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RECYCLING OF TEXTILE WASTEWATERS TREATED WITH VARIOUS COMBINATIONS OF ADVANCED OXIDATION PROCESSES (AOP)

RECIKLIRANJE TEKSTILNIH ODPADNIH VODA OČIŠČENIH Z RAZLIČNIMI KOMBINACIJAMI NAPREDNIH OKSIDACIJSKIH POSTOPKOV (AOP)

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Abstract

Advanced oxidation processes (AOPs) are widely used for treatment of wastewaters containing recalcitrant organic compounds from industrial and municipal wastewater; many advantages over other technologies have been found and good treatment results have been obtained so far. Approaches which reduce fresh water consumption are especially important for regions with shortage in fresh water resources and in high water-consuming industries. Within AOP4Water (a multinational project funded under the CORNET programme), combinations of different AOP methods are being tested with the final aim to enable cost-efficient reuse of AOP-treated effluents from textile industry. The key to wastewater reuse lies in increasing the efficiency of AOP treatment that ensures the required water quality and decreasing operational costs. In the present study a series of experiments was performed with real textile industry effluents using a single AOP method as well as combinations. Following AOP treatments were applied: ozone (O3); O3+ UV irradiation (UV); O3 + hydrogen peroxide (H2O2); and O3 + H2O2 + UV. The most effective combination for colour and COD removal was O3 + H2O2 + UV with 75% - 86% of colour removal and 15% of COD removal.

Keywords: advanced oxidation processes (AOPs), hydrogen peroxide (H2O2), ozonation (O3), UV irradiation, textile effluents, water reuse.

Izvleček

Napredni oksidacijski procesi (AOPs) se pogosto uporabljajo za čiščenje odpadnih voda iz industrije in komunalnih odpadnih voda, ki vsebujejo težko razgradljive organske spojine. Ti postopki imajo veliko prednosti pred ostalimi tehnologijami čiščenja odpadnih voda in so do sedaj pokazali zelo dobre rezultate.

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Pristopi, ki zmanjšujejo porabo sveže vode, so še posebej pomembni v regijah s pomanjkanjem vodnih virov in v industrijskih panogah z visoko porabo vode. V okviru projekta AOP4Water (mednarodni projekt, financiran v okviru programa CORNET) smo preizkusili kombinacije različnih AOP postopkov s ciljem, da bi omogočili stroškovno upravičeno ponovno uporabo AOP očiščenih odpadnih voda iz tekstilne industrije. Glavni ključ do ponovne uporabe leži v povečanju učinkovitosti AOP čiščenja, ki zagotavlja potrebno kakovost vode in zmanjšuje operativne stroške. V predstavljeni raziskavi je bila narejena serija poskusov z odpadno vodo iz tekstilne industrije z uporabo posameznih AOP postopkov, kot tudi njihovih kombinacij. Izvedli smo naslednje poskuse: ozon (O3); O3+ UV sevanje (UV); O3 + vodikov peroksid (H2O2); O3 + H2O2 + UV. Najbolj učinkovita kombinacija pri odstranitvi barve in KPK je bila O3 + H2O2 + UV s 75 % - 86 % odstranitvijo barve in 15 % odstranitvijo KPK.

Ključne besede: napredni oksidacijski postopki (AOPs), vodikov peroksid (H2O2), ozonacija (O3), UV sevanje, tekstilna odpadna voda, ponovna uporaba vode.

1. Introduction

The textile industry is one of the largest consumers of water in the world, and consequently, one of the largest producers of wastewater. An important feature of the textile factories is the use of different types of dyes with multiple colour combinations, resulting in high fluctuations in wastewater composition. Dyes have a complex aromatic and polymeric structure, they are highly soluble in water and are at the same time often toxic and non-biodegradable, since they were intentionally designed to resist degradation. Thus, conventional biological wastewater treatment methods are ineffective in their removal (Wu et al., 2008). The main environmental concern is therefore the amount of wastewater discharged and the chemical (environmental) load it carries (Bulc and Ojstršek, 2008; Balabanič et al., 2012). The textile wastewater effluent discharged into a natural environment represents an aesthetic and environmental problem. Colouration is correlated with pollution and light absorption by dye molecules in the body of water; it interferes with the aquatic biological process like photosynthesis due to reduced light penetration (Alinsafi et al., 2006), and has even more severe consequences, such as toxicity.

The practise of treating textile effluents in municipal wastewater treatment plants (WWTPs) has shown that an industrial-scale discolouration system is needed prior to discharge into sewage works. Regarding the location there are two possibilities where the textile industry effluent can be treated in terms of colour removal. The first one foresees the treatment within the industrial grounds, where wastewater is either first discoloured and then discharged to the sewage, or it is treated to the point that allows its partial or full reuse in the technological process. The second possibility places the discolouration step before or after the treatment process applied at the municipal WWTP (Pearce et al., 2003; Mahne, 2012).

There are currently several different treatment methods applied to abate the textile wastewater pollution; they can be divided into: i) physical and physico-chemical methods, ii) biological approaches and iii) chemical methods. The most prominent drawback of most of the physico-chemical methods is in secondary waste production (sludge), membrane fouling and costly adsorbent regeneration. Biological treatment methods on the other hand are considered to be inherently environmentally friendly and cheaper compared to chemical ones (Harrelkas et al., 2008), but there are some limitations, since it is not certain whether all aromatic amines in dyes can be degraded, and complete removal of other components is also questionable (van der Zee and Villaverde, 2005). Due to environmental implications and limitations of each of the above treatment methods, more and more research is focused on combining one of the biological treatment methods with other techniques such as advanced oxidation processes (AOPs) to ensure a cost-effective and pollution-removing technology as the best approach to pollution abatement (Hai et al., 2007; Mahne, 2012). Because of the poor biodegradability and sometimes even toxicity of the textile wastewater components, an advanced treatment technology is necessary. Especially if reuse of treated wastewater is the objective, extensive removal of organic contents as well as almost complete decolourization are required. The use of AOPs for heavily (bio)degradable components in wastewater is important because AOPs can degrade complex chemical structures to more easily degradable molecules, which can then be treated in a conventional and less expensive way, e.g. biological WWTP.

The project AOP4Water under Cornet programme (www.cornet-aop4water.eu) aims at making new water sources available for high water volume consuming industries like pulp and paper and textile sectors, by (re)using AOP-treated effluents from textile, pulp and paper and food industries as well as municipal waste water. Key to the (re-)use is to improve the efficiency of AOP-treatment to ensure optimum water quality, and to show the possible use of treated waters. Achievable water quality needed for (re-)use will be produced by combination of AOP and biological treatment. For the experimental part, wastewater will be provided by textile industries, paper mills, food industries and municipalities; treated water will then be used in textile factories and paper mills. The textile factories in Slovenia are mostly connected to public sewer networks which are terminated by central treatment facilities and economic viability of installing treatment plants for efficient wastewater pre-treatment is questionable. It is mandatory to achieve the required criteria for discharge into public sewers. More efficient treatment is only justified when it is cost-efficient. Economic viability is assessed in terms of costs, which consist of expenses for fresh water supply, environmental taxes, charges for wastewater collection and treatment and expenses of effective treatment within the factories (Drev et al., 2012). With reuse of AOP-treated wastewater significant cost reductions could be achieved.

The aim of the present study was to test different combinations of AOPs for treatment of raw textile wastewater with the aim to establish which combination is the most efficient for colour and COD removal. After this is achieved, biological treatment will be applied to increase the treated wastewater quality for reuse in textile and (or) paper industry.

2. Material and methods

Experiments were performed on raw wastewater from a textile factory located in Slovenia, which produces 143 tons of socks and stockings per year (data from 2009) and where cotton and polyester fabrics are dyed using reactive dyes. Annual water consumption is 69.9 x 10^6 m^3 (data from 2009). Cooling and neutralization of the wastewater is performed on-site in an egalisation pool and then discharged into a public sewer system.

Wastewater was collected after egalisation and before discharge into the public sewer system. After transportation to the lab, wastewater was filtered with black ribbon filters (Sartorius-stedim, Grade 388, 10-15 µm, basis weight 84 g/m^2) to remove solid compounds and stored in a cooling chamber at 4 °C for maximum 14 days. The experiments were carried out at a lab-scale AOP pilot treatment plant (see Fig. 1) operating in batch mode.

The following AOP experiments were performed: a) ozone (O_3); b) O_3 + ultra violet irradiation (UV); c) O_3 + hydrogen peroxide (H_2O_2); d) O_3 + H_2O_2 + UV.

In the case of experiments with H_2O_2, 30% H_2O_2 was added directly into the wastewater tank at the beginning of the experiments. The amount of added H_2O_2 was calculated according to Kim et al. (1997) and was for our wastewater typically 25 mL of 30% H_2O_2.

2.1 Pilot plant design

The pilot plant (see Fig. 1) consists of a plastic wastewater tank, a water pump (Iwaki Magnet Pump, Iwaki co. LTD), an air pump (KNF Neuberger), an air dryer module (Lufttrockner module LTM 110-60, AquaCare), an O_3 generator

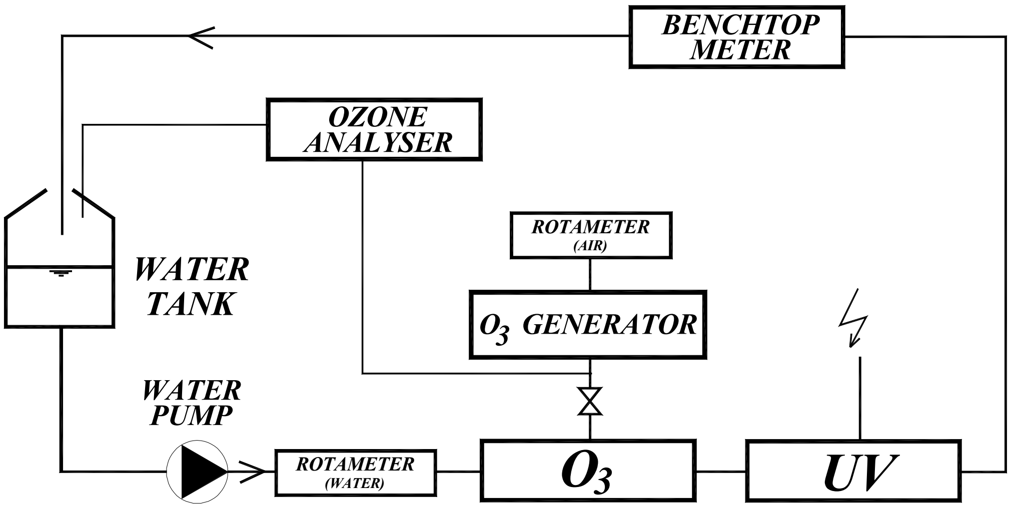

***Figure 1:** Diagram of the laboratory AOP pilot treatment plant.*
***Slika 1:** Shema pilotne laboratorijske AOP čistilne naprave.*

(BasiTech III, AquaCare, 500 mg/h), an O_3 reactor (Ozonreaktor OZR 75, AquaCare), an O_3 analyser (BMT 964 C, BMT Messetechnik), a rotameter (GEMÜ 55/21/14), a benchtop meter (multi-parameter analyser C3040, Consort) and a UV lamp (Sterilight copper, Viqua, 12 W). The volume of the wastewater tank is 2.2 L, while the total volume of the pilot plant is 4 L. O_3 is produced from dried air with maximum O_3 production of 500 mg/h and flow rate of the gas stream 60 L/h. In the O_3 reactor, the O_3-containing gas is led over a frit and rises through the water to be ozonised. Part of the O_3 contained in the gas diffuses into the water, is dissolved and reacts with the substances in the water. O_3 concentration is measured with O_3 analyser constantly shifting between two measuring sites: input (O_3 generator) and output (inflow into the water tank), for 1 minute and 30 minutes, respectively. Measuring O_3 concentration in feed- and off-gas as well as gas and water flow rates serve to balance the O_3 dosage introduced into the sample. The sample is led through the Benchtop meter determining the pH, redox potential, temperature and oxygen content in water.

The system was operating in a continuous mode with a flow rate of the water stream 60 L/h maintained with the rotameter, but the residence time was increased with the wastewater returning back to the beginning of the system. Consequently the system was operating in a batch mode with the water being complete mixed.

2.2 Chemical analyses

Analyses were performed in raw and filtered wastewater for pH, electric conductivity (EC), colour at 436 nm, 525 nm and 620 nm, chemical oxygen demand (COD), biochemical oxygen demand in 5 days (BOD_5) and total suspended solids (TSS). pH and EC were measured with Multimeter HACH HQ40d, colour was measured with portable spectrophotometer (Hach DR 2800), COD was analyzed according to ISO 6060, BOD_5 according to SIST EN 1899-2 and TSS according to SIST ISO 11923.

During the AOP experiments, a 10 mL sample was taken from the circulation loop in the batch system at regular time intervals of 40 minutes (10 cycles) for COD and colour measurements at 436 nm, 525 nm and 620 nm. For each experiment 7 samples were taken. Before each experiment COD and colour were measured to obtain the initial state.

3. Results and discussion

3.1 Chemical analyses

The results of chemical parameters for raw and filtered textile wastewater (black ribbon filters, see Material and Methods) are presented in Table 1. In raw textile wastewater COD, BOD_5, EC and colour are quite high, which is in accordance with findings of other authors (Čvan, 2004; Mahne, 2012). It should be emphasized that textile wastewater is characterized mainly by high organic content and high salinity. Filtration had no effect on pH, EC and BOD_5, while reduction of COD, colour and especially TSS was noticed. Absorbance spectrum of the investigated textile wastewater reveals a high absorbance at 436 nm, most probably due to the aromatic compounds of dyes in the wastewater (Vilar et al., 2011).

Table 1: *Results of chemical analyses of raw and filtered textile wastewater.*
Preglednica 1: *Rezultati kemijskih analiz surove in filtrirane tekstilne odpadne vode.*

Parameter	Unit	Raw wastewater	Filtered wastewater
pH	-	7.96	7.96
EC	mS/cm	2.65	2.65
Colour			
436	m^{-1}	39.4	36.8
525	m^{-1}	35.2	30.8
620	m^{-1}	29.1	23.6
COD	mg/L	1001	978
BOD_5	mg/L	200	200
TSS	mg/L	48	0

3.2 AOP experiments – colour removal

The most efficient method for colour reduction was the combination of O_3 + H_2O_2 + UV (Figure 5) with the reduction of colour by 75.3% (at 436 nm), 83.3% (at 525 nm) and 86.3% (at 620 nm). The treatments of textile wastewater with O_3 alone and with combinations of O_3+ UV and O_3 + H_2O_2 were less effective for colour removal (Figures 2-4). The treatment combination of O_3 + H_2O_2 was the least effective for colour removal (Figure 4). If we compare O_3 and O_3 + UV treatment, UV light did not contribute to better discolouration.

Figures 2-5 present the average discolourization efficiency of the textile wastewater as a function of the AOPs duration. Colour removal within first 80 min was significant. The literature shows that COD and colour removal efficiencies are mainly dependent on dye/organic matter contents, pH, temperature, O_3 transfer to the wastewater solution, and other factors (Kos and Perkowski, 2003; Muhammad et al., 2008).

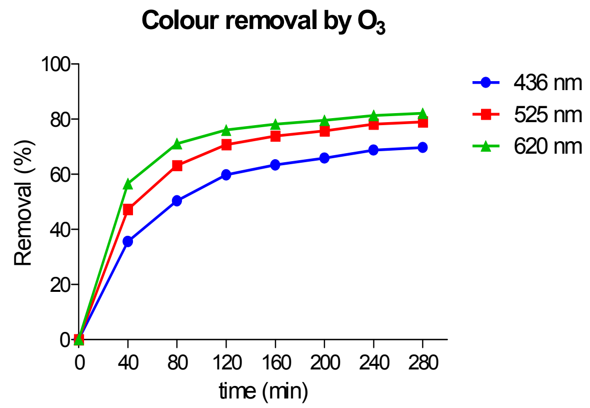

Figure 2: *Average colour removal efficiency at different absorbances for O_3 treatment, n=6.*

Slika 2: *Povprečna učinkovitost odstranitve barve pri različnih absorbancah za poskus z O_3, n=6.*

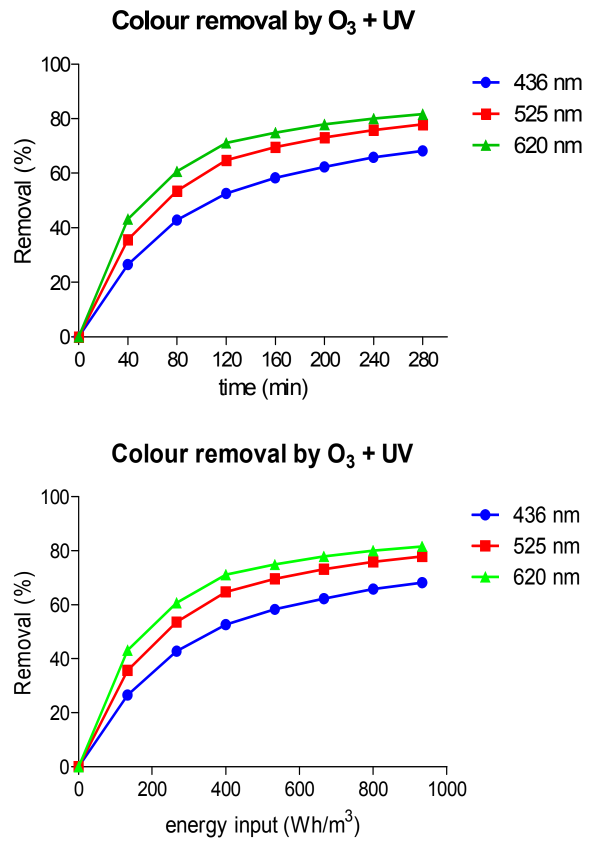

Figure 3: *Average colour removal efficiency at different absorbances for O_3 + UV treatment combination, n=6.*

Slika 3: *Poprečna učinkovitost odstranitve barve pri različnih absorbancah za poskus s kombinacijo O_3 + UV, n=6.*

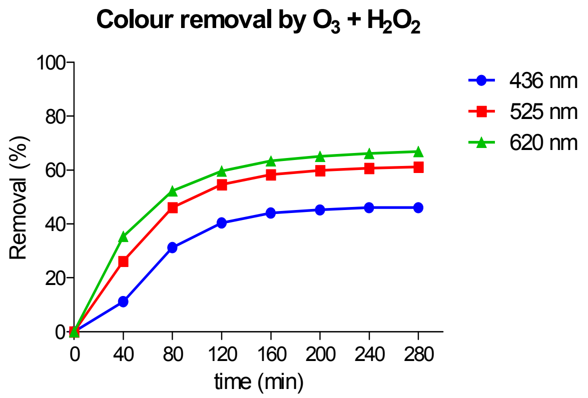

Figure 4: *Average colour removal efficiency at different absorbances for O_3 + H_2O_2 treatment combination, n=6.*

Slika 4: *Povprečna učinkovitost odstranitve barve pri različnih absorbancah za poskus s kombinacijo O_3 + H_2O_2, n=6.*

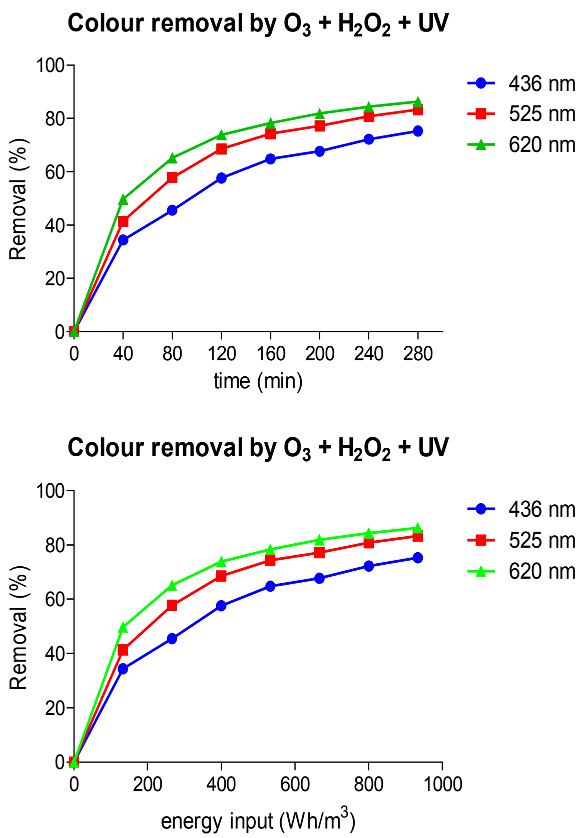

Figure 5: *Average colour removal efficiency at different absorbances for O_3 + H_2O_2 + UV treatment combination, n=6.*

Slika 5: *Povprečna učinkovitost odstranitve barve pri različnih absorbancah za poskus s kombinacijo O_3 + H_2O_2 + UV, n=6.*

3.3 AOP experiments – COD removal

COD is a common parameter used for the characterization of organic matter present in textile wastewaters (Pearce et al., 2003); it depends on the dies used and the type of textile produced. Limited COD removal was obtained in all AOP treatment cases. After 280 min of AOP treatments, COD reduction from 12% (O_3 + H_2O_2) to 15% (O_3 + H_2O_2 + UV) was achieved (Figures 6-9) indicating that combination of O_3 with H_2O_2 and UV is the most efficient in COD reduction. Nevertheless, the differences in COD reduction between AOP combinations applied were not significant indicating that combining O_3 treatment with either H_2O_2 or UV or both does not bring the expected improvement in treatment efficiency.

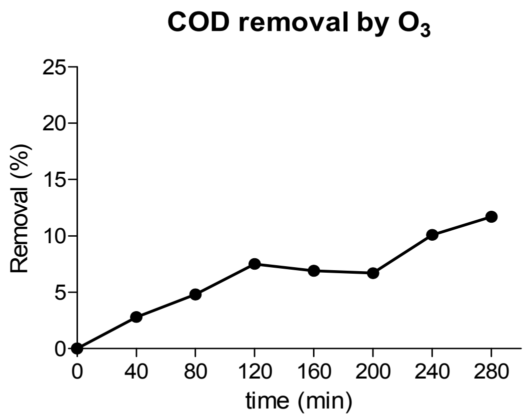

Figure 6: *Average COD removal efficiency for O_3 treatment, n=6.*

Slika 6: *Povprečna učinkovitost odstranitve KPK za poskus z O_3, n=6.*

Since ozonation represents a significant cost, instead of ultimate degradation to complete mineralisation of organic compounds, only partial oxidation down to more readily biodegradable compounds is of (financial) interest. After partial oxidation by AOPs, microorganisms can be used in a post-treatment process for complete mineralization of contaminants in the water matrix. Therefore, the use of chemical oxidation combined (followed) by microbiological degradation may provide more economical and effective process than oxidation or biodegradation alone. In the study presented, dyes and organic matter were not completely destroyed during the AOPs treatments

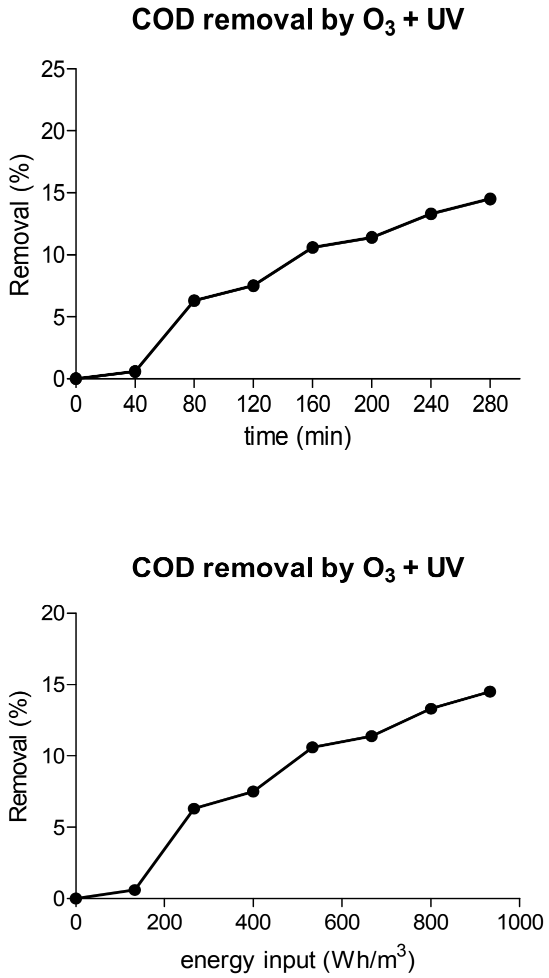

Figure 7: *Average COD removal efficiency for O_3 + UV treatment combination, n=6.*

Slika 7: *Povprečna učinkovitost odstranitve KPK za poskus s kombinacijo O_3 + UV_3, n=6.*

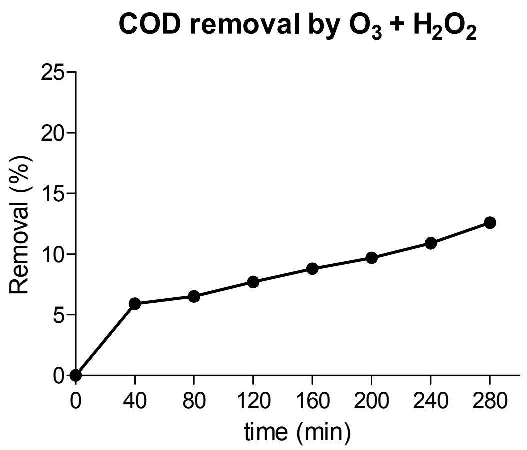

Figure 8: *Average COD removal efficiency for O_3 + H_2O_2 treatment combination, n=6.*

Slika 8: *Povprečna učinkovitost odstranitve KPK za poskus s kombinacijo O_3 + H_2O_2, n=6.*

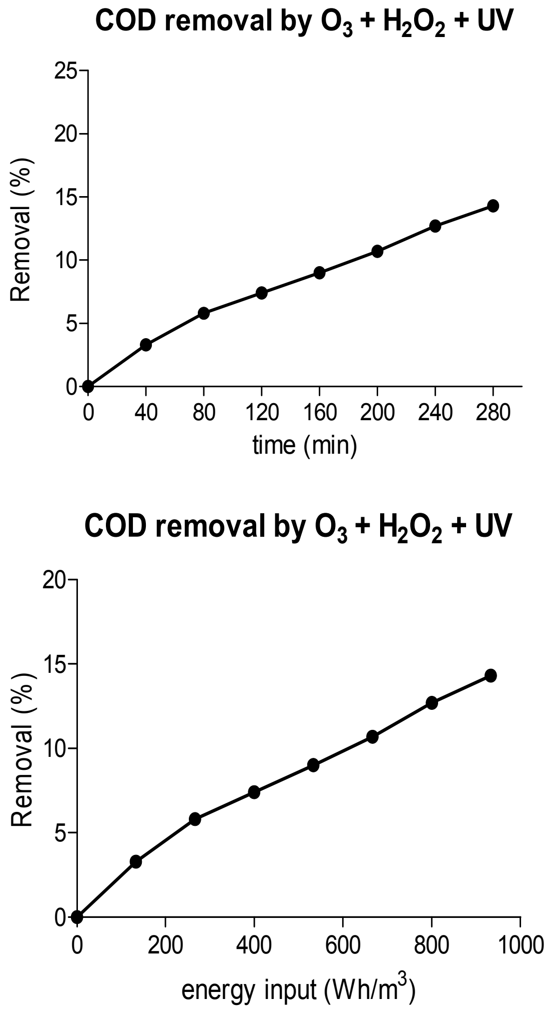

Figure 9: *Average COD removal efficiency for O_3 + H_2O_2 + UV treatment combination, n=6.*

Slika 9: *Povprečna učinkovitost odstranitve KPK za poskus s kombinacijo O_3 + H_2O_2 + UV, n=6.*

used, thus a post-treatment with microbiological degradation is essential. It should also be taken into account that the low COD removal may not mean low efficiency of the AOPs regarding oxidation or destruction of heavily (bio)degradable organic compounds into more readily (bio)degradable compounds. Further tests concatenating AOPs with biodegradation in comparison to biodegradation alone would reveal the real efficiency of the used AOPs for removal of organic compounds from the treated wastewater.

4. Conclusions

The presented pilot-scale AOP treatment of raw textile wastewater was designed to evaluate treatment efficiencies of different AOP combinations for colour and COD removal. The results indicated that the most efficient colour removal was achieved with the combination of O_3 treatment with H_2O_2 and UV with the average efficiencies of colour removal of 75% (absorbance at 436 nm), 83% (absorbance at 525 nm) and 86% (absorbance at 620 nm) after 280 min of water recirculation in the batch reactor system. For COD reduction we noticed no significant differences between the four AOP combinations tested, the average COD reduction varied between 12% (O_3 + H_2O_2) and 15% (O_3 + H_2O_2 + UV). Further tests, upgrading AOPs with subsequent biodegradation will show the real value of the implemented technology to enable a cost-effective reuse of the treated wastewater. Economic viability consist of expenses for fresh water supply, environmental taxes, charges for wastewater collection and wastewater treatment and expenses of effective treatment within the factories. With onsite treatment and reuse of treated wastewater, expenses for fresh water supply, environmental taxes and charges for wastewater collection and treatment could be considerably lower, enabling cost efficiency of the implemented treatment technology.

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References

Alinsafi A., da Motta M., le Bonte S., Pons, M.N., Benhammou A. (2006). Effect of variability on the treatment of textile dyeing wastewater by activated sludge, *Dyes and Pigments* **69**, 31–39.

Balabanič D., Hermosilla D., Merayo N., Krivograd Klemenčič A., Blanco Á. (2012). Comparison of different wastewater treatments for removal of selected endocrine-disruptors from paper mill wastewaters. *Journal of Environmental Science and Health, Part A* **47**, 1350–1363.

Bulc T.G., Ojstršek A. (2008). The use of constructed wetland for dye-rich textile wastewater treatment. *Journal of Hazardous Materials* **155**, 76–82.

Čvan S. (2004). Ekološki in ekonomski vidiki zmanjšanja onesnaženosti odpadnih vod tekstilne industrije (Ecological and economics aspects for pollution reduction of textile wastewater). Master thesis. Univerza v Mariboru, FS, 88 p. (in Slovenian).

Drev D., Krivograd Klemenčič A., Panjan J., Kompare B. (2012). Raziskava onesnaženosti odpadnih voda v slovenski tekstilni industriji in ekonomska upravičenost učinkovitega čiščenja. *Organizacija* **45**, A90–A100.

Hai F.I., Yamamoto K., Fukushi K. (2007). Hybrid treatment systems for dye wastewater, *Critical Reviews in Environmental Science and Technology* **37**, 315–377.

Harrelkas F., Paulo A., Alves M.M., El Khadir L., Zahraa O., Pons M.N., van der Zee F.P., (2008). Photocatalytic and combined anaerobic-photocatalytic treatment of textile dyes. *Chemosphere* **72**, 1816–1822.

Kim, S.M., Geissen, S.U., Vogelpohl, A. (1997) Landfill leachate treatment by a photoassisted Fenton reaction, *Water Science and Technology* **35 (4),** 239–248.

Kos L., Perkowski J. (2003). Decolouration of real textile wastewater with advanced oxidation processes, *Fibres and Textiles in East Europe* **11 (4)**, 81–85.

Mahne D. (2012). Combination of constructed wetland and TiO_2 photocatalysis for textile wastewater treatment. Unpublished Doctoral Thesis. Univerza v Novi Gorici, podiplomski študij, 213 p.

Muhammad A., Shafeeq A., Butt M.A., Rizvi Z.H., Chughtai M.A., Rehman S. (2008). Decolorization and removal of COD and BOD from raw and biotreated textile dye bath effluent through advanced oxidation processes (AOPs), *Brazilian Journal of Chemical Engineering* **25 (4)**, 453–459.

Pearce C.I., Lloyd J.R., Guthrie J.T. (2003). The removal of colour from textile wastewater using whole bacterial cells: a review, *Dyes and Pigments* **58**, 179–196.

van der Zee F.P., Villaverde S. (2005). Combined anaerobic – aerobic treatment of azodyes – A short review of bioreactor studies, *Water Research* **39**, 1425–1440.

Vilar V.J.P., Pinho L.X., Pintor A.M.A., Boaventura R.A.R. (2011). Treatment of textile wastewaters by solar-driven advanced oxidation processes, *Solar Energy* **85(2011)**, 1927–1934.

Wu J., Doan H., Upreti S. (2008). Decolorization of aqueous textile reactive dye by ozone, *Chemical Engineering Journal* **142 (2)**, 156–160.