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The influence of titanium dioxide modifications on photocatalytic oxidation of lignin and humic acids

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ABSTRACT

A few design options of attached photocatalyst reactors were tested in photocatalytic oxidation (PCO) of UV/VIS-irradiated aqueous solutions containing lignin and humic acids (HA). Degussa P25, anode-oxidized titanium and titanium dioxide doped with sulphur and boron atoms attached to various supports were tested. Maximum PCO efficiency with P25 was observed with floating glass plate support submerged at the depth of 7.0 mm, providing beneficial combination of the layer transparency and mixing conditions, thus noticeably exceeding the efficiency of buoyant glass micro-spheres.

The electrolytic titanium dioxide film on metallic titanium demonstrated rather low efficiency: only HA in acidic media was photocatalytically oxidized. The sulphur content in the catalysts active in visible light was found to have an optimum value for the PCO efficiency.

1. Introduction

Lignin and its fragments of complex aromatic structure form the major part of the waste from the pulp and paper industry. Natural decomposition of lignin takes long time and results in the formation of toxic phenolics, aldehydes, ketones, methanol and carboxylic acids [1]. Lignin is resistant to biological degradation and other conventional wastewater treatment: biological oxidation, typically applied to the treatment of pulp and paper mill effluent, does not significantly decrease the content of lignin [2]. Sterile conditions required for white rot fungi-based biological oxidation make its application problematic [3]. Concerning such wastewater treatment as coagulation, only large molecules of lignosulfonates, but not their fragments, can be removed with coagulants [4].

Humic acids (HA) are the ultimate products of plant tissue decomposition of a polyaromatic character with carboxylic and phenolic groups, which are, similarly to lignin, resistant to biological oxidation. Functional groups make HA bonding aqueous toxics such as heavy metals and organic pollutants; this makes the bonded toxics difficult to remove by simple methods [5]. Abundantly formed in landfill leachate due to anaerobic decomposition of lignocellulose [6], HA are of great concern because of high heavy metal and organic toxics contents. Furthermore, HA present a hazard as a source of carcinogenic and mutagenic trihalomethanes (THMs) formed as a result of water chlorination [7,8].

Photocatalytic oxidation (PCO) may appear as promising alternative in elimination of toxic compounds, resistant to biological degradation. The use of suspended titanium dioxide, widely studied as a semiconductor photocatalyst, is difficult due to complications in separation of powdered TiO_2 after the treatment. Alternatively the catalyst may be attached onto the suitable solid support without the need for separation from the effluent streams [9]. Various techniques are known for the fixation of titanium dioxide onto the support matrix, e.g. dip-coating [10], sol–gel technique [11], electrochemical oxidation [9] and chemical vapour deposition [12]. When a photocatalytic film is used, most of the slurries' drawbacks may be avoided, although the PCO efficiency of films is lower and problems in the design of reactors arise.

When using titanium dioxide, one must bear in mind that only ultraviolet light photons have enough energy to displace valence band electrons, as the band-gap energy is 3.2 eV, making only 4% of the solar radiation utilized. To improve the photocatalytic properties of TiO_2 materials, many studies have been performed to enhance the light absorption and delay recombination of photogenerated electron–hole pairs by adjusting its microstructure, processing routs and compositions [13]. To increase visible light absorption of TiO_2 materials, consideration has been made to the doping of third element such as non-metal ions, for example S, B, N, C, or F, to substitute O^{2-} in TiO_2 to reduce the energy band-gap [14–18].

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The attached photocatalyst reactor's design was tested in the present research in oxidation of lignin and HA with the improved efficiency as compared to the photocatalysts attached to buoyant glass hollow micro-spheres. The objective was also to test different modifications of titanium dioxide-based photocatalysts, such as Degussa P25, anode-oxidized titanium and sulphur- and boron-doped titanium dioxide in PCO of lignin and HA.

2. Experiment

Two 200-mL simple batch reactors with inner diameter 100 mm (evaporation dishes) thermostated at 20 ± 1 °C and mechanically agitated with magnetic stirrers were used in the slurry, buoyant micro-spheres and fixed plate PCO experiments: the reactor used for the PCO was called active and the other, containing no photocatalyst, was called the reference one. Both reactors were exposed to identical experimental conditions. The samples from the active reactor were compared to the reference samples to avoid complications caused by water evaporation. With buoyant micro-spheres, samples taken during the experiment were separated from catalyst before analysis by filtration.

For floating plates the volume of reactors was enlarged to 3 L for the convenience in operations (plane surface diameter 295 mm). The reactors were only surface aerated, since the oxygen shortage was not observed even in the PCO experiments with concentrated phenolic solutions [19]. A UV-light source, Phillips TLD 15W/05 low-pressure luminescent mercury UV-lamp with the emission maximum at 360-nm, was positioned horizontally over the reactors as described elsewhere [19], providing irradiance of about 0.7 mW cm^{-2} measured by the optical radiometer UVX at a distance corresponding to the level of the free surface of the reactor. Phillips TL-D 15W/33-640 luminescent lamp was chosen as visible light source with the irradiance on the reactor' plane surface corresponding to 0.54 mW cm^{-2} at 683 nm.

3. Materials and methods

The experiments were conducted with synthetic solutions of alkali lignin and HA purchased from Aldrich. The substrates were prepared in concentrations of 10 mg L^{-1} of sodium salt of HA and 100 mg L^{-1} of alkali lignin solution. The pH of solutions was 7 and 8 respectively. The pH value of solutions was adjusted with 2 M solutions of sulphuric acid or sodium hydroxide. Sulphate ion was chosen as a counter-ion due to its abundant character in groundwater and due to its known non-dramatic effect on the PCO performance [20]. The treatment time was 6 h if not specified otherwise. All the experiments were carried out three times under identical conditions; the average deviation of data in parallel experiments did not exceed 5%.

For HA, colour was determined with the spectrophotometer HACH DR/2010 at 455 nm. The UV-absorbance of HA and lignin samples at 254 and 280 nm respectively was measured by Spectronic Unicam spectrophotometer (Heλios β), which was correlated with the content of HA and lignin by calibration line. The lignin concentration was measured with photometric method developed by HACH Co. Solutions, namely sodium carbonate solution and tannin-lignin reagent, containing sodium molybdate and sodium tungstate (VI), react with lignin forming blue-coloured intermediates. After 25 min of reaction time the colour intensity was measured. Aldehydes, as PCO by-products of lignin, were qualitatively determined by the methods described by Evans and Dennis [21]. The concentration of phenol, another PCO by-product of lignin, was measured by colorimetric method with p-nitroaniline: to the 100-mL sample of treated solution 2 mL of 5% sodium carbonate and 4 mL of diazotizated p-nitroaniline were added; after 15 min of the reaction the optical density at 570 nm was measured. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) were measured by standard procedures [22].

The experiments with ultraviolet radiation were performed using titanium dioxide. TiO_2 (Degussa P25) was attached to buoyant hollow glass micro-spheres and to the surface of the glass plates.

3.1. Buoyant hollow glass micro-spheres

Titanium dioxide was attached to the surface of the micro-beads by the thermal method [23]: equal volumes of dry micro-spheres and the aqueous suspension of titanium dioxide (concentration of 1 g L^{-1}) were thoroughly mixed by stirring and sonication in an ultrasonic bath for 30 min. The micro-spheres used in this study had an average diameter of 60–70 μm and a density 0.27 g cm^{-3}, a product of LP-ImpEx, Estonia. The micro-spheres were then separated from the mixture by filtration through a membrane filter, heated to dryness at 120 °C and calcinated in air at a temperature of 300 °C for 4 h. This procedure was repeated a few times to apply a higher amount of the photocatalyst on the surface of the micro-spheres. It was found that there is an optimum amount of photocatalyst on the surface of the hollow glass micro-spheres, which corresponds to six-time thermal attachments of TiO_2 [24]. Therefore, all experiments were carried out with the photocatalyst prepared following this six-time attachment pattern. Experiments with buoyant hollow glass micro-spheres were carried with lignin at neutral pH for 24 h.

3.2. Fixed glass plate

TiO_2 was attached to the surface of the glass plate by multiple submerging of the plate to the 1 g L^{-1} TiO_2 suspension with subsequent distilled water rinsing and drying at 105 °C after each submersion. Before the attachment of titanium dioxide to the surface of the plate, the surface of the latter was etched by HF and mechanically scratched for better adhesion. The glass plate surface area was 63 cm^2. The glass plates were submerged horizontally in the treated solution and fixed at a depth about 7 mm.

3.3. Floating glass plate

Titanium dioxide was attached to the surface of the floating plate (280 cm^2) similarly as to the fixed plate. The plate was supplied with three foam plastic floats attached to the plate's edge, which kept the plate submerged at a certain depth varied from 0.2 to 2 cm. Fixation of the floating plate at certain depth was provided varying the floats size.

3.4. Titanium anodization

Titanium dioxide film was also produced by low-voltage anodization process of titanium plate, described by Xie and Li [25]. Titanium plates (63 cm^2; thickness 1 mm) were mechanically scratched, cleaned with 5-M sodium hydroxide solution and rinsed with distilled water prior to anodic oxidation. The plate oxidation was conducted in a dual-electrode reaction chamber, in which the Ti plate was used as the anode and a stainless steel plate of the same size was used as the cathode. Both electrodes were submerged in a mixture of electrolyte solution and a direct-current source was used to provide electric current between electrodes. Titanium dioxide films were prepared in H_2SO_4(1.0 M)–H_3PO_4(0.3 M)–H_2O_2(0.6 M)–HF(0.03 M), electrolyte I, and H_3PO_4(0.5 M)–HF(0.1 M), electrolyte II, solutions. The treatment in the electrolyte I solution is supposed to result in micro-structured thick film, whereas the nano-structured thin film is expected with the electrolyte II. Post-calcination at 723 K for 2 h was applied for the titanium dioxide film made with electrolyte II.

3.5. Doped catalysts

The experiments with visible light were carried out with the suspended TiO_2-S and TiO_2-B catalysts. Both catalysts synthesized by hydrolysis of $Ti(OBu)_4$ with $Na_2S_2O_3$ and $Na_2B_4O_7$ as sulphur and boron sources respectively. The procedure of doped catalysts preparation included the rinsing to remove the excess dopant. Calcined catalyst was washed with hot (70–80 °C) distilled water on the membrane filter using about 1 L per 1 g of the catalyst during about 20 to 30 min. With these catalysts, sulphur content in the catalyst varied from 0.83 to 2.79 at.% and boron content was from 1.09 to 3.82 at.%. The atomic concentration of S and B was determined by X-ray photoelectron spectroscopy at the University of Colorado at Boulder.

4. Results and discussion

The performance of PCO with artificial radiation sources was characterized by the process efficiency *E*. The efficiency *E* is defined as the decrease in the amount of lignin or HA divided by the amount of energy reaching the surface of the treated sample:

$$E = \frac{\Delta c \cdot V \cdot 1000}{I \cdot s \cdot t}, \qquad (1)$$

where *E* is the photocatalytic oxidation efficiency in mg W^{-1} h^{-1}; Δc denotes the decrease of pollutants concentration in mg L^{-1}; *V* depicts the volume of the sample to be treated in L; *I* is irradiation intensity in mW cm^{-2}; *s* denotes the solution irradiated plane surface area in cm^2; and *t* depicts the treatment time in h.

It was found that the PCO provided the decrease of pollutants concentrations in time. The catalyst presence was essential, since the decrease of lignin and HA concentration in absence of catalyst was not observed.

4.1. PCO with Degussa P25

The plane surface concentration of the buoyant catalyst attached to the hollow glass micro-spheres varied from 10 to 100 g m^{-2}, resulting in optimum at 25 g m^{-2}. This optimum for lignin coincided with the one found earlier for HA thus confirming indirectly the explanation given before [26]: incomplete coverage of treated solution surface below this number and difficulties in UV penetration through the thick layer of the micro-spheres above that explain lower efficiency apart the optimum.

The efficiency of the Degussa P25 attached to various catalyst supports in PCO of lignin and HA is shown in Fig. 1. As one can see for both substances the maximum PCO efficiency is observed for the floating glass plate submerged to the depth of 7 mm. Buoyant micro-spheres with attached TiO_2 are the least effective. This could be explained by smaller titanium dioxide surface in contact with the treated solution, which is effectively irradiated by UV. The fixed plate, although expected to show the performance similar to the floating one, was less efficient, the reason of which is explained below.

As was confirmed in this study, the thickness of the treated solution layer above the catalyst film is crucial for the PCO efficiency when aromatic compounds are oxidized. For these compounds, this parameter is essential for the UV transparency and, thus, the intensity of the catalyst irradiation. From the other hand, mixing of the solutions above the catalyst film may influence the PCO efficiency for the substrate and oxygen transportation to the catalyst surface. In case with fixed plate in this study, the thickness of the solution layer above the catalyst decreases in time due to water evaporation and sampling from 6 to 2 mm, thus improving the catalyst irradiation on account of the liquid layer thinning, but worsening the stirring. The thickness of the solution layer above the floating plate may be adjusted to an optimum value by the plate submerging depth providing maximum available oxidation rate.

4.2. Optimizing the plate submerging depth

The submerging depth of the catalyst layer was found to play a significant role in the PCO efficiency. As a result of test series with different submerging depths, the maximum PCO efficiency for HA solutions at HA concentrations tested was observed at the depth of 7 mm (Fig. 2). The efficiency decreased with the plate submerging depth above this number obviously due to increased UV absorption, although the depth below 7 mm also resulted in decreased PCO efficiency. The responsibility of worsened stirring above the catalyst layer for the decreased PCO efficiency was confirmed by simple experiment: a drop of a dye tracer placed to the centre of the plate of 19 cm in diameter was completely mixed with the bulk solution in about as long as 80 s at 2 mm depth, whereas at 7 mm depth the complete mixing took five times shorter time, i.e. about 16 s. The reduced concentration of a substrate to be oxidized in the solution layer above the catalyst may thus also result in the reduced PCO rate.

4.3. The amount of attached photocatalyst

The thickness of the TiO_2 film on the glass plate support only slightly affected the PCO efficiency: almost eight times, from 0.076 to 0.6 mg cm^{-2}, increased titanium dioxide surface concentration resulted in less than 10% increased PCO efficiency of HA (Fig. 3). This could be explained by the excess in active adsorption sites over the number of molecules to be adsorbed due to low HA concentration. This minor increase may be explained by unevenness of thicker surfaces, only slightly increasing their contact areas.

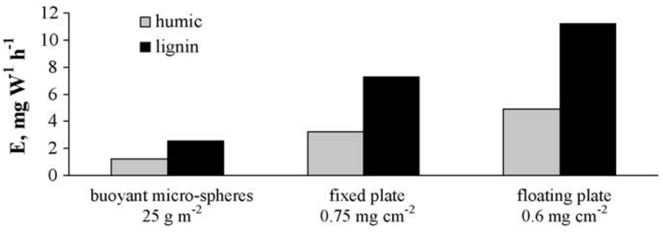

Fig. 1. The efficiency of the photocatalyst supports in PCO of HA and lignin (Degussa P25): treatment time for plates 6 h, for micro-spheres 24 h; neutral pH; HA initial concentration 10 mg L^{-1} and lignin 100 mg L^{-1}.

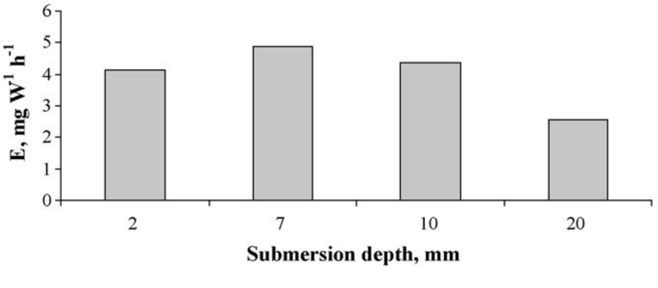

Fig. 2. The influence of photocatalyst layer submerging depth to the PCO efficiency of HA: treatment time 6 h; initial concentration of HA 10 mg L^{-1}; neutral pH; floating plate 0.6 mg cm^{-2}.

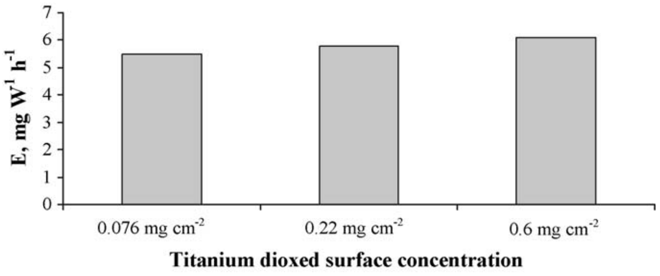

Fig. 3. The influence of thickness of TiO2 film on floating glass plate to the PCO efficiency of HA: treatment time 6 h; initial concentration of HA 10 mg L^{-1}; neutral pH; catalyst layer submersion depth 7 mm.

4.4. PCO with anodized titanium

An alternative method for the preparation of titanium dioxide layers is anodic oxidation (AO) of titanium metal in acidic solutions by applying an electrical current between a Ti anode and a counter electrode. Such titanium dioxide AO-films have certain advantages over others: the nano-structured TiO_2 multi-porous film could provide much larger contact area for pollutant adsorption and UV transmission [25]. In addition, such TiO_2 films show good adhesion to the support [27], whereas titanium dioxide films, attached mechanically, may be unstable [26]. This circumstance deserves attention due to strong ability of lignin and HA solutions to re-suspend attached TiO_2 observed earlier [26].

Although Xie and Li [25] reported the photocatalytic performance of nano-structured TiO_2 film being superior over the one of the micro-structured film in oxidation of endocrine disrupter (bisphenol A) due to larger contact surface area for pollutant adsorption and UV transmission, in the present research only micro-structured film showed positive results in PCO at rather low level: PCO of HA proceeded only in acidic media showing 0.8 to 1.0 mg W^{-1} h^{-1} (compare to Fig. 1). The reason of inefficiency of nano-structured film in lignin and HA PCO could be explained by poor adsorption of big molecules on the nano-structured film surface.

4.5. PCO with doped photocatalysts

The development of visible light active photocatalysts for abatement of environmental pollutants has attracted considerable attention during last years. The band-gap can be reduced by introducing additive atoms into titanium dioxide structure, thus, creating a crystalline structure with a misbalance in charge carries. In the present research the oxidation experiments with lignin and HA under visible irradiation with S- and B-doped catalyst were carried out.

The influence of sulphur content in the doped catalyst to the lignin and HA PCO efficiency was studied. With the increase of the sulphur content from 0.83 to 1.42 at.% the lignin PCO efficiency decreased growing again with further increase in sulphur content (Fig. 4). A similar dependency pattern was observed with HA (Fig. 4b), although the efficiency minimum was observed at sulphur content of 1.66 at.%.

The dependence pattern of lignin adsorption on the sulphur content in the doped catalyst to some extent was similar to the one of the oxidation efficiency: the minimum adsorption, 40 mg g^{-1}, was observed at 1.42 and 1.66 at.% of sulphur compared to 62 mg g^{-1} at 1.08 and 2.46 at.%. Poorer adsorption of lignin by the catalyst at about 1.5 at.% sulphur content may to some extent explain slower lignin PCO. This, however, could not be verified with HA due to complete adsorption of the substrate on the catalysts' surfaces at the low concentrations used in the study. The reason for poorer adsorption and PCO at certain sulphur content lays most probable in the surface/crystal structure properties, which have to be established further.

4.6. Adsorption on the photocatalysts

The lignin and HA adsorption dependence on pH at the surface of S-doped and B-doped catalysts was established in experiments carried out at 25 °C.

We have found that the best adsorption of lignin on S-doped catalyst (2.46 at.%) was observed at pH 3.0, the equilibrium surface concentration was about 87 mg g^{-1} TiO_2, with its gradual decrease to 66 mg g^{-1} TiO_2 at pH 7.0 and 49 mg g^{-1} TiO_2 at pH 10.5. Nevertheless, the pH range of a better adsorption of lignin does not coincide with the pH range of high PCO efficiency (see Section 4.7), which may indicate the prevailing role of OH·-radicals in PCO of lignin. The similar trends were observed in the experiments of lignin and HA adsorption on the surface of titanium dioxide surface [28]: acidic medium is favourable for adsorption, whereas in alkaline solutions lignin and HA practically do not adsorb on the surface of the catalyst.

The best adsorption of HA on the surface of sulphur-doped catalyst was not found due to the low initial concentration of HA: 100% of pollutant adsorbed on the surface of the photocatalyst at all pH values.

The adsorption of both pollutants on the surface of B-doped catalyst was observed only in acidic medium. The best adsorption of lignin and HA coincide with good PCO performance with studied pollutants (see Section 4.7), indicating the prevailing role on positively charged holes in oxidation of pollutants: OH-radicals seem to be unable to oxidize the pollutants for their zero adsorption at the catalyst surface.

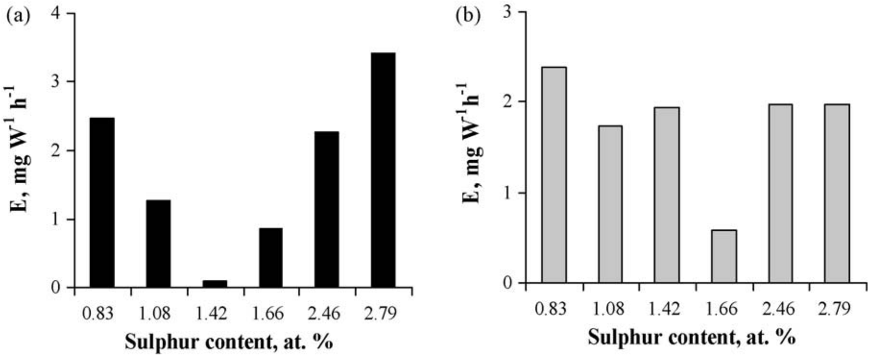

Fig. 4. The influence of sulphur content in doped catalyst to the lignin (a) and HA (b) PCO efficiency: treatment time 24 h; initial concentration of HA 10 mg L^{-1} and lignin 100 mg L^{-1}; neutral pH; catalyst concentration 1 g L^{-1}.

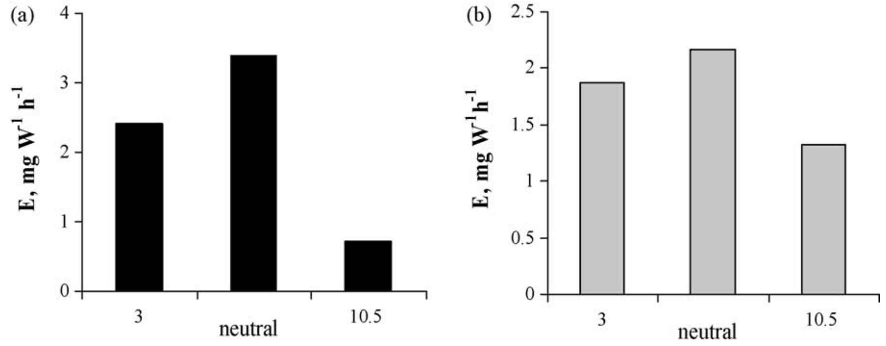

Fig. 5. The dependence of PCO efficiency of lignin (a) and HA (b) on pH with sulphur-doped catalyst under visible light: treatment time 24 h; initial concentration of HA 10 mg L^{-1} and lignin 100 mg L^{-1}; catalyst concentration 1 g L^{-1}; sulphur content 2.79 at.%.

4.7. pH impact with doped photocatalysts

The influence of pH to lignin and HA PCO efficiency with doped photocatalysts was also studied (Fig. 5). Similar to the plain TiO_2 [28], the maximum efficiency of PCO with doped catalyst was also observed in neutral media, which indicates that the oxidation mechanism with OH-radicals is likely to prevail: the most favourable acidic media for lignin and HA adsorption appeared not to be the best for PCO of both substances, the efficiency increased with increasing concentration of OH-ions, the OH-radical precursors. The decrease of PCO efficiency under strong alkaline conditions may be explained by the effect of charges repulsion between both negatively charged lignin/HA molecules and the catalyst particles and accumulation of OH-radical scavenging carbonate ions under alkaline conditions.

One can see that the efficiency of S-doped photocatalysts yielded to the one of Degussa P25 noticeably: attached P25 exhibited efficiencies up to 6 for HA and 11 mg W^{-1} h^{-1} instead of 2.5–3.5 mg W^{-1} h^{-1} for doped catalysts. Therefore, narrowing the band-gap for photocatalysts does widen the effective absorbed light spectrum (PCO proceeds under visible light), although the increase in the PCO efficiency was not observed under tested experimental conditions.

In the experiments with B-doped catalyst, degradation of HA and lignin was observed only in acidic media showing rather low PCO efficiency: 1.3 and 3.8 mg W^{-1} h^{-1} respectively (compare to Fig. 1). The reason for inefficiency in neutral and alkaline media could be explained by zero adsorption of lignin and HA on the B-doped catalysts in these media (see Section 4.6).

5. Conclusions

The present study demonstrated PCO performance of different modifications of titanium dioxide-based photocatalysts, such as Degussa P25, anode-oxidized titanium and sulphur- and boron-doped titanium dioxide. The titanium dioxide attached to a floating glass plate showed a superior PCO efficiency over the others and maximum PCO efficiency was observed at the depth of 7 mm. Buoyant micro-spheres with attached TiO_2 were the least effective due to poor illumination of the surface in contact with the treated solution. The anodic oxidation titanium dioxide film exhibited rather low efficiency. The sulphur-doped photocatalyst, being active in visible light, yields to Degussa P25 in its efficiency.

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