1. Introduction

Composite and other advanced materials can obtain properties of the initial raw [1-3]. Titanium dioxide-based materials attract attention of scientists and engineers due to a set of physical and chemical characteristics (for example, high Ti-O bond strength, low redox potentials).

Due to optical properties, it was mostly widely used in the paint and varnish industry and in the production of pigments. Also, the objects of close attention of researchers are sensor, adsorption, optical, electrical and catalytic properties of TiO₂. The photocatalytic properties of TiO₂ are also a subject of increased interest, which allows increasing efficiency of technological processes for the photocatalytic purification of water and air from toxic organic impurities. Chemical and biological inertness allows creating anticorrosion coatings, matrices for the disposal of radioactive waste, and implants [4-6].

The trend of recent decades has been a directed change of the physical and chemical properties of various materials at the nanoscale [7-11]. Particular attention is drawn to the production of nanostructured TiO₂ particles [12-18], which is associated with the physical and chemical properties of nanoparticles other than macroparticles, such as gravity forces, chemical, electromagnetic, rheological, or optical. The most of published works on the synthesis of nanostructured TiO₂ particles are devoted to synthetic raw materials.

Practically no attention is paid to producing titanium nanodioxide from natural raw – in particular, from a gravity concentrate of titanium ores. When developing new or adapting existing methods, a complex nature of natural raw should be considered. Thus, in ilmenite-leucoxene ores (Pizhemskoe titanium deposit), the main source of valuable components is ilmenite and its alteration products (leucoxene), which are represented by polymineral microaggregates with complex morphostructural features, in which quartz grains occupy up to 30 % (on average). Therefore, during producing nanostructured titanium dioxide directly from the gravity concentrate of ilmenite-leucoxene ore, we should consider possibility of their removal or dissolution.

The aim of this work is to study synthesis of nanostructures based on natural titanium raw – leucoxene ore, and their physical-chemical properties.

2. Materials and experiments

2.1 Materials

We used samples of gravity concentrate of ilmenite-leucoxene ore from the Pizhemskoe deposit, Russia (hereinafter – LC). At hydrothermal synthesis, NaOH (purity ≥98 %), HCl (≥ 85%, NevaReaktiv) were used without additional purification. For the preparation of working solutions, deionized water was used.

2.2 Synthesis of nanostructures

In a typical preparation 0.8 g of starting ore (reduced size) was placed in 100 ml autoclave, where 80 ml of 10 M NaOH solution were added. The autoclave was kept at 110 °C during 24 h (temperature sensor was mounted on the stove, not inside the autoclave). After the hydrothermal reaction the autoclave was cooled to room temperature, and the resulting flaky precipitate was washed successively by distilled water and solution of hydrochloric acid (0.1 M) until neutral pH (6.5-7). The washed samples were dried in the oven at 90 °C for 12 hours.

2.3 Samples characterization

The morphology, phase and chemical composition of the starting ore and as-synthesized samples were studied using a complex of modern analytical equipment in Institute of Geology Komi SC.
UB RAS and Southwest University of Science and Technology. Nanotubes were visualized by scanning electron microscopy (TESCAN Vega 3; SIRMA 300). The crystalline structures of the initial ore and synthesized samples were analyzed by diffractometer (Shimadzu XRD-6000), the material composition was studied by X-ray fluorescence (XRF Shimadzu-1800).

The photocatalytic activity of the samples was studied using a test reaction of decomposition of trichlorophenol in Hereaus circular reactor of a volume of 350 cm³. Vertically to the reactor axis the TQ150 Z2 mercury lamp (150 W, 352–540 nm) was located. The control solutions were analyzed by liquid chromatography (Hypersil C18 reverse phase HPLC column). The solvent was a solution of acetonitrile in water in a ratio of 3:2. The solvent flow was 0.5 ml/min.

3. Results and discussion

3.1 Mineralogical analysis

The titanium minerals in LC sample are represented by ilmenite, rutile, anatase. Leucoxene, an aggregate of rutile and quartz, is represented by grains of yellow and slightly pinkish color and elongated along one of the axes [19].

The phase analysis showed that LC is basically a mixture of two phases: rutile and quartz (Fig. 1, A). The peaks are clear, indicating a high degree of perfection of rutile. Weak reflexes of ilmenite and anatase are present.

LC is represented by rounded isometric and oval flattened aggregates of needle microcrystals of rutile and quartz with relics of pseudorutile (Fig. 1, B-C). Rutile microcrystals form a sagenite lattice of rutile twins, fused at an angle of 60°. There are also areas of development of anatase crystalites, which are a homogeneous mass. The quartz grains have clear crystallographic forms, the surface is porous.

Thus, LC grains are a polynmineragge aggregate, the sizes of individual phases from a few micrometers to 100 micrometers.

Quartz cannot be reliably separated by physical methods.

3.2 Nanostructured titanium dioxide

The synthesized sample, hereinafter NT, (Fig. 2) is a mixture of two phases: quartz and hydrated sodium titanate (Na₂H₂Ti₃O₇). Chemical composition (wt.%) TiO₂ – 74.68, SiO₂ – 12.64, Fe₂O₃ – 5.44, Al₂O₃ – 4.71, Na₂O – 0.14, K₂O – 0.93, MnO – 0.64, CaO – 0.12, MgO – 0.25, P₂O₅ – 0.09, ZrO₂ – 0.08, NbO – 0.14.

The formation of titanium dioxide nanotubes proceeds in several stages: a gradual dissolution of raw is accompanied by epitaxial growth of layered sodium titanate nanosheets → nanolayer delamination → twisting of nanosheets into tubes → nanotube growth along X axis → exchange of sodium ions by protons during washing and separation of nanotubes from each other. When treated with alkali, the crystal lattice of the initial rutile turns into an amorphous product; after treatment with distilled water and a solution of hydrochloric acid, titanium dioxide nanotubes are formed [20]. According to [13], nanotubes consist of titanate layers, the composition of which depends on the synthesis conditions (temperature, processing time, ratio of liquid and solid phases). Tubular twisting of atomic layers is accompanied by a noticeable expansion of the shape of the peaks. Fig. 2A shows indices of planes corresponding to the diffraction pattern. The reflection characteristic of titanium dioxide nanotubes in the region 2θ = 10° can be attributed to H₂Ti₃O₇ or Na₂H₂Ti₃O₇ crystals [21]. Reflexes (200) with an interlayer distance 0.96 nm correspond to the distance between two adjacent TiO₆ octahedra that form the walls of the nanotubes.

Fig. 2 shows an electron microscopic image of the synthesized TiO₂ nanotubes. The channels inside the obtained nanotubes are clearly visible. The resolution of a scanning electron microscope allows estimating their outer diameter (70–100 nm).

Nanostructural rearrangement results in increasing specific surface and changing band gap. Measurements by low temperature nitrogen adsorption (BET) are given in Table 1.
The band gap was calculated by reflection spectra in the visible region based on the relationship of the adsorption coefficient $\alpha$ with the absorbed photon energy $h\nu$ [13]:

$$\alpha = \frac{B_i(h\nu - \Delta E_g)^2}{h\nu},$$

where $B_i$ – adsorption constant for indirect i-transitions. Structural rearrangement at the nanoscale level — the formation of titanium dioxide nanotubes — results in decreasing band gap: anatase — 3.1, LC — 2.8, NT — 2.4 eV.

The change in physical and chemical properties allows considering the obtained nanostructured samples as promising photocatalysts and using them in water treatment systems.

### 3.3 Study of photocatalytic properties

The photocatalytic activity of the samples was studied by a trichlorophenol decomposition reaction test. Commercially available titanium dioxide powders Aeroxide Degussa P25 and Anatase (Aldrich), widely used as an active catalyst in water treatment systems, were used as composites. According to the manufacturer, P25 is a weakly aggregated powder, the surface area is 50 m$^2$/g, the phase composition – 25 % rutile and 75 %. Anatase characteristics are given in Table 1.

The kinetics of the heterogeneous photooxidation reaction in liquid media in the presence of a catalyst is described by the Langmuir – Hinshelwood model [22]. In this model, the reaction rate $r$ is presented as a function of the degree of adsorbate coverage of active surface adsorption centers, which is assumed to be equal to the equilibrium adsorption $\theta$ associated with the concentration of adsorbate C through the equation of the Langmuir adsorption isotherm Eq. (1). The expression for the reaction rate should also contain other parameters, the consideration of which is possible only when constructing an adsorption model and adopting some simplifications. In particular, the size of the catalyst and the rate of transfer of active oxygen can be neglected. However, in this case as well, the process remains rather complicated for modeling, since the adsorption of trichlorophenol and decomposition products proceeds in parallel. Nevertheless, a fairly simple equation can be used if we consider only the process of photocatalytic decomposition of trichlorophenol (neglecting post-absorption).

If we assume that the reaction rate between the adsorbate and the active Bronsted and Lewis surface centers ($h^+$ and $e^-$) can be represented as $k\theta$, and the recombination rate of electron-hole pairs $h^+e^-$ (kr) is quite high (kr>>k), then

$$r = -\frac{dC}{dt} = \frac{I\Phi}{k_r} k\theta = \frac{I\Phi}{k_r} K C = \frac{k_{app} C}{1 + KC}$$

In the above equation, $I$ – intensity of the incident radiation, $\Phi$ – degree of coverage of the surface of the sample by adsorbate, $n$ – surface concentration of active centers, $K$ – equilibrium adsorption coefficient. If the concentration of adsorbate C is small, then Eq. (2) can be represented as:

$$r = \frac{k_{app} C}{1 + KC}$$

In the integrated form, the last two equations, respectively

$$\ln\left(\frac{C}{C_0}\right) + K(C_0 - C) = k_{app} t$$

and

$$\ln\left(\frac{C}{C_0}\right) = k_{app} t$$

In this case, for the decomposition reaction of trichlorophenol, taking into account Eq. (4), the time dependence is linear, and the slope gives the constant $k_{app}$. Graphs of time dependence for the studied samples are presented in Fig. 3.

Linear approximation is applicable only in a certain time interval. This can be explained by the fact that post-absorption processes, i.e. interaction of the surface of the samples with intermediate products of the decomposition reaction of trichlorophenol were not taken into account. When using the Langmuir-Hinshelwood model, it is assumed that the rate of adsorption on the surface significantly exceeds the rate of the reaction proceeding at active surface centers, i.e. the liquid phase and the surface of the sample are constantly in a state of adsorption equilibrium. Although the adsorption and decomposition reactions on the surface proceed...
simultaneously, most likely, they do not determine the reaction rate. In the initial period of time (0–10 min), trichlorophenol is adsorbed on the surface of the sample and the reaction rate increases. Upon reaching complete coverage of the surface with the adsorbate, the reaction rate is maximum and does not change further. At this point, the decomposition reaction of trichlorophenol will be of zero order.

Based on the obtained data, the values of the reaction constants were calculated (Fig. 3 B): 0.005 for LC, 0.006 for anatase, 0.025 for Degussa P25, 0.036 for NT.

4. Conclusions

We have synthesized titanium dioxide nanotubes by the hydrothermal method. Affordable natural raw material — a gravity concentrate of titanium ore from the Pizhemskoe deposit — has been used as an initial material. The synthesized titanium dioxide nanotubes have an external diameter of 70–100 nm. The synthesized material — TiO₂, nanotubes have a developed surface, which gives it good sorption qualities.

We have studied dependence of the kinetics of photoinduced decomposition of trichlorophenol in aqueous solutions in the presence of various types of catalysts based on titanium dioxide: commercially available Degussa P25 and anatase (Aldrich), leucoxene concentrate (Pizhemskoe deposit), titanium dioxide nanotubes. The reaction constants of photoinduced decomposition of trichlorophenol are calculated. We have shown that titanium dioxide nanotubes are not inferior in characteristics to commercial analogues currently used as the basis for catalysts.

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References

[1] T.N., Schemelinina – A. L., Gomze – O. B., Kotova – J.E.F.M., Ibrahim – D. A., Shushkov – M., Harja – G. V., Ignatiev – E. M., Anchugova (2019): Clay- and zeolite-based biogeoabsorbers: modelling and properties Építőanyag–JSBCM, Vol. 71, No.4, pp.131–137. p. https://doi.org/10.14382/epitoanyag-jscbm.2019.23

[2] T., Schemelinina – O., Kotova – M., Harja – E., Anchugova (2019): Biogeoabsorbers for solving ecological problems // IOP Conf. Series: Materials Science and Engineering Vol. 613, 012042 https://doi.org/10.1088/1757-899X/613/1/012042

[3] E., Kurovics – O.B., Kotova – A. L., Gomze – D. A., Shushkov – G.V., Ignatiev – P. A., Sitnikov – Y. I., Ryabkov – I. N., Vaseneva – L. N., Gomze (2019): Preparation of particle-reinforced mullite composite ceramic materials using kaolin and IG-017 bio-origin additives Építőanyag–JSBCM, Vol. 71, No.4, pp.114–119. https://doi.org/10.14382/epitoanyag-jscbm.2019.20

[4] K. D., Kumar – G. P., Kumar – K. S., Reddy (2015): Rapid Microwave Synthesis of Reduced Graphene Oxide-supported TiO₂ Nanostructures as High Performance Photocatalyst. Materials Today. No. 2, pp. 3736–3742.

[5] W., Zhang – C. R., Ou – Z.G., Yuan (2017): Precipitation and growth behaviour of metatitanic acid particles from titanium sulfate solution. Powder Technology, No.315, pp. 31–36.

[6] O. B., Kotova – I. L., Shabalin – D. A., Shushkov – A. V., Ponaryadov (2015): Sorbents based on mineral and industrial materials for radioactive wastes immobilization. Vestnik of Institute of Geology, Vol. 2, pp. 32–34.

[7] J. E. F. M., Ibrahim – A. L., Gomze – O. B., Kotova – T. N., Schemelinina – D. A., Shushkov – G.V., Ignatiev – E. M., Anchugova (2019): The influence of composition, microstructure and firing temperature on the density, porosity, and shrinkage of new zeolite-alumina composite material. Építőanyag–JSBCM, Vol.71, No.4, pp.120–124. https://doi.org/10.14382/epitoanyag-jscbm.2019.21

[8] D. P., Penaloz Jr. (2019): Enhanced mechanical, thermal and barrier properties of clay-based polymer nanocomposite systems. Építőanyag–JSBCM Vol. 71 No. 3 pp. 74–79. https://doi.org/10.14382/epitoanyag-jscbm.2019.13

[9] O. B., Kotova – D. A., Shushkov – A. L., Gomze – E., Kurovics – G. V., Ignatiev – P. A., Sitnikov – Y. I., Ryabkov – I. N., Vaseneva (2019): Composite materials based on zeolite-montmorillonite rocks and aluminosilicate wastes. Építőanyag–JSBCM, Vol. 71, No.4, pp. 125–130. https://doi.org/10.14382/epitoanyag-jscbm.2019.22

[10] F., Hu – Y., Wen – K. C., Chan – T. M., Yue – Y. Z., Zhou – S. L., Zhu – X. J., Yang (2015): Synthesis of self-detached nanoporous titanium-based metal oxide. Journal of Solid State Chemistry Vol. 229, Pages 78-86 https://doi.org/10.1016/j.jssc.2015.05.021

[11] S., Illas – A. K., Mahapatro (2019): Hydrothermally grown rutile titanium dioxide nanostructures with various morphologies. Materials Science in Semiconductor Processing, Vol. 104, 104676. https://doi.org/10.1016/j.mssp.2019.104676

[12] O. B., Kotova – M., Harja – L. N., Kotov – A. V., Ponaryadov (2018): Titanium minerals as prototypes of functional materials with pronounced electromagnetic properties. Vestnik IG Komi SC UB RAS. No. 4. C. 34–39.

[13] L. H., Huang – C., Sun – Y. L., Liu (2007): Pt/N-codoped TiO₂ nanotubes and its photocatalytic activity under visible light. Applied Surface Science, Vol. 253, pp. 7029–7035.

[14] H. L., Kuo – C. Y., Kuo – C. H., Liu – J. H., Chao – C. H., Lin (2007): A highly active bi-crystalline photocatalyst consisting of TiO₂ (B) nanotube and anatase particle for producing H₂ gas from neat ethanol. Catalysis Letters, Vol. 113. P. 7–12.

[15] T. W. P., Seadira – G., Sadanandam – T., Ntho – C. M., Masuku – M. S., Scurrel (2018): Preparation and characterization of metals supported on nanostructured TiO₂ hollow spheres for production of hydrogen via photocatalytic reforming of glycerol. Applied Catalysis B: Environmental, Vol.222, pp.133–145

[16] N. Wang – X., Li – Y., Wang – X., Quan – G., Chen (2009): Evaluation of bias potential enhanced photocatalytic degradation of 4-chlorophenol with TiO₂ nanotube fabricated by anodic oxidation method. Chemical Engineering Journal, Vol. 146, pp. 30–35.

[17] Duduman C. N., – Gómez de Salazar y Caso de Los Cobos Harja M., – Barrena Pérez M. I., Gómez de Castro C., Lutic D., Kotova O., Cretescu (2018): Preparation and characterisation of nanocomposite materials based on TiO₂-Ag for environmental applications. Environmental Engineering and Management Journal. Vol.17, No. 4, pp. 2813-2821.

[18] O., Kotova – E., Ozhogina – A., Ponaryadov – I., Golubeva (2016): Titanium minerals for new materials. IOP Conf. Series: Materials Science and Engineering, 012025 https://doi.org/10.1088/1757-899X/123/1/012025

[19] A. V., Ponaryadov (2017) Mineralogical and technological features of ilmenite-leucoxene ores of Pizhemskoe deposit, Middle Timan. Vestnik of the Institute of Geology, Komi SC UB RAS. No. 1, pp. 29–36. https://doi.org/10.19110/2221-1381-2017-1-29-36 (in Russian)

[20] O. B., Kotova – A. V., Ponaryadov – L. A., Gomze (2016): Hydrothermal synthesis of TiO₂, nanotubes from concentrate of titanium ore Pizhemskoe deposit (Russia). Vestnik IG Komi SC UB RAS, No.1, pp. 34–36.

[21] Th., Streethawong – Y., Suzuki – S., Yosikawa (2005): Synthesis, characterization, and photocatalytic activity for hydrogen evolution of nanocrystalline mesoporous titania prepared by surfactant-assisted templating sol-gel process. Journal of Solid State Chemistry, Vol.178, pp. 329–338.

[22] Alouisi, O. Tahiri – Nguyen, Q. T. – Mbarnek, C. – Rhlalou, T. (2009): Elaboration and study of poly (vinylidene fluoride)–anatase TiO₂ composite membranes in photocatalytic degradation of dyes, Applied Catalysis A General Vol. 358, pp. 13–20.

Ref: Ponaryadov, Aleksii V. – Kotova, Olgia B. – Titih, Mohammed – Sun, Shiyong: Natural titanium dioxide nanotubes Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 72, No. 5 (2020), 152–155. p. https://doi.org/10.14382/epitoanyag-jscbm.2020.25