Efficiency Evaluation for Titanium Dioxide-Based Advanced Materials in Water Treatment

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Abstract. We present a comparative evaluation of efficiency of titanium dioxide polymorphs as an active photocatalyst (commercially available DegussaP25, anatase (Sigma Aldrich), natural leucoxene concentrate (Pizhenskoe deposit, Russia) and titanium dioxide nanotubes based on it). The materials obtained on the basis of relatively inexpensive and affordable ilmenite-leucoxene ore have the same efficiency as more expensive commercial products.

Keywords: Anatase · Ilmenite-leucoxene ores · Nanotube · Water treatment

1 Introduction

In recent years, advanced oxidation processes have been proposed as alternative methods for eliminating toxic organic pollutants from aquatic systems. Semiconductor heterogeneous photocatalysis is one of the most promising and effective method. This method is environment friendly, because the reaction products of the oxidation of organic pollutants are carbon dioxide and water. A comparative analysis of the economic efficiency of water purification showed that the photocatalytic method was the cheapest (Duduman et al. 2018, Kotova et al. 2016b).

The treatment of water from phenols, in particular, containing chlorine (2, 4, 6 - trichlorophenol, TCP), is an important public health task because of their estrogenic, mutagenic or carcinogenic effects. Their toxicity depends on the degree of chlorination and the position of chlorine atoms in relation to the hydroxyl group. Removing these compounds from the water is necessary to protect both human health and the environment. To produce semiconductor photocatalyst based on titanium dioxide, multi-stage synthesis methods are most often used, using orthotitanium acid or titanium tetrachloride as precursors.

The aim of the work is the comparative evaluation of efficiency of commercially available titanium dioxide (Degussa P25, Anatase Sigma Aldrich), natural (leucoxene concentrate, Pizhetskoe deposit, Russia) and titanium dioxide nanotubes based on natural leucoxene as active photocatalysts (TiNT).

2 Methods and Approaches

Titanium dioxide. Degussa P25 (80% anatase, 20% rutile; Sigma Aldrich, France) was used as photocatalyst without any purification. It has a BET surface (average) of 50 m²/g, a particle size of 20–50 nm. Anatase (Sigma Aldrich) was used as photocatalyst without any purification. It has a BET surface (average) of 80 m²/g, elongated particles with a size of 15–30 nm.

Leucoxene concentrate (LC) was obtained from the Pizhetskoe deposit (Russia). Chemical composition (wt%): TiO₂ – 42.12, SiO₂ – 46.57, Fe₂O₃ – 1.04, Al₂O₃ – 7.57, K₂O – 1.61, MnO – 0.06, CaO – 0.13, MgO – 0.37, SO₃ – 0.06, P₂O₅ – 0.17, ZrO₂ – 0.05, NbO – 0.11. The particle size is about 20–40 μm.

Titanium dioxide nanotubes (TiNT) were obtained using a hydrothermal treatment procedure. The detailed description is given elsewhere (Kotova et al. 2016a).

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

The initial leucoxene (Fig. 1A) is a mixture of two phases: rutile and quartz. The peaks are clear, which indicates a high crystallinity of these phases. There are weak reflexes of ilmenite and anatase. Leucoxene is a rutile microcrystalline matrix, saturated with the finest inclusions of quartz (Ponaryadov 2017). The synthesized sample (Fig. 1B) is a mixture of two phases: quartz and sodium titanate Na₂Ti₆O₁₃. The chemical composition (semi-quantitative): TiO₂ – 74.68%, SiO₂ – 12.64%, Fe₂O₃ – 5.44%, Al₂O₃ – 4.71%, K₂O – 0.93%.

The structural rearrangement at the nanoscale level – formation of titanium dioxide nanotubes – leads to decreasing band gap: anatase – 3.1, LC – 2.8, TiNT – 2.4 eV. Another important parameter is the specific surface area. During formation of titanium dioxide nanotubes we observed increasing specific surface, which is associated with formation of external and internal surfaces. For the studied samples, the specific surface area was: anatase – 80, LC – 13, TiNT – 230 g/m².

Fig. 1. XRD patterns for leucoxene concentrate, heavy fraction (A) and as-synthesized TiNT (B)

Kinetics of heterogeneous photooxidation reaction in liquid medium in the presence of a catalyst is described by the Langmuir-Hinshelwood model. For the reaction of decomposition of trichlorophenol, the time dependence $\ln(C_0/C)$ is linear, at that the slope ratio gives a constant k_{app} . The time dependence graphs for the studied samples are presented in Fig. 2.

Fig. 2. Curves of decomposition of trichlorophenol in water medium (▲ - leucoxene concentrate, ■ - anatase, ◆ - DegussaP25, × - titanium dioxide nanotubes)

The adsorption and decomposition reaction on surface occur simultaneously, most likely, they do not determine the reaction rate. In the initial period of time (0–10 min), trichlorophenol is adsorbed on the sample surface and the reaction rate increases. Upon reaching the full coverage of the surface with adsorbate, the reaction rate is maximal and does not change in the future. Based on the received data, the values k_{app} of reaction constants were calculated: 0.005 for leucoxene concentrate, 0.006 for anatase, 0.025 for Degussa P25, 0.036 for titanium dioxide nanotubes.

Thus, TiNT, produced by the hydrothermal method from ilmenite-leucoxene ore, are competitive photocatalysts in water treatment from organically contaminants in comparison to the above stated synthetic analogues.

4 Conclusions

We studied the dependence of the kinetics of photoinduced decomposition of trichlorophenol in water solutions in the presence of various types of catalysts based on titanium dioxide: commercially available DegussaP25 and anatase (Aldrich), leucoxene concentrate (Pizhenskoe deposit), titanium dioxide nanotubes. We calculated reaction constants of the photoinduced decomposition of trichlorophenol. It is shown that advanced materials on the basis of relatively inexpensive and affordable ilmenite-leucoxene ore have the same efficiency as expensive commercial products.

Acknowledgements. This research was supported by UB RAS project № 15-18-5-44 and project AAAA-A17-117121270037-4 “Scientific basis for effective development and use of the mineral resource base, development and implementation of innovative technologies, geological and economic zoning of the Timan-North Ural region”.

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