PHOTOCATALYTIC OXIDATION OF POORLY BIODEGRADABLE ORGANIC COMPOUNDS PRESENT IN OVERBALANCED WATERS FROM MUNICIPAL WASTE LANDFILLS

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Abstract
The contribution deals with the study of photocatalytic oxidation as one of the stages of treatment of overbalanced wastewater from municipal landfills. This is either complete oxidation of organic compounds that are poorly biodegradable to carbon dioxide, water and inorganic salts or partial oxidation to products which are readily degradable in biological sewage treatment plants. Model wastewater containing humic substances and real sample of wastewater from the landfill Nasavrky were used in experiments. Anatase type TiO_2 photocatalyst and efficient LED UV radiation source with a very narrow range of wavelengths of $\lambda = 365 \pm 8.5$ nm were basic parts of the experimental set up. The results showed that by using this technology it is possible to reduce the content of non-biodegradable organic substances in wastewater. The problem remains in process efficiency at extremely high concentrations of pollutants.

Key words:
Landfill Leachate, Humic substances, Photocatalysis, Titanium Dioxide, Anatase

Introduction

Solid municipal waste landfill leachate is a complex multicomponent system whose composition is highly variable. It depends mainly on the composition of solid waste, on the type and method of waste disposal, on the internal structure and age of the landfill, on the extent and method of leachate recirculation, and the climatic conditions in a given location. Chemical substances contained in landfill leachate can be toxic and environmentally dangerous, and their combinations can also lower effectiveness of technologies used potentially for leachate treatment. (Malý 2002).

Leachate discharge into the watercourses is strictly limited by European legislation. The main focus of landfill leachate treatment is to reduce effluent BOD5 values (which also leads to associated COD reduction). Furthermore, it is mostly also needed to reduce overall salinity, total nitrogen content and heavy metals.

Leachate treatment generally combines simple mechanical treatment (mixing, sedimentation, filtration) with chemical, physical and biological purification. If possible, the leachate recycling back to the immature areas of the landfill, is one of the first treatment steps. Another option is to treat leachate together with conventional municipal sewage. Only then is realized separate treatment utilizing various combinations of standard and lesser-known technologies. Within potential technologies biological purification is preferred as the first step. This removes a significant part of organic substances. Nevertheless, non-biodegradable organic compounds, such as humic compounds, remain in leachate. These non-biodegradable organic compounds dominantly cause high BOD values of treated water and simultaneously are able to reduce the efficiency of many advanced separation processes. To remove these compounds, which are typically present in older mature landfill, the coagulation, flocculation, precipitation, adsorption and flotation are commonly used today. (Pivokonský, Pivokonská, Bubáková, 2010). The problem is, however, high residual concentration of pollutants (both organic and inorganic) in output streams after the implementation of these processes. This means that the processes are not sufficient for complete leachate cleaning. Thus new technologies, such as membrane separation (mostly hybrid microfiltration, reverse osmosis and/or electrodialysis) are being tested and developed. (Li, Zhou, Hua, 2010)

Reverse osmosis permeate can satisfy even the most strict quality demands on discharged water. The use of reverse osmosis is, however, limited by particularly high operating pressure (up to 100 bar). This operating pressure has to exceed the osmotic pressure of treated wastewater, which is highly saline. The use of reverse osmosis is also limited by membrane fouling by some (mainly non-biodegradable organic) substances. Similar membrane fouling is a negative side effect also when using the electrodialysis which is particularly suitable for the removal of ionic inorganic compounds from the leachate. Hybrid membrane microfiltration is a combination of microfiltration (with separation in tenths of micrometer) and adsorption on active carbon (or zeolite, bentonite, titanium dioxide or other). Although microfiltration own separates only solid particles and fine colloid compounds, large portion of soluble organic compounds and heavy metal ions can be bound to sorbent which is also retained by microfiltration membrane. (Palatý 2012).

It appears, that for non-biodegradable organic compounds removal may be advantageous to include alternatively advanced oxidation processes (AOPs) as a part of complex landfill leachate treatment technology. AOPs are radical processes based on production and reaction of hydroxyl radicals. These are highly reactive and can react with any compound present in landfill leachate which is capable of oxidation. Hydroxyl radical can be generated in many ways, which makes advanced oxidation processes highly convenient for wastewater treatment. (Linsebigler, Lu, Yates Jr. 1995)
Because of new developments in the field of efficient UV sources (LED lamps), it may be interesting to study organic compound photocatalytic oxidation with UV light and titanium dioxide as catalyst. The process can be run either to complete oxidation (to carbon dioxide, water, and inorganic salts) or partially (to smaller organic compounds which can be recycled, and degraded biologically). (Mills, Raymont, 2013).

This contribution therefore focuses on experimental study of photocatalytic oxidation wastewaters which can be produced by solid municipal waste landfill leachate treatment technology.

Experimental

For modeling of wastewater with high content of humic acids (typical for leachate from old matured landfills) was used potassium humate Dralig (Humatex a.s., CR). It is a mixture of potassium salts of humic and fulvic acids produced from natural oxyhumolite. In 25 l of deionized water was dissolved 12.5 g of solid powdered substance. From the resulting solution were subsequently removed undissolved portions using microfiltration bundle of hollow polypropylene fibers P-50 (Zena, CR) with a pore size of 0.1 x 0.5 microns. The value of chemical oxygen demand (COD) of the model water obtained was 36.5 mg/l and the value of total organic carbon (TOC) was 15.72 mg/l.

For experiments with real leachate the wastewater from Nasavrky municipal landfill (Czech Republic) was used. A sample of leachate was taken from the retention tank with capacity of about 1700 m^3. In the technology the retention tank is used to collect leachate from the entire landfill. Basic data on the composition of the leachate sample are summarized in Table 1.

Tab. 1: Selected parameters of waste leachate from Nasavrky landfill

Parameter	Unit	Used sample value	Maximum acceptable value for watercourse discharge
Conductivity	mS/cm	10.99	
pH		7.94	6-8
COD	mg/l	708	30
BOD	mg/l	-	15
TSS	g/l	6.33	
Undissolved solids	mg/l	-	12
Total carbon	mg/l	1125.6	
TOC	mg/l	395.2	
Anorganic carbon	mg/l	770.4	
Total nitrogen	mg/l	277	
Amonium nitrogen	mg/l	-	18
Sodium	mg/l	1100	
Potasium	mg/l	960	

UV Inspector 711 LED lamp (made by Helling, Germany) was used as source of UV radiation. This lamp was originally designed for non-destructive material testing and crime scene investigation. Peak wavelength is declared by manufacturer as 365 nm (± 8.5). Radiant flux in the considered wavelength region was determined using YK-35UV meter (Lutron, CR) as 1.23 W.

As a catalyst anatase titanium dioxide, type AV-01, produced by Precheza Company (CR) was used. The particle size was determined by laser diffraction method, using Malver Mastersizer 2000 (UK). At pH = 7 was found particle diameter ranging from 0.08 to 3.30 microns with average value equal to 0.301 micron. Photocatalyst particle morphology was determined using JEOL-JSM 5600LV scanning electron microscope(Japan) (Ditrich et al., 2014).

Wastewater dispersion with catalyst concentration of 1g/l was used in all experiments. The dispersion was prepared by intensive dispergation (mixing) of powdered catalyst into water (model or real leachate) with simultaneous action of ultrasound (Kraintek, SK) to enhance dispergation. After 30 min dispergation the UV lamp was switched on. Reaction mixture samples were taken I regular intervals and analyzed for COD, TOC and absorbance (200 nm). For measurements DR 6000 spectrophotometer (Hach-Lange, Germany) was used in combination with cuvette COD tests LCI 500 and LCI 400. TOC was determined using FORMAX TOC/TN Analyzer (Skalar, NL).

Experimental results and discussion

The results of experiments are summarized in Figs 1 to 3 as ratios of actual and initial values of COD, TOC and absorbance at 200 nm. In Fig.1 are depicted the results of experimental study of the photocatalytic degradation of model leachate wastewater containing humic compounds. It is obvious, that with time there was a decline of monitored parameters. The highest decline was recorded for absorbance. This means, that there was a destruction of the functional groups characteristic for humic substances because these groups have absorption maxima around wavelength of 200nm. The TOC value is the measure of organic carbon presence. The results show, that after 3 hours of the experiment there was a 60% decline of organically bound carbon content (from 15.72 mg/l to 6.08 mg/l). These carbon compounds were oxidized by hydroxyl radicals to carbon dioxide. The COD decline (from 36.5 mg/l to 12.5 mg/l) follows the course of the TOC decrease, suggesting that in this model system do not occur except the organic carbon any other oxidizable substances.

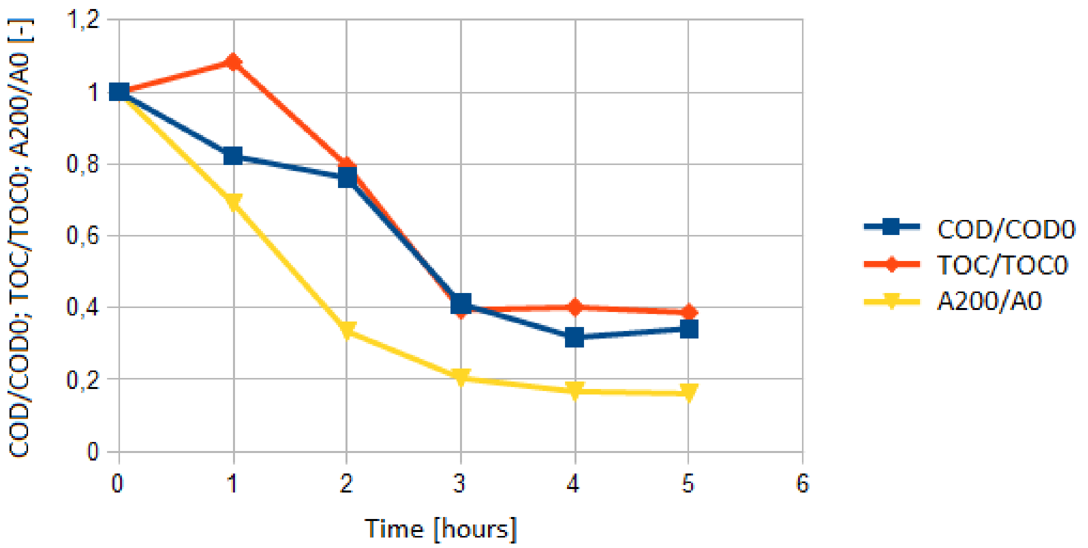

Fig.1: Dependences of COD/COD$_0$, TOC/TOC$_0$ and A200/A200$_0$ ratios on time. Photocatalytic oxidation of humic substances with initial concentration 168 mg/l, reaction volume 400ml, UV Inspector 711 lamp, catalyst concentration 1 g/l

Fig. 2 shows similar dependences for photocatalytic oxidation of diluted real landfill leachate wastewater. Dilution was selected in proportion one part of the leachate to nineteen parts of demineralized water. Using this dilution ratio, the COD and TOC were of comparable order of magnitude with model wastewater. From the figure it is clear that there was again a reduction of organic material content with time. The value of COD dropped from an initial value of 51.5 mg/l to 15.8 mg/l and TOC from 22.56 mg/l to 13.32 mg/l. The reduction of COD was higher and reached almost 75%. It was probably caused by the presence of other oxidizable substances in a complicated system of real leachate wastewater. The TOC decline was only 40%. The value of absorbance at 200 nm remained during the experiment practically unchanged. The reason for this behavior can be extremely high amounts of organic and inorganic carbon content (see Table 1). For example, carbonates and bicarbonates contained also exhibit very high absorbance at wavelengths around 200 nm.

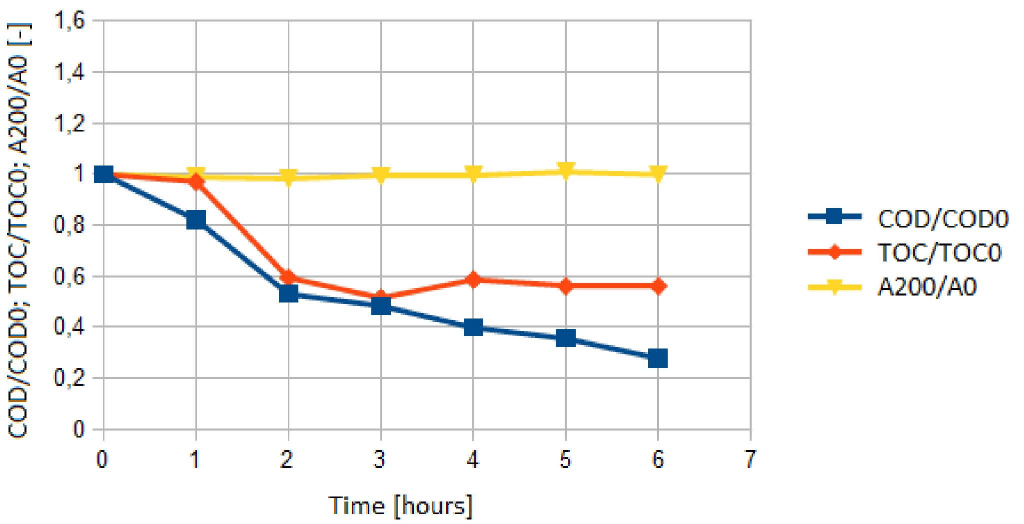

Fig. 2: Dependences of COD/COD$_0$, TOC/TOC$_0$ and A200/A200$_0$ ratios on time. Photocatalytic oxidation of diluted real landfill leachate (dilution 1:19), reaction volume 400ml, UV Inspector 711 lamp, catalyst concentration 1 g/l

Results obtained by photocatalytic oxidation of undiluted landfill leachate are summarized in Fig.3.

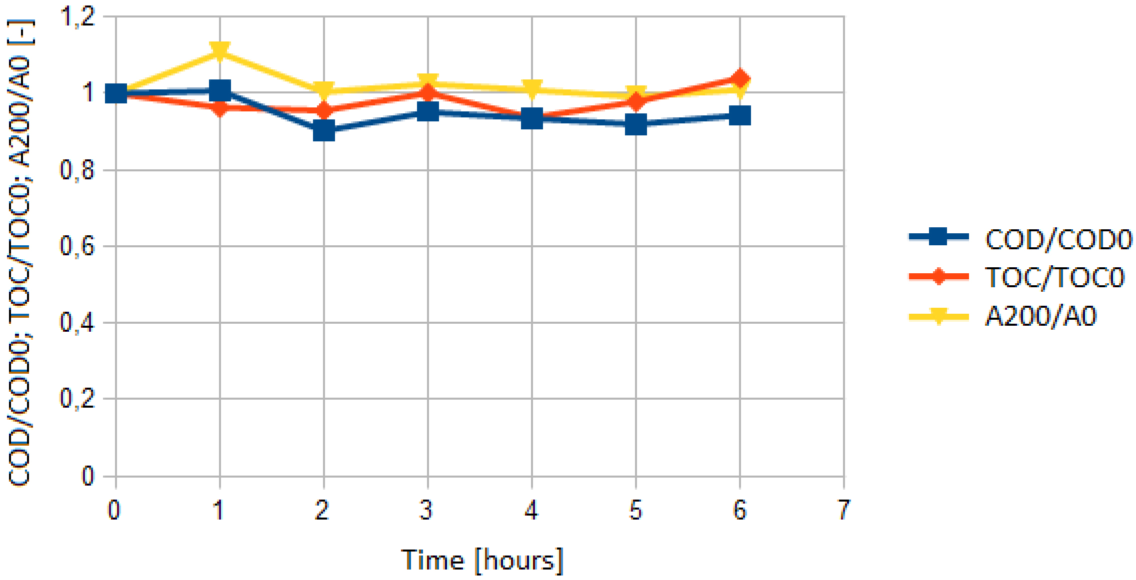

Fig. 3: Dependences of COD/COD_0, TOC/TOC_0 and $A200/A200_0$ ratios on time. Photocatalytic oxidation of undiluted landfill leachate, reaction volume 400ml, UV Inspector 711 lamp, catalyst concentration 1 g/l

Figure 3 shows that the values of COD, TOC, and absorbance remained constant during the whole experiment (6 hrs). Minor variations may be due to incomplete sampling and analysis scatter. During the experiment, however, it was visually detected partial decolorization of the reaction mixture. Subsequently, there were also detected insignificant changes in the absorbance of samples at wavelengths between 400 and 600 nm. The course of photocatalytic reaction was not influenced neither by aeration of the reaction volume. In total, we can say that the experimental arrangement used in this experiment was not appropriate for real landfill leachate containing high amounts of organic compounds - LED lamp output was too low.

Conclusions

The UV-A LED lamp used in experiments is source of ultraviolet radiation with wavelength suitable for anatase photocatalyst valence electron excitation. The lamp produces radiation with fairly narrow range of wavelengths; doesn't produce ozone and potentially has high energy efficiency. Experiments with model water containing humic substances clearly show that these nonbiodegradable compounds can be removed by photocatalytic oxidation. The oxidation transforms humic compounds into carbon dioxide, water and inorganic salts. Experiments with real landfill leachate show, that radiant flux of UV-lamp used is too low to be used for undiluted landfill leachates containing high amount of humic substances. More experiments are needed to determine process limits and optimal reaction conditions. For these experiments, LED lamp with higher light power output will be needed.

Acknowledgement

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