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Photocatalytic Oxidation of Natural Polymers in Aqueous Solutions

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Declaration: Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

Elina Portjanskaja

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ELINA PORTJANSKAJA

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INTRODUCTION

The growth of the global population, agriculture and industry has led to the generation of large quantities of polluted industrial and municipal wastewaters posing a serious threat to humans. This makes the scientists and technologists to look for effective, economic, and environmentally benign water treatment technologies, harmless to the environment. Advanced oxidation technologies, including photocatalytic oxidation (PCO), have been proposed as an alternative to water treatment strategies currently in use. The PCO of organic pollutants is based on the photochemical production of an electron-hole pair in a solid semiconductor under irradiation by light of energy greater than its optical band gap. Photocatalytic oxidation is believed to proceed via a dual mechanism: (1) the adsorption of the pollutant by the surface of a semiconductor followed by direct subtraction of the pollutant's electrons, i.e. oxidation, with positively charged holes; (2) the oxidation at the surface or in its vicinity with hydroxyl radicals (Linsebigler et al., 1995).

In the present research the experimental study in PCO of aqueous solutions of natural polymers, humic acids (HA) and lignin, was undertaken. The main source of these pollutants is natural organic material. They may be present in groundwater due to the dissolution of bark mulch, buried organic debris such as tree stumps, landfills, the waste-waters of leather and wood-working industries, and pulp and paper mill effluents. Both substances are resistant to biological degradation. Humic acids and lignin may affect the taste, colour, and odour of drinking water; the chlorination of water containing HA or lignin leads to the formation of toxic and carcinogenic chlorinated substances.

The objective of the present research was to clarify the PCO potential in degradation of HA and lignin under various experimental conditions. The control parameters under the study include pH, the presence of H_2O_2 and ferrous ions, the initial concentration of pollutants, the attached photocatalyst reactor’s design, and different modifications of titanium dioxide-based photocatalysts including sulphur-, nitrogen- and boron-doped catalysts active in visible light.

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My deepest thanks go to my family and friends for understanding, patience, encouragement, support and for being with me through all years of the study.

LIST OF ORIGINAL PAPERS

The present doctoral thesis is based on the following papers, which are referred to the text by their Roman numerals I-IV.

I. **Portjanskaja, E.**, Krichevskaya, M., Preis, S., Kallas, J. 2004. Photocatalytic oxidation of humic substances with TiO_2-coated glass micro-spheres. *Environmental Chemistry Letters*, 2(3), 123-127. http://apps.isiknowledge.com/full_record.do?product=WOS&search_mode=GeneralSearch&qid=1&SID=N13pAcjoMkb6l5Jgjog&page=1&doc=4

II. **Portjanskaja, E.**, Preis, S., Kallas, J. 2006. Aqueous photocatalytic oxidation of lignin and humic substances with supported TiO_2. *International Journal of Photoenergy*, Vol. 2006, Article ID 85927, doi: 10.1155/IJP/2006/85927, 1-7. http://apps.isiknowledge.com/full_record.do?product=WOS&search_mode=GeneralSearch&qid=1&SID=N13pAcjoMkb6l5Jgjog&page=1&doc=3

III. **Portjanskaja, E.**, Preis, S. 2007. Aqueous photocatalytic oxidation of lignin: the influence of mineral admixtures. *International Journal of Photoenergy,* Vol. 2007, Article ID 76730, doi:10.1155/2007/76730, 1-7. http://apps.isiknowledge.com/full_record.do?product=WOS&search_mode=GeneralSearch&qid=1&SID=N13pAcjoMkb6l5Jgjog&page=1&doc=2

IV. **Portjanskaja, E.**, Stepanova, K., Klauson, D., Preis, S. 2009. The influence of titanium dioxide modifications on photocatalytic oxidation of lignin and humic acids. *Catalysis Today*, in press, doi:10.1016/j.cattod.2008.12.021 http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6TFG-4VH334W-2&_user=10&_rdoc=1&_fmt=&_orig=search&_sort=d&view=c&_acct=C000050221&_version=1&_urlVersion=0&_userid=10&md5=1ff910e050d31388fefa5f65166d6829

In the appendix I, copies of these publications are included.

The author's contribution to the publications

Paper I
The author carried out experiments and analyses, interpreted obtained results and wrote the paper. The results were presented also at International Conference Eco-Balt, May 6-7 2004, Riga, Latvia.

Paper II
The author carried out experiments and analyses, interpreted obtained results and wrote the paper. The results were reported at the Sixth European Meeting on Environmental Chemistry, December 6-10 2005, Belgrade, Serbia and Montenegro.

Paper III
The author planned experimental work, carried out the experiments, interpreted the results and wrote the paper. The results were also reported at the 4th European Meeting "Solar Chemistry and Photocatalysis: Environmental Applications", November 8-10 2006, Las Palmas, Spain.

Paper IV
The author planned and supervised the experimental work carried out together with BSci-student, analysed results and wrote the paper. The results were presented at 5th European Meeting "Solar Chemistry and Photocatalysis: Environmental Applications", October 4-8 2008, Palermo, Italy.

ABBREVIATIONS

AO	Anodic oxidation
AOPs	Advances oxidation processes
BOD_5	5-day biochemical oxygen demand
CAT	Catalyst
COD	Chemical oxygen demand
e^{-}	Electron
E_{gap}	Band gap energy
EU	European Union
h^{+}	Positively charged hole
HA	Humic acids
HS	Humic substances
PCO	Photocatalytic oxidation
THMs	Trihalomethanes
UV	Ultraviolet light
UV_{254}	Ultraviolet absorbance at 254 nm
UV_{280}	Ultraviolet absorbance at 280 nm
VIS	Visible light

1. LITERATURE REVIEW

Since the early 1970s, advanced oxidation processes (AOPs) have been used considerably to remove both low and high concentrations of organic compounds from diverse sources such as groundwater, municipal and industrial wastewater, sludge digestion, and volatile organic compounds control. AOPs are effective against majority of organic compounds, and the chemicals used in the process decompose to harmless or beneficial by-products (Peyton, 1992). In the AOPs the organic compounds can be completely mineralized to carbon dioxide and water mostly by hydroxyl radicals, the second most powerful oxidizing agent generated *in situ* in the reaction environment.

The hydroxyl radical (•OH) is a non-selective chemical oxidant, which reacts very rapidly with most organic compounds (Carp et al., 2004). Several methods are available for generating •OH radicals. These include both non-photochemical and photochemical methods:

- Ozonation at elevated pH (> 8.5)
- Ozone + hydrogen peroxide (O_3/H_2O_2)
- Ozone + catalyst (O_3/CAT)
- Fenton system (H_2O_2/Fe^{2+})
- O_3/UV
- H_2O_2/UV
- O_3/H_2O_2/UV
- Photo-Fenton/Fenton-like systems
- Photocatalytic oxidation (UV/TiO_2)

Photocatalytic oxidation (PCO) benefits from very low capital and operation costs and from the possibility of using solar energy directly without energy transformation.

1.1. Basis of Photocatalysis

Heterogeneous PCO is a promising technique for the degradation of many contaminants in water, in air and on solid surfaces. The photocatalytic destruction of organic compounds involves the excitation of a semiconductor (mostly titanium dioxide) by irradiation with light of energy greater than its optical band gap. When the photon with energy equal to or exceeding the band gap energy of the semiconductor ($h\upsilon \geq E_{gap}$) reaches the surface, an electron (e^-) is promoted from the valence band to the conduction band. At the valence edge an electronic vacancy or hole (h^+) is created. Both energy carriers can participate in various reactions: the holes and electrons can recombine and the energy will be lost as heat, they can get trapped in metastable surface states, or they can migrate to the surface of semiconductor and participate in redox reactions with electron donors and electron acceptors adsorbed at the surface (Schiavello and Sclafani, 1989, Hoffman et al., 1995).

$h\upsilon$ + (semiconductor) $\rightarrow e^{-} + h^{+}$ (1)
$A_{(ads)} + e^{-} \rightarrow A_{(ads)}^{-}$ (2)
$D_{(ads)} + h^{+} \rightarrow D_{(ads)}^{+}$ (3)

Each ion formed subsequently reacts to form intermediates and final products. As a consequence of reactions (1-3), the photonic excitation of the catalyst appears as the initial step of the activation of the whole catalytic system (Herrmann, 1999).

There is experimental evidence (Carey, 1992) for the produced hydroxyl radical remaining adsorbed at the interface. Thus in order for it to react with organic compounds, these probably also need to be adsorbed or be present very near the surface at the time of excitation. For very dilute solutions, the rate of reaction is very likely limited by the rate of mass transfer of the substrate to the surface.

To prevent the electron-hole recombination, a suitable scavenger or surface defect state must be available to trap the electron or hole. Howe and Grätzel (1985) showed that the conduction band electrons in an oxygen-free aqueous solution are trapped at the particle surface, possibly with the formation of Ti^{3+}. In the presence of most common electron acceptor, molecular oxygen, the electrons are trapped by oxygen, forming the superoxide radical anion in reaction (4). Superoxide ions readily protonate and disproportionate in reactions (5) and (6) forming hydrogen peroxide and oxygen. The holes in the valence band migrate to the surface where they can react with water or hydroxide ions to produce hydroxyl radicals in reaction (7). These hydroxyl radicals are assumed to be the primary oxidizing species in the PCO of organics, but also the positive holes can attack organic species at the surface (Turchi and Ollis, 1990).

$e^{-} + O_2 \rightarrow \bullet O_2^{-}$ (4)
$\bullet O_2^{-} + H^{+} \rightarrow \bullet O_2H$ (5)
$2\ \bullet O_2H \rightarrow H_2O_2 + O_2$ (6)
$h^{+} + H_2O \rightarrow H^{+} + \bullet OH$ (7)

Various catalysts have been used in PCO: TiO_2 , ZnO, CeO_2 , CdS, ZnS, etc. As generally observed, the best photocatalytic performances with maximum quantum yields are always obtained with titania. Anatase is the most active allotropic form among the various ones available, either natural (rutile and brookite) or artificial (TiO_2-B. TiO_2-H). Anatase is thermodynamically less stable than rutile, but its formation is kinetically favoured at lower temperatures (<600°C) (Herrmann, 1999).

Titanium dioxide (anatase) is a semiconductor photocatalyst with an energy band gap of 3.2 eV thus being activated by UV illumination with a wavelength up to 387.5 nm (Zhang et al., 1994). The strong oxidizing power of the photogenerated holes, the chemical inertness, and non-toxicity of TiO_2 has also made it a superior photocatalyst (Reddy et al., 2002).

It has been shown that the photocatalytic effect of TiO_2 is dependent on crystal structure, particle size and surface area and that the effectiveness of the process is governed by the lifetime or recombination probability of the electron-hole pair (Dalton et al., 2002).

The catalyst in water treatment can be either immobilized or suspended in the reactor. So far, suspended systems have received most attention in literature. Although, the suspended system has the advantage of a larger surface area as compared to the immobilized system, the necessary separation of the fine catalyst powder from the treated water is expensive and constitutes a major drawback in the commercialization of this system (Sakthivel et al*.,* 2002).

A major problem associated with suspended system is that a large amount of catalyst is needed, but only the thin exterior layer of the typical unsupported photocatalyst actually absorbs UV light. Consequently, only a small fraction of the solid is active with respect to its capability to bring about photocatalytic reactions (Sirisuk et al., 1999).

The common disadvantage of the immobilised photocatalysts is their reduced photocatalytic activity due to the reduced contact surface and, often, the screening effect of the water layer above the catalyst. It could thus be beneficial to bring up the support with the photocatalyst close to the irradiated plane surface of water to be treated.

Optimal catalyst/support options could be identified (Zhang et al., 1994) by considering: (a) type of photocatalyst, (b) support material, (c) catalyst dosage on the support, (d) support particle size, (e) method of attaching the photocatalyst onto the support, and (f) calcination temperature. Various techniques are known for the fixation of titanium dioxide onto the support matrix, e.g. dip-coating (Herrmann et al., 1999), sol-gel technique (Neppolian et al., 2007), electrochemical oxidation (Byrne et al., 1998) and chemical vapour deposition (Bessergenev et al., 2006).

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 (Chang et al., 2005). To increase visible light absorption of TiO_2 materials, consideration has been made to the doping of the 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 (Umebayashi et al., 2003; Asahi et al., 2001; Irie et al., 2003; Yu et al., 2002; Ling et al., 2008).

1.2. Pollutants: an overview

1.2.1. Lignin

The pulp and paper industry causes serious pollution problems of the aquatic bodies. Manufacturing good quality paper, the pulp and paper industry discards lignin as an unwanted constituent of raw material, discharging a significant amount of lignin-containing wastewater.

Since lignins are irregular complex natural tri-dimensional polymers with random bonds, the exact chemical structure is not known. Lignin, which is the second, after cellulose, most abundant macromolecule in wood, contains various aromatic, mostly phenolic units. Physical and chemical properties of lignins differ depending on the wood (fir or foliferous) and extraction technology (Nikitin et al., 1987). For example, lignosulfonates are hydrophilic, whereas kraft lignins are hydrophobic (Agryropoulos and Menachem, 1997).

The lignins are resistant to natural decomposition processes: the lifetime in aqueous media in nature is about 200 days. Natural decomposition of lignins results in formation of toxic phenolics, aldehydes, ketones, methanol and carbonic acids (Cotrim et al., 2001). Toxic behaviour is under suspicion to be a reason for depressed immunity of population consuming water from polluted sources, especially in vicinity of pulp and paper plants, and, as a result, for two-fold increased endocrine systematic diseases observed if even the polluted water passed conventional treatment procedure (Manahan, 1994). The current strategies of wastewater treatment are ineffective against lignins: only large molecules of lignosulfonates, but not their fragments, may be removed with coagulants (Dilek and Gokçay, 1994). White rot fungi-based biological oxidation systems may present a promising solution, although application in non-sterile conditions is problematic (Mester and Tien, 2000). Concerning potable water treatment, increased chlorination is hazardous due to formation of more toxic chlorinated substances (Chang et al., 2004). Lignin is also abundantly present in landfill leachates as a product of decomposition of lignocellulose comprising mostly cardboards.

1.2.2. Humic substances

Humic substances (HS) are the water-soluble compounds with the molecular weight from several hundreds to a few hundred thousands. Being mainly ultimate products of plant tissue decomposition, HS are resistant to biological oxidation. They are not toxic, although the intensive colour given by HS to water may irritate customers and make water inappropriate for use in food industry, laundering, paper, and textile making (Manahan, 1994). The colouring of water, however, is not the only and far not the main negative property of HS. A branched mainly aromatic carbon skeleton of HS molecules contains large number of carboxylic and phenolic groups making HS bonding heavy metals, pesticides, insecticides, herbicides etc., consequently making them difficult to remove by simple methods (Manahan, 1994). Besides, HS are well-known precursors of trihalomethans (THMs) formed by chlorination (Eggins et al., 1997, Wang et al., 2001).

The strongest concern is associated with the HS formation in landfill leachate containing heavy metals and organic toxics. Curiously, HS are not formed from lignin in its natural aqueous decomposition process being abundantly present in landfill leachate due to anaerobic decomposition of lignocellulose (Sánchez-Monedero et al., 1999). This may be explained by the thermophilic phase of composting, at which white-rot fungi do not survive and cannot take part in lignin degradation (Tuomela et al., 2000).

The abatement strategies for HS include some conventional and advanced methods such as coagulation, adsorption, nanofiltration and various oxidation methods. All these strategies have certain drawbacks such as sludge accumulation, necessity for material safe regeneration, membrane fouling and high capital investment and operation costs.

1.2.3. Concerns in Estonia

The pulp and paper industry in Estonia is a potential and actual source of aqueous pollutants under consideration. Since the industry is under development sometimes on account of relocation of old paper mills from the EU countries (Reimer, 2003), there is a reasonable doubt about the best available techniques served the needs of the environment. Other sources of lignin-laden wastewaters and leachates are expected with further development of the wood-processing industry (Kunda puitmassitehas, 2002) and accumulation of municipal solid wastes in landfills (Pajula and Arusoo, 2002). Landfills, in their turn, will create problems such as formation of noxious compounds with high heavy metal and toxic organics content. Humic substances are also characteristic to shallow groundwater used by summer cottages owners in the towns' vicinity.

1.3. The objectives of the present study

Since there are currently no treatment units certified specifically for the reduction of HS and lignin in water, PCO looks to be promising treatment method for reducing their levels in potable and waste water.

The objective of the present research was to clarify the PCO potential in degradation of humic acids (HA) and lignin under various experimental conditions. The declared objective was achieved in the experimental research undertaken into the PCO of pollutants, dependently on various process parameters. The control parameters under the study include pH, the presence of radical promoters, i.e. H_2O_2 and ionic admixtures, i.e. ferrous ions, the initial concentration of pollutants, the buoyant photocatalyst plane surface concentration and the amount of TiO_2 attached to the glass micro-spheres. The attached photocatalyst reactor's design was tested 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 and anode-oxidised titanium in PCO. Also, the experimental study of the action of sulphur-, nitrogen- and boron-doped catalysts active in visible light was carried out.

pH is a key parameter determining the adsorption of pollutants onto a photocatalyst surface, their dissociation state and the red-ox potential of oxidizing agents. Hydrogen peroxide is a well-known OH-radical precursor and helps not only acceleration of the reaction but also allows studying the reaction pathways by radical and/or non-radical route. Iron is often abundantly present in groundwater; therefore its influence to the PCO presents an interest. The PCO of aromatic compounds is known to exhibit maximum reaction rate at certain optimum pollutants' concentration (Preis et al., 2002).

Practical limitation in use of powdered catalyst for PCO, such as difficulties in separation of the fine catalyst powder from the treated water, often makes immobilized catalyst application the only alternative, as observed in the present study. Special attention was paid to the design of the PCO reactors in order to achieve higher efficiency with the least potential expenses.

Anion-doped TiO_2 photocatalysis has good potential for the utilization of the solar energy to eliminate environmental pollutants in water. Besides, doping of titanium dioxide with such ions as S, N, or B can reduce energy ban-gap, but the effect of dopant ions to the photocatalytic activity of TiO_2 often remains unpredictable.

The experiments were carried out with the pollutants' synthetic solutions as well as with groundwater polluted with HA under both artificial UV/VIS and solar radiation. The observation made on course of the study improved the knowledge of the reaction mechanisms and the feasibility of PCO in treatment of polluted waters.

2. EXPERIMENTAL PART

The experimental conditions are briefly given here. For more details see experimental parts of *Papers I-IV*.

2.1. Experimental device

Two 200-mL simple batch reactors with inner diameter 100 mm (evaporation dishes) thermostatted at 20±1 ºC and mechanically agitated with magnetic stirrers were used in the slurry (*Paper I*), buoyant micro-spheres (*Paper I, II, IV*) and fixed plate (*Paper II, III, IV*) 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.

For floating plates (*Paper IV*) 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 (Preis et al., 1997).

A UV–light source (*Paper I-IV*), 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 (Preis et al., 1997), 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 (*Paper III, IV*) was chosen as visible light source with the irradiance on the reactor's plane surface corresponding to 0.54 mW cm^{-2} at 683 nm. The experiments with solar radiation *(Paper I*) were carried out by sunny days in Tallinn, Estonia (59º25'N), from May to June under conditions identical to these of experiments with artificial radiation. The intensity of solar radiation was not measured. All the experiments were carried out three times under identical conditions; the average deviation of data in parallel experiments did not exceed 5%.

2.2. Materials and methods

2.2.1. Treated solutions

The experiments were conducted with synthetic solutions of alkali lignin and HA purchased from Aldrich. The coloured groundwater was taken from two different water wells in Estonia (*Paper I*). The pH value of solutions was adjusted with 2M solutions of sulphuric acid or sodium hydroxide. Sulphate ion was chosen as a counter-ion due to its known moderate effect on the PCO performance (Krichevskaya et al., 2003).

2.2.2. Catalysts

The experiments with ultra-violet radiation were performed using titanium dioxide (Degussa P25), TiO_2 attached to buoyant hollow glass micro-spheres and to the surface of the glass plates. Electrolytic titanium dioxide film on metallic titanium was also used with UV-light.

Titanium dioxide was attached to the surface of **the buoyant hollow glass micro-spheres** (*Paper I, II, IV*) by the thermal method (Jackson et al., 1991): 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 were then separated from the mixture by filtration through a membrane filter, heated to dryness at 120 ºC and calcinated in air at a temperature of 300 ºC for 4 h. This procedure was repeated a few times to apply a desired amount of the photocatalyst on the surface of the micro-spheres.

TiO_2 was attached to the surface of **the glass plates** (*Paper II, III, IV*) by multiple submerging of the plates in the TiO_2 suspension with subsequent rinsing with distilled water and drying after each submersion, or by spraying the TiO_2 suspension over the surface of the plates and drying. 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. Floating glass plate (*Paper IV*) was prepared similarly to the fixed plates. The plate was supplied with three plastic foam floats attached to the plate’s edge, which kept the plate submerged at a certain depth varied from 2 to 20 mm. Fixation of the floating plate at certain depth was provided varying the floats size.

Titanium dioxide film was also produced by low-voltage anodization process of titanium plate (*Paper IV*), described by Xie and Li (2006). Titanium plates (63 cm^2; thickness 1mm) 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 with the Ti anode and the stainless steel cathode, supplied with a direct-current source.

The experiments with visible light were carried out with the suspended TiO_2-N, TiO_2-S and TiO_2-B catalysts. Last two catalysts (*Paper IV*) were synthesised by hydrolysis of $Ti(OBu)_4$ with $Na_2S_2O_3$ and $Na_2B_4O_7$ as sulphur and boron sources respectively. With these catalysts, sulphur content in the catalysts varied from 0.83 to 2.79 at. % and boron 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. The TiO_2-N catalyst (*Paper III*) was made after Gandhe and Fernandes (2005).

2.2.3. Analytical methods

An overview of the analytical methods, applied for HA and lignin samples are summarized in the Table 1.

Table 1. Analytical methods used for samples

Analysis/Parameter	Method/Analytical instrument	Source
UV_{254} and UV_{280} absorbance	Spectronic Unicam spectrophotometer (Heλios β)	Standard Methods, 1995
Colour	Spectrophotometer HACH DR/2010	The manual
COD	Closed reflux colorimetric method, spectrophotometer HACH DR/2010	Standard Methods, 1995
BOD_5	BOD Incubator Sanyo MIR-153, oxygen analyser Marvet Junior MJ97	Standard Methods, 1995
Lignin concentration	Spectrophotometer HACH DR/2010	The manual
Aldehyde concentration	Spectrophotometer HACH DR/2010	Evans and Dennis, 1973
Phenol concentration	Spectrophotometer HACH DR/2010	Lurje, 1971

3. RESULTS AND DISCUSSION

The performance of photocatalytic oxidation with artificial radiation sources was characterised by the process efficiency *E*. The efficiency *E* is defined as the decrease in the amount of pollutant divided by the amount of energy reaching the surface of the treated sample (Preis et al., 1997):

$$E = \frac{\Delta c \cdot V \cdot 1000}{I \cdot s \cdot t}, \qquad (8)$$

where *E* is the photocatalytic oxidation efficiency in mg W^{-1} h^{-1}; Δc denotes the decrease of pollutant 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 HA and lignin concentrations in time. The presence of the photocatalyst was essential, since the decrease of concentrations in absence of titanium dioxide under UV/VIS was not observed.

3.1. Influence of pollutants' initial concentration

Photocatalytic oxidation of pollutants with initial concentrations of HA ranging from 5 to 50 mg L^{-1} at pH 7 and lignin from 35 to 400 mg L^{-1} at pH 8 with TiO_2 attached to the hollow glass micro-spheres gave a close to linear dependence of PCO efficiency on the pollutant concentration: the efficiency of HA PCO increased from 0.2 mg W^{-1} h^{-1} at 5 mg L^{-1} to 3.4 mg W^{-1} h^{-1} at 50 mg L^{-1} *(Paper I)* and for lignin these numbers were 2.0 mg W^{-1} h^{-1} at 35 mg L^{-1} and 6.5 mg W^{-1} h^{-1} at 400 mg L^{-1}. *(Paper II)*. This indicates that the reactions under experimental conditions may be described by first-order or Langmuir-Hinshelwood equations *(Paper I)*. The minor difference in pH for HA and lignin was caused by the natural reasons: commercially available lignin exhibited slightly alkaline reaction whereas HA remained neutral.

Aromatic compounds are generally UV absorbers. This should lead to a decreased UV transparency of the solution at increased HA and lignin concentrations, and thus to a decrease in PCO efficiency. However, it was found, within the experimental limits, that PCO efficiency increased with the increased concentration of pollutant. The optimum concentration corresponding to the maximum efficiency was not found within the studied interval of pollutant concentrations. The author should note, however, that the mentioned interval covers most of the possible concentrations in polluted natural and wastewaters.

3.2. The effect of pH

The results of PCO of HA and lignin solutions are presented in *Paper II* (Figure 2) and show that the process efficiency depends on pH. Both substances showed maximum PCO efficiency under neutral and slightly basic media conditions. The PCO efficiency for HA at pH between 7.0 and 9.0 with the buoyant photocatalyst was equal to 1.1 mg $W^{-1}h^{-1}$, and at pH 5.0 this number averaged 0.67 mg $W^{-1}h^{-1}$. The decrease of PCO efficiency under alkaline conditions could be explained by the effect of charges repulsion between both negatively charged lignin molecules and TiO_2 particles (see below) and accumulation of OH-radical scavenging carbonate ions under alkaline conditions.

The relationship between pollutant adsorption on the TiO_2 surface and the PCO efficiency at different pH and in the presence of radical promoters may indicate the mechanism prevailing in oxidation of the pollutant. For example, it was found that the best adsorption of HA on TiO_2 was observed at pH 3.0 (*Paper II*, Figure 3a). However, the maximum PCO efficiency for HA was observed at the lowest adsorption pH range, in neutral and alkaline media, which may point to the prevailing oxidation of HA with OH-radicals, abundantly formed at elevated pH (*Paper II*, Figure 2). Low PCO efficiency in acidic media could be explained by less effective direct oxidation of the pollutant with positively charged holes due to complex molecular structure of the adsorbed pollutant and the higher resistance towards oxidation of non-dissociated phenolic moieties in acidic media; oxidation of HA with OH-radicals appears to be more successful: the radicals are formed in neutral and alkaline media at a higher rate due to the abundant presence of OH-ions as OH-radicals precursors. In acidic media, the formation of OH-radicals is poor due to low OH-ions concentration.

The isotherms for lignin adsorption on the TiO_2 surface at different pH are shown in Figure 3b *(Paper II)*. One can see that lignin adsorption depends on pH similarly to HA: an acidic medium is favourable for adsorption, whereas in alkaline solutions lignin practically does not adsorb on the TiO_2 surface. Nevertheless, the pH range of good adsorption of lignin does not coincide with the pH range of high PCO efficiency (*Paper II-III*, Figure 2), which also may indicate the prevailing role of OH-radicals in PCO of lignin.

3.3. Influence of H_2O_2 addition

Another way to estimate the contribution of OH-radicals to PCO of HA and lignin is to study the influence of a well-known OH-radical source, hydrogen peroxide (*Paper II*). Resulting from the addition of H_2O_2, the increased PCO rate may be attributed to a decrease in electron-hole recombination rate because of the conduction band electrons scavenged by hydrogen peroxide or superoxide ions and generation of OH-radicals (Bekbölet and Balçioglu, 1996).

Hydrogen peroxide was added to the solutions of HA and lignin prior to PCO at pH 3, 7, 9 and 11 in amounts from 0.7 to 50 mM. In all cases the addition of H_2O_2

led to the oxidation of HA in both the PCO-treated sample and the reference. Thus, an increase in the sum reaction rate was observed, however the efficiency of PCO decreased since a part of the HA was reacting directly with H_2O_2 in the reference sample. The higher was the H_2O_2 dose, the lower the efficiency observed, that is, photocatalytic decomposition of H_2O_2 with additional hydroxyl radicals' generation did not result in more energy-efficient decomposition of HA.

The addition of hydrogen peroxide to the lignin solutions enhanced the degradation rate considerably in the acidic medium (*Paper II*, Figure 4). The rate improvement is due to the OH-radical generation subsequent to the conduction band electron scavenging with hydrogen peroxide:

$$e^{-} + H_2O_2 \rightarrow \bullet OH + OH^{-} \qquad (9)$$

In neutral media, the PCO efficiency gradually and slightly decreased with increasing H_2O_2 concentration. This can be explained by competition of H_2O_2 with the contaminant for adsorption sites on titanium dioxide. In alkaline media one can see a sudden decrease in the PCO efficiency at an H_2O_2 concentration of 1 mM. This fact can be explained by scavenging of the valuable OH-radicals by hydrogen peroxide and the forming of the much weaker oxidant - hydroperoxide radical $HO_2\bullet$ (Sun et al., 1997):

$$H_2O_2 + \bullet OH \rightarrow H_2O + HO_2\bullet \qquad (10)$$

With further growth of H_2O_2 concentration, the secondary formation of OH-radical from hydroperoxide radical is likely to prevail:

$$HO_2\bullet + H_2O_2 \rightarrow \bullet OH + H_2O + O_2 \qquad (11)$$

This may lead to the increase of the PCO efficiency with increasing H_2O_2 concentration observed in Figure 4 (*Paper II*) for alkaline media. Abundant presence of OH-ions in the solution at high pH levels results in massive OH-radical formation in both direct PCO oxidation of OH-ions and secondary formation of OH-radicals from hydrogen peroxide, which explains increasing PCO efficiency with increasing pH.

3.4. Influence of ferrous ions

The role in PCO of ferrous ions, abundantly present in waters under anoxic reductive conditions, such as groundwater or landfill leachate, was also studied in this research. A drastic increase in lignin PCO efficiency at low, below 0.05 mM, concentrations of Fe^{2+} (*Paper II*, Figure 5b) could be explained by the decrease in recombination rate between positively charged holes and conductivity band electrons, which is considered as a PCO limitation stage. Conductivity electrons may be scavenged by ferrous ions adsorbed on TiO_2 surface at their higher oxidation ferric stage, extending the lifetime and thus the oxidation performance of the positively charged holes.

In contrast to many substances, in the experiments with HA the addition of Fe^{2+} up to 0.1 mM leads solely to a sharp decrease in PCO efficiency from 4.15 to 1.65 mg $W^{-1}h^{-1}$ (*Paper II*, Figure 5a). A further increase in Fe^{2+} ions concentration up to 0.3 mM resulted in stabilisation of PCO efficiency value at 1.6 mg $W^{-1}h^{-1}$. A similar dependency pattern was observed with buoyant photocatalyst, although the efficiency rates were lower. Since the influence of ferrous ion was studied in acidic media, where OH-radicals give little contribution to PCO performance, the observed inhibitive effect of ferrous ions on the PCO efficiency for HA could be explained by the complications in HA adsorption: not only do Fe^{2+}-ions block the adsorption sites at the TiO_2 surface, but also the partial chelation of carboxylic and phenolic groups of the humic molecules with the Fe^{2+}-ions may obstruct their adsorption at the TiO_2 surface. Under these circumstances, the prolonged lifetime of positively charged holes may weaken due to obstructions in the adsorption of chelated humic molecules (Klauson et al., 2005).

In contrast to HA, chelation of lignin with Fe^{2+} ions was probably not pronounced due to the small number of carboxylic groups in the structure of the lignin molecule. Ferrous ions thus only occupy the adsorption sites on the surface of TiO_2 without further complications for the adsorption of chelated iron complex molecules. This made the PCO efficiency increase from 5.6 to 7.0 mg $W^{-1}h^{-1}$ with increasing concentration of ferrous ions from 0 to 0.05 mM. The decrease in PCO efficiency from 7.0 to 4.4 mg $W^{-1}h^{-1}$ with further increase in ferrous ion concentration is, presumably, caused by the blockade of absorption sites by metallic ions. The lack of precipitates observed with lignin at concentrations up to 200 mg L^{-1} in presence of ferrous ions indirectly confirmed the absence of chelation with lignin molecules. Humic acids, however, easily precipitate in the presence of ferrous ion at concentrations slightly above the experimental limits of this study.

3.5. Oxidation by-products

The oxidation by-products were observed in the PCO-treated lignin solutions. These solutions were analysed for free phenols, aldehydes and the biodegradability expressed as the BOD_5/COD ratio. The initial concentration of free phenols in the solution containing 100 mg L^{-1} of lignin, measured by the standard method, was found to be 16 mg L^{-1}. As a result of 24-h PCO under neutral media conditions, 80% of free phenols were removed, i.e. their concentration decreased five times; the final concentration of phenols was 3.25 mg L^{-1}. The biodegradability of this sample increased from 3 to 15%, i.e. also five times. The analogous effect was observed for the samples PCO-treated under different pH (see *Paper III*, Figure 3), although the neutral media was the most beneficial for the increased biodegradability. It may be interesting to notice that the five-fold decrease in phenols' concentration resulted in five times increased biodegradability, indicating possible correlation between these two parameters.

The PCO treatment never resulted in an increased phenols concentration to any extent (*Paper III*, Figure 4). This may be explained by the degradation of phenolic compounds exceeding the degradation of lignin by its rate: the free phenols degraded for about 80%, whereas lignin degradation did not exceed 50%. The reduced concentration of toxic free phenols together with the formation of biodegradable oxidation by-products may be the reason for increased biodegradability of the lignin solutions.

During the PCO of lignin, the formation of aldehydes, another PCO by-product, was observed (*Paper II*; *Paper III*, Figure 5). The neutral pH was beneficial for the aldehyde formation with the rate similar to the lignin oxidation rate and the biodegradability growth rate. However, in contrast to the oxidation of phenol and lignin, acidic medium was favourable for aldehydes formation. In general, the rate of aldehyde accumulation, determined by the balance between the formation and oxidation of aldehydes, increased with the pH increasing from 3 to 7 and decreased with the further increasing pH, having the maximum rate at pH 7.

The formation of aldehydes in PCO of HA was not noticed due to, probably, concentrations of HA too low for aldehyde measurements.

In the experiments with lignin, the decrease of pH was observed (*Paper II*), which was probably due to the formation of carboxylic groups and carboxylic acids in PCO, known to go via formation of aldehydes. For example, in the PCO of aqueous solution containing 100 mg L^{-1} of lignin pH from 8.37 changed to 6.45 in 24 hours. However, pH of photocatalytically treated HA solutions behaved differently: pH remained neutral when the experiment started at pH 7.0. Furthermore, in experiments with pH initially adjusted above or below 7.0, for example to 5.0 or to 9.0, it showed a tendency to approximate pH 7.0 during the PCO, i.e. HA under oxidation exhibit a buffering capacity. Since molecules of HA contain nitrogen atoms, the author suppose the behaviour of pH explained by the transformation of HA structural nitrogen to ammonia. Presumably, the decrease of pH of the PCO-treated HA basic aqueous solutions can be explained by the escape of free ammonia and formation of carboxylic acids, whereas the increase of pH in acidic media is a result of partial binding of acidity with free ammonia formed in the solution.

3.6. PCO with Degussa P25

3.6.1. Buoyant photocatalyst

The plane surface concentration of the buoyant catalyst immobilized to the hollow glass micro-spheres varied from 10 to 100 g m^{-2}, resulting in optimum at 25 g m^{-2} (*Paper I,* Figure 2; *Paper IV*). 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 amount of the photocatalyst at the surface of the micro-spheres was adjusted by the number of TiO_2 attachment operations. The single attachment of TiO_2 to the surface of hollow glass micro-spheres is less effective in the HA decomposition than the multiple ones (*Paper I*, Figure 3). The photocatalytic oxidation efficiency is increased with the increased number of attachment operations until this number comes to six. Further attachments resulted in small oscillations within ±5 % of the photocatalytic oxidation efficiency.

The observed dependence is most likely shaped by the following factors. The solitary attachment did not provide the complete cover for the surface of the hollow glass micro-spheres with TiO_2. This results in the decreased contact surface of the photocatalyst, which leads to the oxidation efficiency decrease. Further attachments increase the coverage of the buoyant support surface until it is completely coated with TiO_2 at six operations under the described conditions. The attachments operations exceeding six by the number did not result in the efficiency improvement, which indirectly proves that the surplus TiO_2 attachments to the micro-beads simply make the photocatalyst layer thicker without significant increase in the buoyant photocatalyst active contact surface.

3.6.2. Titanium dioxide immobilized to the plates

The attached photocatalyst reactor's design was tested in oxidation of lignin and HA with the improved efficiency as compared to the photocatalysts attached to the buoyant glass hollow micro-spheres.

The efficiency of the Degussa P25 attached to various catalyst supports in PCO of lignin and HA is shown in Figure 1 of *Paper IV*. As one can see, the maximum PCO efficiency for both substances is observed with 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.

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.

The submerging depth of the catalyst layer is playing 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 (*Paper IV*, Figure 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 with a tracer indicating five-times faster mixing at the depth of 7 mm than at 2 mm. 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.

The impact of thickness of the TiO_2 film on the glass plate supports was also studied. Within the tested limits of the photocatalyst surface concentration (0.3-0.75 mg cm^{-2}) the increased efficiency was observed for the increased amount of the catalyst on the fixed plate (*Paper III*). This could be explained by the UV-light penetration to a certain depth of the TiO_2 layer, which is active in PCO reactions. A similar phenomenon was observed earlier with the photocatalyst attached to the microspheres: the oxidation efficiency increased with increased thickness of the catalyst layer until a certain limit, above which the PCO efficiency did not increase further (*Paper I)*.

The attachment mode of titanium dioxide to the glass plates makes a difference in the PCO efficiency: the spraying attachment appeared to be more effective (*Paper III*, Figure 2). However, under acidic conditions, the washing-off of titanium dioxide from the plate made by spraying was observed as the decrease in the PCO efficiency of lignin.

3.7. PCO with anodized titanium

The titanium dioxide films prepared by anodic oxidation should have certain advantages of larger contact area for pollutant adsorption and UV transmission (Xie and Li, 2006) and good adhesion to the support (Yerokhin et al., 1999). This circumstance deserves attention due to strong ability of lignin and HA solutions to re-suspend attached TiO_2 and form its stable suspensions observed in *Paper III*.

In the present research only low efficiency results of PCO of HA in acidic media were observed showing 0.8 to 1.0 mg $W^{-1}h^{-1}$ (Figure 1, *Paper IV*). The reason of inefficiency of anodized titanium film in lignin and HA PCO could be explained by poor adsorption of large molecules on the film surface.

3.8. PCO with doped photocatalysts

The band-gap extensive in titanium dioxide can be reduced by introducing additive atoms into its structure, thus, forming a crystalline structure with a misbalance in charge carries sensitive towards visible light radiation. In the present research the oxidation experiments with lignin and HA under visible irradiation with N-, S- and B-doped catalysts were carried out.

3.8.1. Sulphur-doped catalyst

The PCO efficiency dependent on sulphur content in the doped catalyst was studied. With the increase of the sulphur content from 0.83 to 1.42 atomic % the lignin PCO efficiency decreased growing again with further increase in sulphur content (*Paper IV*, Figure 4a). A similar dependency pattern was observed with HA (*Paper IV*, Figure 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 at 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.

The influence of pH to lignin and HA PCO efficiency with sulphur-doped photocatalysts (*Paper IV*, Figure 5) was similar to the one of plain TiO_2 (*Paper II*): the maximum PCO efficiency 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 for lignin and HA adsorption acidic media 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 observed also with the doped catalysts 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.

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 $W^{-1}h^{-1}$ for lignin instead of 2.5 and 3.5 mg $W^{-1}h^{-1}$ respectively for doped catalysts. Therefore, narrowing the band gap for photocatalysts does widen the effective absorbed light spectrum (PCO proceeds under visible light) although an increase in the PCO efficiency was not observed under experimental conditions.

3.8.2. Boron-doped catalyst

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 Figure 1, *Paper IV*). 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. The best adsorption of lignin and HA coincide with good PCO performance with studied pollutants, indicating the prevailing role on positively charged holes in oxidation of pollutants: OH-radicals seem to be unable to oxidise the pollutants for their zero adsorption at the catalyst surface.

3.8.3. Nitrogen-doped catalyst

In the experiments of lignin oxidation under visible irradiation with N-doped catalyst synthesized after Gandhe and Fernandes (2005) no degradation of lignin was observed in wide range of pH conditions, catalyst and lignin concentration (*Paper III*). The reason for this inefficiency was found in zero adsorption of lignin on the N-doped catalysts. In fact, the catalyst synthesized according to Gandhe and Fernandes (2005) did not even form the stable suspensions with lignin solutions like Degussa P25 did. The efficiency of the catalyst in respect of other compounds, i.e. MTBE and TBA, however, was noticeable (Klauson et al., 2008)

CONCLUSIONS

Process efficiency increased with increasing HA and lignin concentrations. Maximum efficiency, observed with aromatic compounds, was not achieved during PCO of HA and lignin within the experimental limits.

The highest PCO efficiency with Degussa P25 for both substances was observed in neutral and slightly basic media, despite the best adsorption in acidic media. This indicates that the PCO of HA and lignin may proceed mainly by the radical mechanism.

The addition of hydrogen peroxide to the solution of HA increased the PCO rate, although the apparent PCO rate did not change: hydrogen peroxide itself also oxidized HA in the reference sample. Photocatalytic oxidation of lignin benefited from introduction of hydrogen peroxide in acidic medium due to promoted OH-radical formation. Lignin was not oxidized with hydrogen peroxide in absence of the photocatalyst.

Ferrous ions did not increase the rate of HA PCO. However the addition of Fe^{2+} ions, up to 0.05mM, to the lignin solution leads to the drastic increase of PCO efficiency. A further increase in ferrous ion concentration results in a decrease in PCO efficiency of lignin.

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. The submersion depth is conveniently adjusted and held constant with the floating catalyst plate. 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 sulphur-doped photocatalyst, being active in visible light, yields to Degussa P25 in its efficiency.

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ABSTRACT

The present research considers aqueous photocatalytic oxidation of two common water pollutants: lignin and humic acids. The objective of the present research was to clarify the PCO potential in degradation of these pollutants under various experimental conditions.

The dual mechanism of PCO includes pollutants oxidation by hydroxyl radicals and positively charged holes. Due to this complex reaction mechanism the PCO performance depends on experimental parameters.

The study demonstrated that the performance of the photocatalytic oxidation of humis acids and lignin is influenced by the following factors: initial pollutants concentration, pH, the presence of hydroxyl radical promoters, such as hydrogen peroxide, and the addition of ferrous ions.

Special attention was paid to the design of the PCO reactors in order to achieve higher efficiency with the least expenses. Various modifications of titanium dioxide-based photocatalysts, such as Degussa P25 and anode-oxidised titanium in PCO of lignin and humic acids were tested. The titanium dioxide attached to a floating glass plate showed a superior PCO efficiency over the others and maximum PCO efficiency was observed under experimental conditions at the depth of 7 mm.

The experiments with the sulphur-, nitrogen- and boron-doped catalysts active in visible light were carried out to observe their effect on pollutants degradation. The sulphur-doped photocatalyst, being active in visible light, yields to Degussa P25 in its efficiency; N- and B-doped catalysts showed their inefficiency in HA and lignin oxidation.

KOKKUVÕTE

Käesolevas töös uuriti laialt levinud vee saasteainete, ligniini ja humiinhapete, fotokatalüütilist oksüdatsiooni (FKO). Uurimistöö eesmärgiks oli selgitada välja FKO võimalik efektiivsus nimetatud ainete lagundamisel erinevatel katsetingimustel.

FKO mehhanism seisneb saasteaine oksüdatsioonis nii hüdroksüülradikaalidega kui ka positiivselt laetud aukudega. Keerulise reaktsioonimehhanismi tõttu sõltub FKO protsess ning selle tulemus konkreetsetest katsetingimustest. Teostatud uuringud näitasid, et humiinhapete ja ligniini FKO protsessi efektiivsust mõjutavad järgmised tegurid: saasteaine algkontsentratsioon, pH, hüdroksüülradikaalide tekke promootorite, nagu näiteks vesinikperoksiidi, ning rauaioonide lisamine.

Erilist tähelepanu pöörati töös FKO reaktori kujundamisele saavutamaks kõrgemat efektiivsust väiksemate kuludega. Samuti uuriti humiinhapete ja ligniini FKO-d erinevate fotokatalüsaatori titaandioksiidi modifikatsioonide - Degussa P25 ja anood-oksüdeeritud titaandioksiidi - juuresolekul. FKO oli kõige efektiivsem, kui kasutati ujuvale klaasplaadile kantud titaandioksiidi, maksimaalne efektiivsus saavutati sellistes katsetingimustes, kus plaadile kantud katalüsaator oli uputatud 7 mm sügavusele vette.

Lisaks teostati FKO katsed, milles kasutati nähtavas valguses aktiivseid väävli, lämmastiku ja booriga dopeeritud katalüsaatoreid, selgitamaks titaandioksiidi dopeerimise mõju saasteainete lagundamisele. Väävliga dopeeritud fotokatalüsaatori kasutamisel oli FKO efektiivsus väiksem, kui Degussa P25 kasutamisel saavutatud efektiivsus; N- ja B-ga dopeeritud katalüsaatorid oli humiinainete ja ligniini fotokatalüütilisel lagundamisel ebaefektiivsed.

APPENDIX I

PUBLICATIONS

Paper I

Portjanskaja, E., Krichevskaya, M., Preis, S., Kallas, J. 2004. Photocatalytic oxidation of humic substances with TiO_2-coated glass micro-spheres.

The paper has been published in *Environmental Chemistry Letters*, 2(3), 123-127

Paper II

Portjanskaja, E., Preis, S., Kallas, J. 2006. Aqueous photocatalytic oxidation of lignin and humic substances with supported TiO_2.

The paper has been published in *International Journal of Photoenergy*, Vol. 2006, Article ID 85927, doi: 10.1155/IJP/2006/85927, 1-7.

Paper III

Portjanskaja, E., Preis, S. 2007. Aqueous photocatalytic oxidation of lignin: the influence of mineral admixtures.

The paper has been published in *International Journal of Photoenergy,* Vol. 2007, Article ID 76730, doi:10.1155/2007/76730, 1-7

Paper IV

Portjanskaja, E., Stepanova, K., Klauson, D., Preis, S. 2009. The influence of titanium dioxide modifications on photocatalytic oxidation of lignin and humic acids.

The paper has been published in *Catalysis Today*, in press, doi:10.1016/j.cattod.2008.12.021.

APPENDIX II

CURRICULUM VITAE

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perekonnanimi: Elina Portjanskaja
Sünniaeg ja -koht: 27.03.1981, Tallinn
Kodakondsus: Eesti

2. Kontaktandmed

Aadress: TTÜ, Ehitajate tee 5, Tallinn, 19086, Eesti
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E-posti aadress: elina.portjanskaja@mail.ee

3. Hariduskäik

Õppeasutus (nimetus lõpetamise ajal)	Lõpetamise aeg	Haridus (eriala/kraad)
Tallinna Tehnikaülikool	2005	Tehnikateaduste magistrikraad
Lappeenranna Tehnikaülikool	2005	Magistrikraad Keemiatehnoloogias
Tallinna Tehnikaülikool	2003	Tehnikateaduste bakalaureusekraad
Tallinna Õismäe Üldgümnaasium	1999	Keskharidus

4. Keelteoskus (alg-, kesk- või kõrgtase)

Keel	Tase
Eesti keel	Kõrgtase
Vene keel	Kõrgtase
Inglise keel	Kõrgtase

5. Täiendusõpe

Õppimise aeg	Täiendusõppe läbiviija nimetus
Juuli - November, 2003	Lappeenranta Tehnikaülikool, Soome
Juuli – Detsember, 2004	Lappeenranta Tehnikaülikool, Soome

6. Teenistuskäik

Töötamise aeg	Tööandja nimetus	Ametikoht
2008 - ...	OÜ Besur	Keemik-arendusjuht
2000 - 2008	Tallinna Tehnikaülikool, Keemiatehnika instituut	Lepinguline/Erakorraline teadur

7. Kaitstud lõputööd

Tehnikateaduste magistritöö: Humiinainetega ja ligniinidega saastatud vete oksüdatiivne töötlemine. Tallinna Tehnikaülikool. 2005. Juhendajad: Sergei Preis, Marina Kritševskaja

Magistritöö Keemiatehnoloogias: Photocatalytic oxidation of humic substances and lignin in aqueous solutions. Lappeenranta Tehnikaülikool. 2005. Juhendaja: Sergei Preis

Tehnikateaduste bakalaureusetöö: Humiinainete fotokatalüütiline oksüdeerimine vesilahustes. Tallinna Tehnikaülikool. 2003. Juhendajad: Sergei Preis, Marina Kritševskaja

CURRICULUM VITAE

1. Personal data

Name: Elina Portjanskaja
Date and place of birth: 27.03.1981, Tallinn
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2. Contact information

Address: TTÜ, Ehitajate tee 5, Tallinn, 19086, Estonia
Phone: +372 6202857
E-mail: elina.portjanskaja@mail.ee

3. Education

Educational institution	Graduation year	Education (field of study/degree)
Tallinn University of Technology	2005	MSc in Engineering
Lappeenranta University of Technology	2005	MSc in Chemical Engineering
Tallinn University of Technology	2003	BSc in Engineering
TÕÜG High School	1999	High school education

4. Language competence/skills (fluent, average, basic skills)

Language	Level
Estonian	Fluent
Russian	Fluent
English	Fluent

5. Special courses

Period	Educational or other organisation
July - November, 2003	Lappeenranta University of Technology, Finland
July – December, 2004	Lappeenranta University of Technology, Finland

6. Professional employment

Period	Organisation	Position
2008 - ...	OÜ Besur	Chemist-Product Development Manager
2000 - 2008	Tallinn University of Technology, Department of Chemical Engineering	Researcher

7. Theses Performed

MSc thesis in Engineering: Oxidation treatment of water containing humic substances and lignin. Tallinn University of Technology, 2005. Supervisors: Sergei Preis, Marina Krichevskaya

MSc thesis in Chemical Engineering: Photocatalytic oxidation of humic substances and lignin in aqueous solutions. Lappeenranta University of Technology. 2005. Supervisor: Sergei Preis

Bachelor's thesis: Photocatalytical Oxidation of Humic Substances in Aqueous Solutions. Tallinn University of Technology. 2003. Supervisors: Sergei Preis, Marina Krichevskaya

DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *CHEMISTRY AND CHEMICAL ENGINEERING*

1. **Endel Piiroja**. Oxidation and destruction of polyethylene. 1993.

2. **Meili Rei**. Lihatehnoloogia teaduslikud alused. Fundamentals of Food Technology. 1995.

3. **Meeme Põldme**. Phase transformations in hydrothermal sintering processing of phosphate rock. 1995.

4. **Kaia Tõnsuaadu**. Thermophosphates from Kovdor and Siilinjärvi apatites. 1995.

5. **Anu Hamburg**. The influence of food processing and storage on the N-nitrosamines formation and content in some Estonian foodstuffs. 1995.

6. **Ruth Kuldvee**. Computerized sampling in ion chromatography and in capillary electrophoresis. 1999.

7. **Külliki Varvas**. Enzymatic oxidation of arachidonic acid in the coral *Gersemia fruticosa*. 1999.

8. **Marina Kudrjašova**. Application of factor analysis to thermochromatography and promotion studies. 2000.

9. **Viia Lepane**. Characterization of aquatic humic substances by size exclusion chromatography and capillary electrophoresis. 2001.

10. **Andres Trikkel**. Estonian calcareous rocks and oil shale ash as sorbents for SO_2. 2001.

11. **Marina Kritševskaja**. Photocatalytic oxidation of organic pollutants in aqueous and gaseous phases. 2003.

12. **Inna Kamenev**. Aerobic bio-oxidation with ozonation in recalcitrant wastewater treatment. 2003.

13. **Janek Reinik**. Methods for purification of xylidine-polluted water. 2003.

14. **Andres Krumme**. Crystallisation behaviour of high density polyethylene blends with bimodal molar mass distribution. 2003.

15. **Anna Goi**. Advanced oxidation processes for water purification and soil remediation. 2005.

16. **Pille Meier**. Influence of aqueous solutions of organic substances on structure and properties of pinewood (*Pinus sylvestris*). 2007.

17. **Kristjan Kruusement**. Water conversion of oil shales and biomass. 2007.

18. **Niina Kulik**. The application of Fenton-based processes for wastewater and soil treatment. 2008.

19. **Raul Järviste**. The study of the changes of diesel fuel properties a its long term storage. 2008.

20. **Mai Uibu**. Abatement of CO_2 emissions in Estonian oil shale-based power production. 2008.

21. **Valeri Gorkunov**. Calcium-aluminothermal production of niobium and utilization of wastes. 2008.