Korobochkin et al., 2004; Watson et al., 2003; Zwilling et al., 1999).

The coatings crystallization can be reached by the specimens annealing at the temperatures above 390-420ºC. It is mentioned in some works (Ali et al., 2011; Liu et al., 2012), that the coatings with poor adhesion are exfoliated from the substrate layer during the annealing. In its turn, it is possible to control the crystal structure by changing the annealing conditions. Such coatings have undoubted advantages for applications as photocatalysts, namely: opened porosity, narrow pores' size distribution, high surface of light absorption.

An important task consists in the improving of nanotubular structure of titanium dioxide, through the modification of electrolytic solution composition, justifying the mechanism of its formation, as well as the studies of the amorphous structure transformation into the crystal one during the annealing, in order to provide its stable photocatalytic properties.

The final scope of this research was to elaborate the efficient photocatalytic destruction method of persistent organic pollutants (xenobiotics) in water systems. To this end, it was necessary to modify the electrochemical technology of nano-structured titanium oxide production, with the obtaining of compact nanotubular coatings with the improved adhesion. At the same time, the estimation of the barrier layer's role in the tubular structure formation was of a certain interest. Based on these studies, it became possible to develop and test the operation of an integrated photocatalytic reactor in the process of photocatalytic decomposition of hard-degradable pollutants in water systems.

2. Material and methods

The anodic treatment of titanium was performed in the solution containing, vol.%: ammonium fluoride ($NH_4F \cdot HF$) - 2-5; sulfuric acid (H_2SO_4, spec. weight 1,84) - 2-3; potassium-titanium oxalate ($K[Ti(C_2O_4)_2]$, Standard 5868-78) - 3-5; diethylene glycol ($(OHCH_2CH_2)_2O$ – the rest (Covaliova and Enachi, 2010a).

An important function of potassium-titanium oxalate in electrolyte composition is to reduce the chemical solubility of forming titanium dioxide particles which are separated from the barrier layer, thus increasing their yield. At the same time, this double salt promotes an increase in the electric conductivity of electrolyte, decreasing the electrode voltage during the electrolysis, thus ensuring the appropriate reducing of energy costs of this process.

To synthesize the nanotubular TiO_2, technically pure 300 mkm Ti (BT-1.0 brand) was used, which surface was polished to remove the oxide film. For obtaining of high quality porous structure, prior to oxidation, Ti samples/plates were treated with ultrasound in 2M HCl and acetone solution for 1-2 min, in order to remove the impurities and to ensure degreasing. The coatings of nanotubular TiO_2 were formed only on one side of a plate; the other side was covered with the electro-insulation lacquer. Anodic oxidation of titanium was performed under the potentiostatic regime, in the electrolytic cell under the constant temperature, using the constant current source B5.120. The voltage on the cell was varied from 100 to 114 V. The gap between the cathode and anode made 2 cm.

Two electrolysis regimes were applied: 1) when the temperature was maintained within the range 10-20°C, in order to avoid exfoliating of growing nanotubes from the barrier layer on Ti surface, and 2) maintaining the temperature of 10-20°C during 30-40 min, and then 30-40°C during 10-15 min; the growing coating was thus exfoliating from the amorphous barrier layer composed of $TiO(OH)_2$. The processes occurring during the annealing were studied by thermogravimetric analysis (TG) using the thermo-derivatograph Q1500 (Hungary), structural-phase transformations were analysed with X-ray method on DRON IM-1 equipment (Russia). The morphology of nanotubular layers obtained was studied with Scanning Electron Microscope SEM "VEGA45TS 5130MM" equipped with the device for surface chemical analyzing "Oxford Instrument Analytical".

As photoinductors, TiO_2 and TiO_2/H_2O_2 systems served, whereas the decomposing photocatalytic processes were studied using the water solutions of xenobiotic - benzothiazol BT (C_7H_5NS) with molar mass 135.19 g/Mol (Aldrich Ltd, Gillingham, Kent, UK, >98%).

The concentrations of BT and photo-destruction products were determined by gas-liquid chromatography using the HPLC Agilent Technology chromatographic equipment on the column (15 x3 mm) with the reverse phase C_{18}, in the acetonitrile: water (20:80) system under the room temperature, the flow rate was 1 mL/min, UV detector - 265 nm. In photocatalytic reactor, the high-pressure UV lamps CVD-120A were used, with energy illumination of 18.9 Wt/m^2 within the wavelength 300-400 nm.

3. Results and discussion

3.1. Specifics of the electrolysis process and formation of nanostructural coatings on titanium

As a result of the anodic oxidation of titanium in fluoride-containing electrolyte, the nanostructured coatings were obtained, consisting from the thin barrier layer adjacent to metal and the external pore-ridden layer of TiO_2 nanotubes (Fig. 1). The parameters of these coatings can be varied, modifying the oxidation conditions. The structure of a surface layer formed during the anodic treatment is characterized by the coherent system of tightly adjoining nanotubes with the internal diameter within 60-80 nm and wall thickness up to 60-65 nm. The tube height is determined by the electrolysis duration and can reach 200 mkm and more. An internal tube diameter is thus characterized with the layered structure with thin needle-like protrusions, which ensure the higher specific active surface of nanotubes. The diameter of forming nanotubes is narrowing along their depth, whereas the wall thickness mainly depends on the anodic current density and electrode voltage (Thompson et al., 2006). The mechanism of titanium dioxide nanotubular structure formation can be explained on the base of the structural geometrical theory stipulations. Formation and growth of tubular structure starts as a result of partial dissolving of a barrier layer under the action of electrolyte having the optimal aggressiveness with regard to the material of barrier layer. If this aggressiveness is insignificant, formation of porous external layer practically does not occur and the thickness of anodic film on titanium is only dependent on the barrier layer thickness.

At the initial period of electrolysis (Fig. 2), the voltage on cell terminals is sharply increased up to the point “A” corresponding to the maximal thickness of forming barrier layer. The point “B” corresponds to the eqilibrium state between the dissolving processes and oxide layer renewal; after 5-10 min (portion “A-B”) the voltage drop occurs (portion “B-C”), then the voltage is stabilized with the insignificant upward bias.At this stage the film etching starts with the insignificant decrease in local thickness of barrier layer, within the centers of the external ends of elementary cells. At the same time, the local Ohmic heating occurs, and within this zone the etching is increasing.

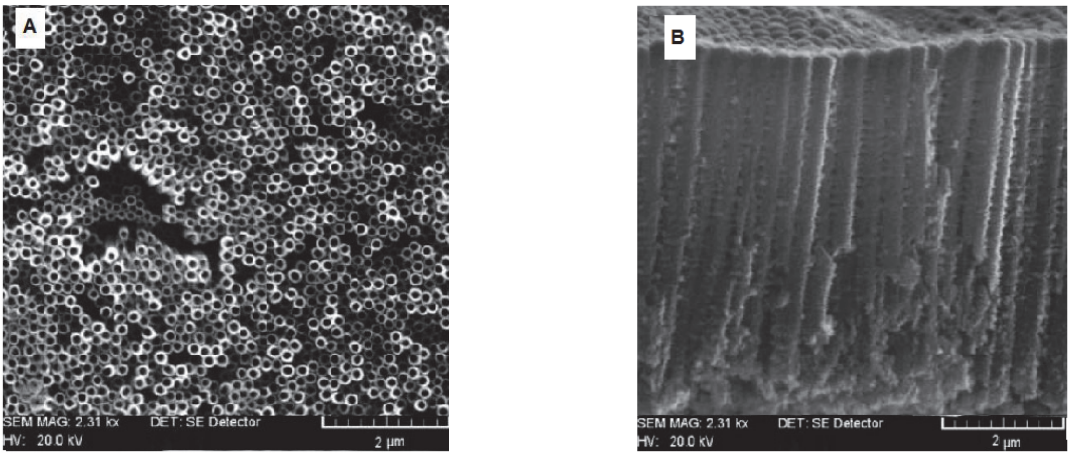

Fig. 1. The nanotubes structure: A – morphology of tubular surface; B – cross-section of anodized titanium

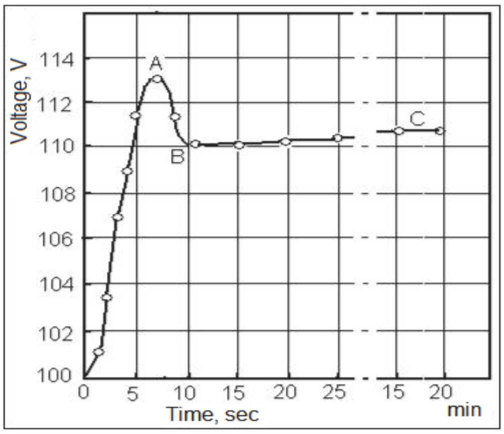

Fig. 2. The specifics of voltage change (by oscillogramms) on the electrodesduring the titanium anodizing

Such specifics of the formation, destruction and renewal of the barrier layer determines the character of tubular structure of anodic titanium coatings. The bottom of the TiO_2 pores ridding the external layer, coincides with the external surface of the barrier layer. The pore walls are placed practically stictly perpendicular to the metal surface and are composed from the undissolved part of material, which served for the construction of permanently renewable barrier layer. During the oxidation process, the external layer is thickened due to the continuous transformation of deeper metal layers in oxides.

In this way, the formation of the anodic-oxide layer of TiO_2 is connected with the dissolving effect of electrolyte towards the barrier layer. This dissolving should be running with such rate that the loss of the oxide layer material could be replenished by the renewal of the barrier layer. And the barrier layer is renewed as a result of the further metal transformation into the oxide, occurring in such a way that its thickness remains unchanged. Excessively rapid dissolving of barrier layer prevents the nanotubular structure formation in the external layer; in this case only the metal electropolishing occurs.

The thickness of the barrier layer mainly depends on the voltage value. The barrier layer is destroyed in a selective way: the central areas of elementary cells are most likely built from the amorphous titanium hydroxyl-oxide $TiO(OH)_2$, whereas the peripheral areas – from the more stable titanium dioxide, which are not destroyed.

Appearance of the barrier layer and its continuous dissolving during the anodic treatment was discovered during the studies of the porous thick-layer anodic coatings formation on aluminum (Vermei, 1954), for which the porous columnar structure is also typical. It can be admitted that the similar mechanism of porous nanostructure formation is also valid for the case of the anodic treatment of titanium. Thus, it was suggested (Akimov et al., 1946) that the counter migration of $Ti^{4+}$and O^{2-} ions occurs within the barrier layer. Similarly, under the anodic polarization of the electric field, Ti(IV) ions can migrate through the barrier layer, and their excess inside this layer is created.

The graphic model of an elementary cell was earlier developed for the case of aluminum oxide layers formation during the anodic processes (Keller et al., 1953). Proceeding from this model, an axonometric model of anodic tubular structure of TiO_2 layer on metallic Ti was proposed (Fig. 3). The growth of a nanotubular titanium cell starts with the destruction in the central point, the end of an elementary cell of the barrier layer being turned towards the electrolyte.

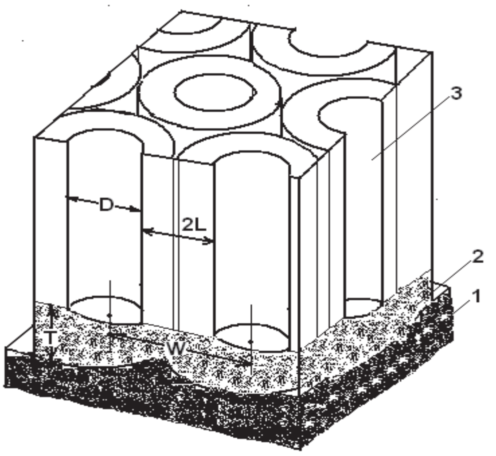

Fig. 3. Axonometric model of the anodic tubular structure ofthe TiO_2 layer on the basis of the metal Ti: 1 – base metal; 2 – barrier layer; 3 – pore

The oxide growth around the pores' bottom provokes the formation of a series of parallel tightly packed cylinders with the internal pores, practically equally sized, which are gradually expanded towards the external side of a pore. Regardless the anodic treatment regime, the ratio between the elementary cell dimensions and applied voltage is maintained the same (Eq. 1):

$$W = 2SE + D = 2L + D \tag{1}$$

where: W – cell size (diameter), nm; E – voltage promoting the oxide formation, V; D – pore diameter, nm; S – specific depth of cell's wall, characterizing the share of depth (nm) per each Volt of the forming voltage, nm/V; L – cell's wall depth, nm.

The depth of the barrier layer and that of the elementary cell's wall is expressed with the ratio: $T = 1.2$ L. The ratio between the pore diameter, cell diameter and the depth of the barrier layer is expressed with the following general type equation (Eq. 2):

$$D = W - 1.67\,T \tag{2}$$

The specific amount of the elementary cells of nanotubes, calculated on the base of the cell size, makes $(3\text{-}5)\cdot 10^8$ per 1 cm^2 and is changing inverse proportionally to the voltage.

3.2. Formation of fine dispersed TiO_2 particles

The barrier layer is mainly composed of the amorphous Ti hydroxyl-oxide $TiO(OH)_2$ and possesses the increased electric resistance. Therefore, it creates the strong valve effect, similar to semiconducting materials: its conductivity is essentially higher when the current is passing from titanium towards its oxo-hydroxo compounds, as compared to the opposite direction. As a result, practically all the voltage drop during the anodic treatment is determined by the resistance of a barrier layer.

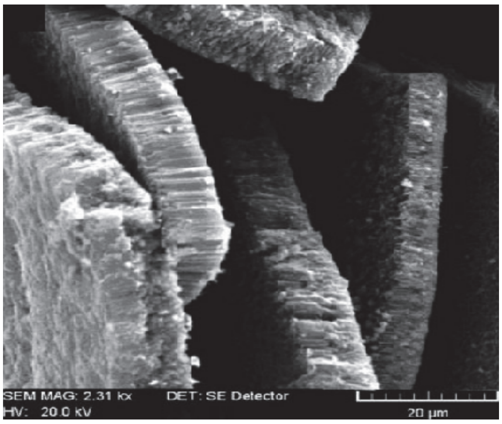

Fig. 4. Morphology of the crossover section of the dispersed particles of nanotubular TiO_2

An increase in the chemical aggressiveness of electrolyte due to the higher contents in fluoride-ions, or temperature, provokes the destruction of the barrier layer, exfoliation of oxide layer of nanotubes and exposure of a titanium surface. The dissolving of titanium dioxide is a purely chemical process, occurring on the phase boundary surface between the barrier layer and electrolyte, filling/entering the pores. The temperature on the pore bottom, developed due to the Joule’s heat evolving, can reach high values, thus enhancing the chemical aggressiveness of electrolyte and provoking the exfoliating of nanotubes.

On one hand, titanium anodizing process must be performed with the minimal heat evolving within the barrier layer, to promote the formation of canals and nanotubes growth. On another hand, the elevated electric resistance of electrolyte causes the evolving of the Joule’s heat and the spontaneous increase in the temperature during the electrolysis, which leads to the exfoliating of the nanotubular coating (Fig. 4).

Therefore, to obtain the higher thickness coatings, it is necessary to carry out the process with the electrolyte cooling. However, the specifics of this process allowed us to propose the appropriate conditions of the dispersed nanotubes obtaining, with the scope to apply them in the photocatalytic water treatment systems containing the recalcitrant organic pollutants.

On the first stage of this process it is important to maintain the temperature regime of working electrolyte within the range of 10-20°C to avoid exfoliating of growing nanotubes from the barrier layer on titanium. But, because of the high Ohmic resistance in the barrier layer, the electrolysis is accompanied with the evolving of Joule’s heat in the nanotubes’ bottom part. The maintenance of the lower temperature can be provided with various ways, specifically: cooling of the total bulk of electrolyte, cooling of the anodized metal by heat convey from the electrodes, carrying out the electrolysis under the higher, within the optimal limits, current density, which will allow to reduce the time of the dissolving action of electrolyte with regard to the oxide.

On the second stage of the process, with temperature increase up to 30-50°C, the electrolyte aggressiveness is enhanced, too. Under these conditions, the nanotubes are exfoliating from the barrier layer and are falling down on the electrolytic cell’s bottom as a dispersed sediment, which can be periodically removed for subsequent washing, drying and annealing. The length of the pass-through nanotubes thus formed can be strictly regulated by the electrolysis time during the first, low temperature stage of the process.

In this way, the synthesis of the titanium dioxide nanotubes can be performed according to two alternative ways. By the first way, electrolysis can be carried out with the gradual increase in temperature. Under the decreased temperatures the nanotubes growth occurs, and then, after the critical temperature is reached within the range of 30-50°C, the exfoliating of nanotubes fragments and their sedimentation starts. In this case the nanotubes length will be determined by the rate of temperature change with time.

According to the second alternative, the anodic treatment in the beginning is carried out in the cold electrolyte with the temperature maintained within the limits of 10-20°C. Then, the electrodes are transferred into the electrolyte heated up to 30-50°C, where electrolysis is carried out with the scope to exfoliate the nanotubular titanium dioxide coating from the base, with subsequent renewal of the anodic treatment cycle. This approach makes it possible to regulate the formation conditions of nanotubes with targeted parameters and properties.

As a result of two-stage electrochemical oxidation of metal titanium, with the meticulous control of the external conditions, the highly-ordered porous TiO_2 coatings were obtained. The structure of such coatings includes tightly packed arrays of titanium oxide, oriented in a perpendicular way with regard to the metal base.

3.3. Structural-phase transformations of nanostructured titanium dioxide

During the annealing of nanotubular titanium dioxide samples, a series of structural-phase transformations occur, which promote transformations of the initial coating from the amorphous state into the crystalline one, which affects its photocatalytic properties. As follows from Fig. 5, on the curves TG and DTG, starting from 20°C, an insignificant weight loss is observed, most likely associated with water removal. However, starting from 360°C, an essential mass loss takes place, with the maximal rate under 390°C, making approximately 6 % from the initial sample weight.

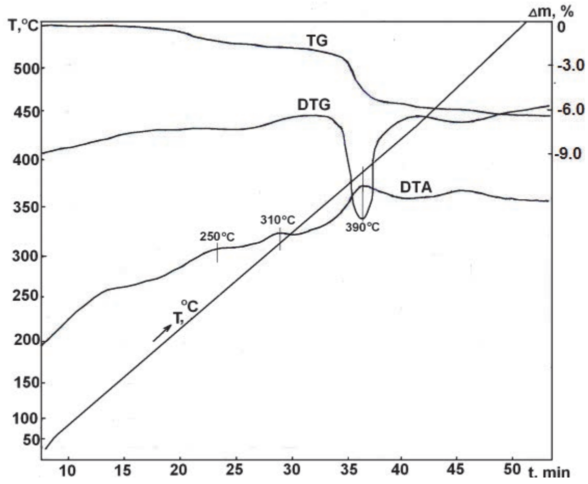

Fig. 5. Thermoderivatogram of the nanotubular TiO_2: sample mass – 30 mg; annealing speed – 10 degr/min

Under these conditions two weak exothermal peaks are detected on the DTA curve at 250 and 310°C. At the same time, within the range from 360 to 430°C strong enough exothermal effect can be seen, with peak maximum at 390°C, which, however, has lower slope as compared to the initial part of this peak.

This temperature maximum which almost coincides with other research data (Korobochkin et al., 2004), can be attributed to the phase transfer temperature, associated with the formation of the TiO_2 crystalline form out of the amorphous phase. The mass reduction within the range 360-430°C, and the coincidence of an exothermal peak on the DTA curve and mass loss on the TG curve testify on the columnar structure products transformation from the amorphous state into the anatase crystalline structure. As a result, OH^- groups and water molecules are liberated (Eq. 3):

$$TiO(OH)_2 \xrightarrow{T=390^o C} TiO_2 + H_2O\uparrow \qquad (3)$$

The sloping nature of the peak loss on the back side of the exothermic peak, associated with the partial consumption of heat for evaporation of the released water during the phase crystallization of anatase, may indicate a possible mechanism of this reaction.

With further temperature increase up to 600°C no essential changes on the curves were observed. The scope of our work was to obtain the particles of anatase structure having the high photocatalytic properties. To obtain an efficient photo-catalyst, following the washing and drying of the obtained nanotubes, their annealing was performed at 350-450°C. The amorphous forms of titanium dioxide are thus mainly transformed into the crystal form of anatase, with the specific tetragonal structure, in which lattice each Ti atom is placed as a distorted octahedron with the crystalline lattice parameters a = 3.73 E, c= 9.37 E, d = 1.95 E. An active surface of the formed TiO_2 nanoparticles is two-three orders higher than that of the particles obtained under the conventional conditions.

Photocatalytic activity of crystallized TiO_2 particles with nanotubular structure, having high specific surface, was attributed to the fact that the light quanta under the UV-irradiation with the wavelength l<385 nm excite the electrons from the valence zone to the conductivity zone, forming the electron-hole pair, i.e.$TiO_2 + h\nu \rightarrow TiO_2\ (e^- + h^+)$ (Covaliova et al., 2009). Their formation, in its turn, promotes water oxidation with positively charged holes, which splits into $^{\bullet}OH$ and H^+. Since oxygen is an easily reducible substance, its reduction with photo-electron within the conductivity zone leads to generation of superoxide-radical anions ($^{\bullet}O_2^-$). In their turn, these react with H^+, generating dioxide-hydrogen radical ($^{\bullet}HO_2$, hydroperoxyl). During the further collisions with electron, the hydrogen-dioxide radical is formed (HO_2^-), followed by the possible formation of hydrogen ion and H_2O_2 molecule. The above described chain of reactions, as well as the other reactions which have not been described here, results in the formation of other highly reactive oxygen-containing species, such as H_2O_2, $^{\bullet}O_2$-, etc.

3.4. Studies of the photocatalytic properties of the nanotubular titanium dioxide

Photocatalytic activity of nanostructured samples of compact coatings on Ti, as well as that of the exfoliated dispersed TiO_2 fragments was studied using the especially developed reactor (Fig. 6). One of the specifics of the reactor proposed is a conical form of perforated light reflectors, alternating by height, which surface was covered with nanotubularTiO_2. The dispersed fragmented TiO_2 particles with the pass-through nanotubes were introduced additionally into the reactor. This promotes an active surface increase in heterogeneous photocatalytic processes and more complete using of the light flow. At the same time, hydrodynamic conditions of liquid movement in the reactor are improved, and, accordingly, the mass-exchange and mass-transfer processes in the treated water bulk are improved, too.

To ensure the solution mixing, the magnetic fluidization principle was applied, with the intensive movement of magnetized spherical particles in the polygradient electromagnetic field. Experimental data demonstrate (Fig. 7), that the efficiency of xenobiotic BT photo-degradation when using the nanostructured titanium dioxide as photoinductor, is increased essentially in the presence of hydrogen peroxide additives. Benzothiazol destruction process occurs with the formation of the intermediates (Fig. 8).

On the first stage the photocatalytic oxidation occurs stepwise, with the OH-group grafting to the 4th position of phenol ring and the formation of acid functional groups, with further bonds breakage within the intermediate OBT molecules. With the increase of treatment time and H_2O_2 concentration, the rates of these processes are noticeably increased, too.

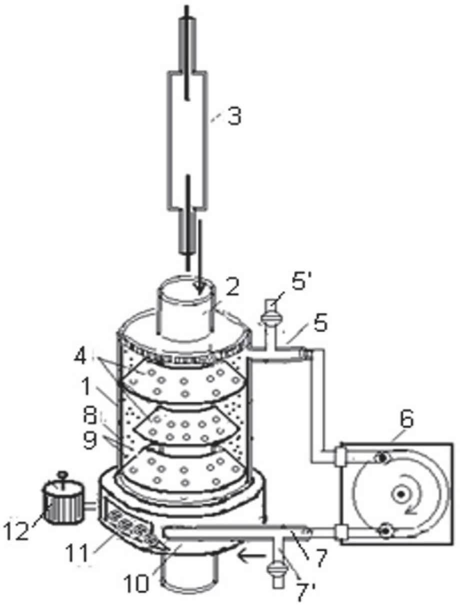

Fig. 6. The scheme of the experimental photocatalytic reactor: 1 – cylindrical body; 2- internal quartz cylinder; 3 – UV-lamp; 4 – perforated conical photocatalytic reflectors covered with nanotubularTiO_2; 5, 7– recirculation pipes; 6 – peristaltic pump; 5’7’ – outlet and inlet valves of studied BT solution; 8 – internal cylinder mirror reflector; 9 – dispersed TiO_2 nanoparticles; 10 – solenoid; 11 – spherical magnetized particles; 12 – voltage regulator (Covaliova and Enachi, 2010b)

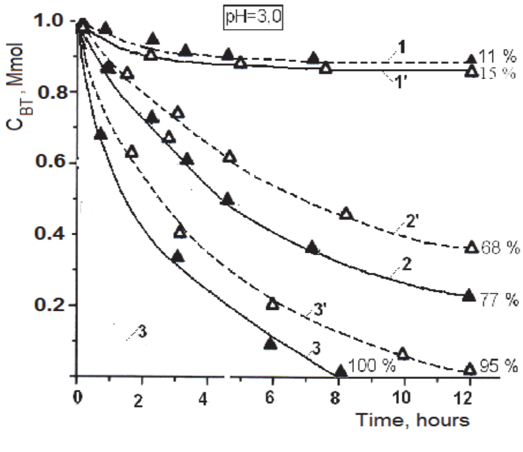

Fig. 7. hange in the BT (1.0 mmol) photo-degradation degree under pH = 3on the compact nanotubular TiO_2 surface (curves 1, 2 and 3) and on the compact surface in combination with the TiO_2 fine dispersed particles (curves 1’, 2’ and3’) in dependence on H_2O_2 concentration:
1 – 0.3 mmol without irradiation; 2 - 0.3 mmol with photo-irradiation; 3 - 3.0 mmol with photo-irradiation

4. Conclusions

Obtaining of titanium dioxide nanotubular coatings is a perspective way to improve the efficiency of photocatalytic treatment of polluted water systems, containing the persistent organic compounds. Anodizing of titanium surface under the special conditions, in the electrolytic solution with modified composition, makes it possible to obtain the 150-200 nm diameter nanotubes with cells thickness of 60-100 nm.

The nanotubular systems obtained can be applied as photo-catalysts as compact coatings and in the dispersed form in the integrated photoreactor presented. The efficiency of the organic pollutants photodestruction is thus ensured due to the combination of chemical and physical effects.

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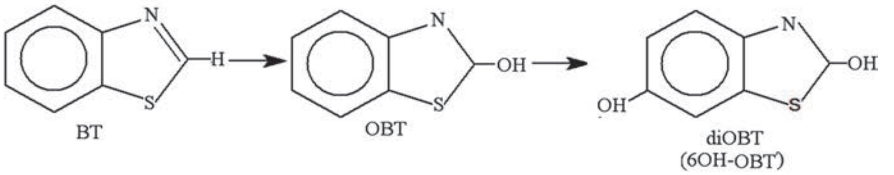

Fig. 8. The scheme of BT photo-destruction with the formation of intermediates (Andreozzi et al., 2000; 2001)

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