



Jelena MOLNAR JAZIĆ, Tajana ĐURKIĆ,  
 Marijana KRAGULJ ISAKOVSKI, Malcolm WATSON,  
 Snežana MALETIĆ, Aleksandra TUBIĆ, Jasmina AGBABA<sup>1</sup>

## UTICAJ pH VREDNOSTI I VODENOG MATRIKSA NA UV/H<sub>2</sub>O<sub>2</sub> OKSIDATIVNU DEGRADACIJU 1,2,3-TRIHLOBENZENA

### IMPACT OF pH AND WATER MATRIX ON THE UV/H<sub>2</sub>O<sub>2</sub> OXIDATIVE DEGRADATION OF 1,2,3-TRICHLOROBENZENE

#### APSTRAKT

Hlorovani benzeni predstavljaju značajnu grupu polutanata životne sredine, što ih svrstava na listu prioriternih supstanci prema Okvirnoj Direktivi o Vodama (2000/60/EC). Trihlorobenzeni se koriste kao intermedijeri u proizvodnji herbicida, pigmenta i boja, a u životnu sredinu dospevaju tokom proizvodnje, upotrebe, odlaganja otpada ili kao posledica razlaganja organohlorinih pesticida. U radu su prikazani rezultati ispitivanja uticaja pH vrednosti i vodenog matriksa (huminskih kiselina i hidrogenkarbonata) na oksidativnu degradaciju 1,2,3-trihlorobenzena (TCB). Primenom direktne UV fotolize postignuto je 4-48% degradacije TCB, pri čemu pH vrednost nije imala značajniji uticaj na efikasnost fotolitičkog razlaganja ispitivanog polutanta. Najveća efikasnost degradacije TCB u sintetičkoj vodi (>99%) postignuta je primenom UV/H<sub>2</sub>O<sub>2</sub> unapređene oksidacije pri nižoj pH vrednosti (pH 5) i prati kinetiku pseudo-prvog reda. Prisustvo huminskih kiselina i hidrogenkarbonata značajno smanjuje efikasnost unapređenog oksidacionog tretmana u odnosu na fotodegradaciju TCB u sintetičkom matriksu bez dodatka interferirajućih agenasa.

**Ključne reči:** 1,2,3-trihlorobenzen, UV/H<sub>2</sub>O<sub>2</sub>, UV fotoliza, huminske materija, uticaj matriksa

#### ABSTRACT

Chlorinated benzenes represent a significant group of environmental pollutants which have been identified as priority pollutants by the European Water Framework Directive (2000/60/EC). Trichlorobenzenes are used as intermediates in the production of herbicides, pigments and dyes, and are found in the environment during the production, usage and disposal of waste, or as the result of organochlorine pesticides decomposition. This paper investigates the influence of pH and water matrix (humic acids and carbonate species) on the oxidative degradation of 1,2,3-trichlorobenzene (TCB). Under direct UV photolysis 4-48% of TCB degradation was achieved wherein the pH did not have a significant effect on the photolytic decomposition efficiency of the investigated pollutant. The highest efficacy of TCB degradation in synthetic water (> 99%) was achieved using UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation at a lower pH (pH 5), following pseudo-first order kinetics. The presence of humic acids and hydrogen carbonates significantly reduces the efficiency of the advanced oxidation treatment relative to the photodegradation of TCB in the synthetic matrix with no scavengers added.

**Key words:** 1,2,3-trichlorobenzene, UV/H<sub>2</sub>O<sub>2</sub>, UV photolysis, humic matter, matrix effect

#### 1. UVOD

Prisustvo velikog broja zagađujućih materija u životnoj sredini, uključujući prioritne supstance i emergentne polutante, predstavlja veliki rizik za kvalitet kako površinskih, tako i podzemnih voda. Prioritetni polutanti regulisani su na međunarodnom i nacionalnom nivou usled toksičnosti, perzistentnosti i bioakumulativnog potencijala, a samim tim i visokog rizika po ljudsko zdravlje i akvatičnu biotu. Uzimajući u obzir prioritetni status navedenih polutanata i njihov značaj, uklanjanje ovih supstanci iz vode predstavlja veliki izazov. Proces pripreme vode mora se optimizovati tako da odgovori zahtevima kvaliteta sirove vode, koja je podložna varijacijama usled klimatskih promena, korišćenja zemljišta u poljoprivredne svrhe, ispuštanja nedovoljno prečišćenih otpadnih voda itd. (Teodosiu i sar., 2018).

#### 1. INTRODUCTION

The presence of a large number of pollutants in the environment, including priority substances and emerging pollutants, poses a significant risk to the quality of surface and groundwater. Priority pollutants are regulated at international and national levels due to the toxicity, persistence and bioaccumulative potential, and they can pose a high risk to human health and aquatic biota. Considering the priority status of the listed pollutants and their significance, drinking water treatment plants face great challenges in terms of optimizing technologies that will enable efficient removal of the priority substances. Water preparation needs be optimized to meet the requirements of raw water quality in the source, which is subjected to variations due to the climate change, use of land for agricultural purposes,

<sup>1</sup> Jelena MOLNAR JAZIĆ, Tajana ĐURKIĆ, Marijana KRAGULJ ISAKOVSKI, Malcolm WATSON, Snežana MALETIĆ, Aleksandra TUBIĆ, Jasmina AGBABA, Univerzitet u Novom Sadu, Prirodno-matematički fakultet, Departman za hemiju, biohemiju i zaštitu životne sredine, Trg Dositeja Obradovića 3, 21000 Novi Sad, Republika Srbija, e-mail: jelena.molnar@dh.uns.ac.rs



Proces pripreme vode za piće dodatno komplikuje prisustvo prirodnih organskih materija (POM). Novija istraživanja ukazuju na značajan uticaj klimatskih promena na karakteristike huminskih materija (kao gradivnih jedinica POM), njihovu strukturu i reaktivnost, što se dalje odražava i na interakcije huminskih supstanci sa polutantima relevantnim za kvalitet akvatičnih ekosistema. Pored toga, sa porastom temperature favorizuju se i procesi biodegradacije zemljišnih organskih materija, čime dolazi do povećanja sadržaja rastvorenih organskih materija, koje se pod uticajem obilnih padavina transportuju i spiraju u površinske vode (*Lipczynska-Kochany, 2018*).

Konvencionalni fizičko-hemijski i biološki procesi nisu dovoljno efikasni da omoguće uklanjanje prioritarnih polutanata iz vode. Među novim, unapređenim tehnologijama pripreme vode posebno se ističu unapređeni oksidacioni procesi (AOPs), koji se zasnivaju na generisanju visoko reaktivnih intermedijera, kao što su hidrosil radikali ( $\text{HO}^\cdot$ ), koji reaguju brzo i neselektivno sa gotovo svim organskim polutantima, dovodeći do njihove potpune oksidativne degradacije i uklanjanja iz vode (*Antonopoulou i sar., 2014; Massima Mouele i sar., 2015*). Hidrosil radikali, kao izuzetno jaka oksidaciona sredstva (oksidacioni potencijal 2,8 V) mogu biti generisani na različite načine, što omogućava prilagođavanje različitim potrebama u tretmanu voda. AOPs se široko primenjuju za tretman voda kontaminiranih različitim polutantima uključujući pesticide i proizvode njihove degradacije, farmaceutike, proizvode za ličnu higijenu, usporivače gorenja, koji se kontinualno ispuštaju u životnu sredinu usled njihove primene u industriji, medicini i poljoprivredi (*Sharma i sar., 2018*).

Kombinacija ultraljubičastog zračenja sa vodonik-peroksidom (UV/ $\text{H}_2\text{O}_2$  proces) predstavlja jednostavnu i efikasnu tehnologiju za degradaciju organskih polutanata u vodi posredstvom direktnog UV fotolitičkog razlaganja i oksidacije generisanim hidrosil radikalima (*Liao i sar., 2016; Molnar Jazić i sar., 2015*). Na dekompoziciju vodonik-peroksida i formiranje  $\text{HO}^\cdot$  u vodenim rastvorima osim UV zračenja veliki uticaj imaju i pH vrednost, prisustvo katalizatora i ozona. Efikasnost fotokatalitičkih procesa u velikoj meri zavisi i od prisustva, odn. sadržaja POM, hidrogenkarbonata/karbonata i drugih neorganskih materija, koje mogu da stupaju u kompetitivne reakcije i troše, odn. „hvataju“ (eng. *scavengers*) hidrosil radikale.

Cilj ovog rada bio je ispitivanje uticaja pH vrednosti i vodenog matriksa na oksidativnu degradaciju 1,2,3-trihlorbenzena (TCB) primenom UV/ $\text{H}_2\text{O}_2$  procesa. Poseban fokus istraživanja obuhvatao je ispitivanje uticaja huminskih materija i alkaliteta na efikasnost unapređenog oksidacionog tretmana. TCB je odabran kao model komponenta hlorovanih benzena, koji predstavljaju značajnu grupu

wastewater discharge, etc. (*Teodosiu et al., 2018*).

The presence of natural organic matter (NOM) additionally complicates drinking water preparation. Recent studies have shown the significant impact of climate change on humic matter (an integral part of NOM structure) characteristics, including their structure and reactivity, which is further reflected in the interactions between humic substances and pollutants relevant for the quality of aquatic ecosystems. Furthermore, increasing the temperature of the soil organic matter biodegradation processes favours an increase in dissolved organic matter content, which undergoes transport to natural waters by erosion or leaching caused by floods (*Lipczynska-Kochany, 2018*).

Conventional physico-chemical and biological processes are not efficient enough to enable the removal of priority pollutants from water. Among a new generation of treatment technologies, advanced oxidation processes (AOPs), which are based on highly reactive intermediates, such as hydroxyl radicals ( $\text{HO}^\cdot$ ) generation, are particularly promising. The reactions of most organic pollutants with  $\text{HO}^\cdot$  are very fast and unselective, leading to their complete oxidative degradation and removal from water (*Antonopoulou et al., 2014; Massima Mouele et al., 2015*). Hydroxyl radicals, as very strong oxidizing species (oxidation potential of 2.8 V) can be generated in different ways, allowing adjustments to different requirements in water treatment. AOPs are widely used for the treatment of water contaminated with various pollutants including pesticides and their degradation products, pharmaceuticals, personal care products, flame retardants, etc. which continuously have been discharged to the environment as a consequence of applications in industry, medicine and agriculture (*Sharma et al., 2018*).

The combination of ultraviolet light with hydrogen peroxide (UV/ $\text{H}_2\text{O}_2$  process) is a simple and efficient technology for the degradation of organic pollutants in water which works via direct UV photolytic decomposition and oxidation by generated hydroxyl radicals (*Liao et al., 2016; Molnar Jazić et al., 2015*). Apart from the UV irradiation, pH value, the presence of catalysts and ozone also have a great influence on the hydrogen peroxide decomposition and formation of  $\text{HO}^\cdot$  in water. The efficiency of photocatalytic processes depends to a large extent on the presence and content of NOM, carbonate species and other inorganic substances, which can compete with target pollutants and act as hydroxyl radicals' scavengers.

The aim of this study was to investigate the effect of pH and water matrix on the oxidative degradation of 1,2,3-trichlorobenzene (TCB) using the UV/ $\text{H}_2\text{O}_2$  process. The influence of humic substances and carbonate species on the advanced oxidation process efficiency was also addressed. TCB has been selected as a model compound of chlorinated benzenes, a

polutanata životne sredine, što ih svrstava na listu prioritarnih supstanci prema Okvirnoj Direktivi o Vodama (2000/60/EC) i Američkoj agenciji za zaštitu životne sredine (USEPA, 2014).

## 2. MATERIJAL I METODE

### 2.1. Hemikalije i reagensi

U laboratorijskim ispitivanjima primenjeni su standardi 1,2,3-trihlorbenzen (*Pestanal*<sup>®</sup>, *Sigma-Aldrich*, CAS No. 87-61-6) i pentahloronitrobenzen (u koncentraciji od 5000 µg/ml u metanolu, *Supelco*, CAS No. 82-68-8), kao interni standard. Organski rastvarači heksan (*J.T. Baker*, CAS No. 110-54-3) i metanol (*J.T. Baker*, CAS No. 67-561) su bili visokog stepena čistoće za analizu organskih tragova. Za pripremu sintetičkog matriksa korišćeni su komercijalna huminska kiselina (HK) (*Fluka*, CAS No. 1415-93-6), rastvor natrijum-hidrogenkarbonata (*Merck*, CAS No. 144-55-8) i ultračista dejonizovana voda ASTM tipa I, dobijena pomoću sistema za prečišćavanje (LABCONCO, WaterPro Ro/Ps Station) (sadržaj rastvorenog organskog ugljenika (eng. *dissolved organic carbon*, DOC) <0,5 mg C/L; električna provodljivost 0,0558 µS/cm). Ostale hemikalije primenjene u istraživanju: 30% rastvor H<sub>2</sub>O<sub>2</sub> (*POCH, S.A.*, CAS No. 7722-84-1), natrijum-hidroksid (*Centrohem*, CAS No. 1310-73-2) i hlorovodonična kiselina (*Merck*, CAS No. 7647-01-0).

### 2.2. Priprema sintetičkog vodenog matriksa

Za pripremu sintetičkog matriksa korišćen je radni rastvor komercijalne huminske kiseline, kao model supstance POM, koji je pripremljen rastvaranjem standarda HK u ultračistoj dejonizovanoj vodi, prema proceduri datoj u literaturi (*Mosteo i sar., 2009*). Radni rastvor TCB u dejonizovanoj vodi pripreman je u koncentraciji od ~10 mg/l. Sadržaj huminskih kiselina u sintetičkom matriksu iznosio je 5 mg C/l DOC, sadržaj hidrogenkarbonata 500 mg/l, a početna koncentracija TCB ~100 µg/l. Tačna početna koncentracija TCB u sintetičkom matriksu određivana je neposredno pre svakog eksperimenta. U cilju ispitivanja uticaja pH vrednosti na efikasnost oksidativne degradacije TCB u vodi pH vrednost je korigovana pre fotohemijjskih eksperimenata.

### 2.3. Fotohemijjski eksperimenti

UV/H<sub>2</sub>O<sub>2</sub> oksidativna degradacija TCB u sintetičkoj vodi vršena je u komercijalno dostupnom reaktoru od nerđajućeg čelika zapremine 0,7 l. Kao izvor zračenja korišćena je živina lampa niskog pritiska, sa maksimumom emisije na 254 nm, proizvođača Philips, koja je postavljena u centralni deo reaktora od kvarcnog stakla i povezana preko balasta sa

significant group of environmental pollutants which are on the priority substances list according to the Water Framework Directive (2000/60/EC) and the United States Environmental Protection Agency (USEPA, 2014).

## 2. MATERIALS AND METHODS

### 2.1. Chemicals and reagents

The following standards were used in the laboratory investigation: 1,2,3-trichlorobenzene (*Pestanal*<sup>®</sup>, *Sigma-Aldrich*, CAS No. 87-61-6) and pentachloronitrobenzene (5000 µg/ml in methanol, *Supelco*, CAS No. 82-68-8), as an internal standard. Organic solvents hexane (CAS No. 110-54-3) and methanol (CAS No. 67-561) were for organic residue analysis and were supplied by *J.T. Baker*<sup>®</sup>. The commercial humic acid (HA) (*Fluka*, CAS No. 1415-93-6), sodium hydrogencarbonate (*Merck*, CAS No. 144-55-8) and ultra-pure deionised water ASTM type I, obtained from a LABCONCO (*WaterPro Ro/Ps Station*) system (dissolved organic carbon, DOC <0.5 mg C/L; electrical conductivity 0.058 µS/cm) were used to prepare synthetic matrices and solutions. The other chemicals used were: 30% H<sub>2</sub>O<sub>2</sub> (*POCH, S.A.*, CAS No. 7722-84-1), sodium hydroxide (*Centrohem*, CAS No. 1310-73-2) and hydrochloric acid (*Merck*, CAS No. 7647-01-0).

### 2.2. Preparation of the synthetic water matrix

A working solution of commercial humic acid, as a model of NOM, was prepared by dissolving HA in deionised water according to *Mosteo et al. (2009)* and used for preparation of the synthetic water matrix. A TCB working solution in deionized water was prepared at concentrations of ~10 mg/L. Synthetic matrices were prepared containing: humic acids (5 mg C/L DOC), alkalinity (500 mg HCO<sub>3</sub><sup>-</sup>/L) and initial concentrations of TCB ~ 100 µg/L. The initial concentrations of TCB were measured prior to each experiment to control for any loss of the compound. In order to investigate the effect of pH on the TCB oxidative degradation efficiency, the pH value was corrected prior to the photochemical experiments.

### 2.3. Photochemical experiments

UV/H<sub>2</sub>O<sub>2</sub> oxidative degradation of TCB in synthetic water was carried out in a stainless steel photoreactor (0.7 L). An low pressure mercury lamp (*Philips*) with a UV emission peak at 254 nm was used as a source of UV irradiation and was placed in a quartz reaction vessel in the center of the reactor. The photon flux was determined to be 2.33 x 10<sup>-6</sup> Einsteins s<sup>-1</sup> by ferrioxalate actinometry method, described by *Hatchard and*



izvorom napajanja (Molnar Jazić i sar., 2015). Pre počeka svakog eksperimenta lampa je zagrevana 20 minuta kako bi se stabilizovao intenzitet UV zračenja. Foton fluks je određen primenom aktinometrijske metode sa ferioksalatom, prema proceduri Hatchard i Parker (1956), i iznosi  $2,33 \times 10^{-6}$  Einsteins $\cdot$ s $^{-1}$ . Primenjene doze UV zračenja bile su u opsegu 0-1400 mJ/cm $^2$ , a koncentracija vodonik-peroksida, koji je doziran u vodu neposredno pre fotohemijskih eksperimenata 1 i 10 mg/l. UV/H $_2$ O $_2$  oksidativna degradacija TCB u sintetičkoj vodi ispitivana je pri dve pH vrednosti (pH 5 i 7).

## 2.4. Analitičke metode

Koncentracija TCB u uzorcima vode analizirana je nakon tačno-tečne ekstrakcije sa heksanom primenom gasne hromatografije sa detektorom sa zahvatom elektrona (6890 with  $^{63}\text{Ni}$   $\mu\text{ECD}$ , Agilent Technologies) sa DB-XLB kolonom (J&W Scientific) prema proceduri datoj u literaturi (Kragulj i sar., 2013). Granica detekcije metode iznosi 10 ng/l.

Sadržaj organskih materija u vodi pre i nakon tretmana određivan je merenjem sadržaja DOC u vodi na instrumentu Elementar Liqui TOC II (Model 35072028). pH vrednost određivana je na instrumentu pH/ION 735 (Model 04520006).

## 3. REZULTATI I DISKUSIJA

### 3.1. Degradacija TCB u sintetičkom matriksu - uticaj huminskih materija i hidrogenkarbonata

Rezultati ispitivanja uticaja direktne UV fotolize i UV/H $_2$ O $_2$  unapređenog oksidacionog tretmana na degradaciju TCB u sintetičkoj vodi pri različitim pH vrednostima prikazani su na slikama 1 i 2. Sadržaj organskih materija i hidrogenkarbonata u sintetičkom vodenom matriksu odabran je tako da simulira sadržaj ovih materija u podzemnoj vodi dela Panonskog basena (sa lokaliteta AP Vojvodine, Republika Srbija) i omogućiti poređenje sa prirodnim vodenim matriksima kroz dalja istraživanja. Primenom direktne UV fotolize postignuto je 4-48% degradacije TCB u sintetičkom matriksu, pri čemu je povećanje efikasnosti procesa zabeleženo sa povećanjem primenjene doze UV zračenja. Utvrđeno je da pH vrednost nije imala značajniji uticaj na efikasnost uklanjanja TCB iz vode direktnom UV fotolizom.

Značajno brža i efikasnija degradacija TCB u vodi postignuta je primenom UV/H $_2$ O $_2$  procesa, koji je omogućio gotovo potpuno uklanjanje trihlorbenzena iz vode (>99%). Dobijeni rezultati ukazuju na značajan uticaj primenjene doze oksidacionog sredstva, vodonik-peroksida i inicijalne pH vrednosti rastvora

Parker (1956). Before the beginning of each treatment, the lamp was warmed for 20 minutes in order to stabilize the intensity of UV irradiation. After warm-up, the reactor was filled with the water sample and hydrogen peroxide added, at concentrations of 1 or 10 mg H $_2$ O $_2$ /L. Applied UV doses were in the range 0-1400 mJ/cm $^2$ . UV/H $_2$ O $_2$  oxidative degradation of TCB in synthetic water was investigated at two pH values (pH 5 and 7).

## 2.4. Analytical methods

The concentration of TCB in water samples was analyzed after liquid-liquid extraction with hexane by gas chromatography with electron capture detection (6890 with  $^{63}\text{Ni}$   $\mu\text{ECD}$ , Agilent Technologies) with a DB-XLB column (J&W Scientific), according to a procedure given in the literature (Kragulj et al., 2013). The method detection limit was 10 ng/l.

The content of organic matter in water before and after treatment was determined by measuring the content of DOC in water using an Elementar LiquiTOC II. pH measurements were made using pH/ION 735 instrument (Model 04520006).

## 3. RESULTS AND DISCUSSION

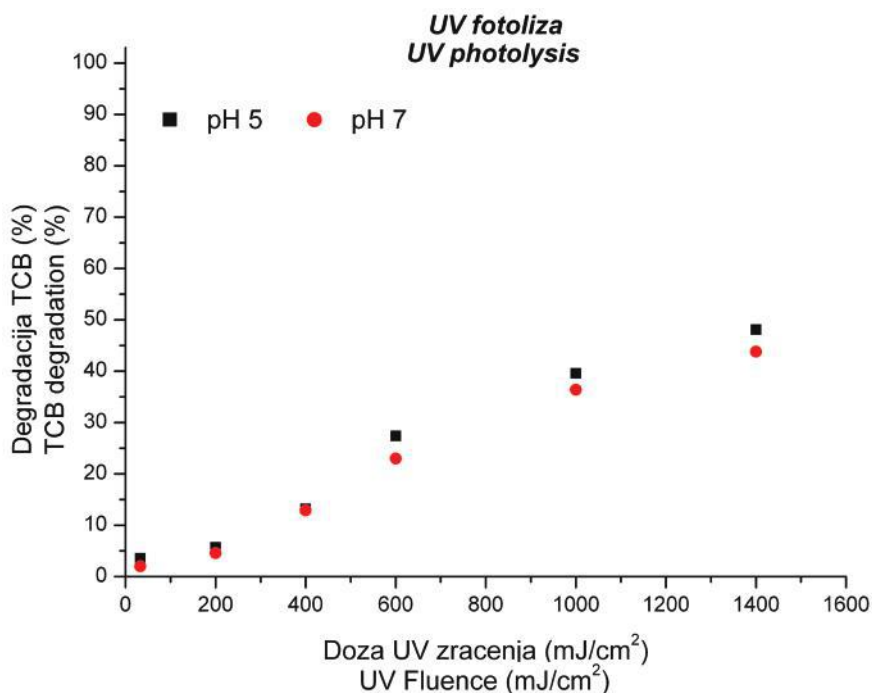
### 3.1. TCB degradation in synthetic matrices – effects of humic acids and hydrogen carbonates

The effects of direct UV photolysis and UV/H $_2$ O $_2$  advanced oxidation processes on the TCB degradation efficacy in a synthetic water under different pH conditions are presented in figures 1 and 2.

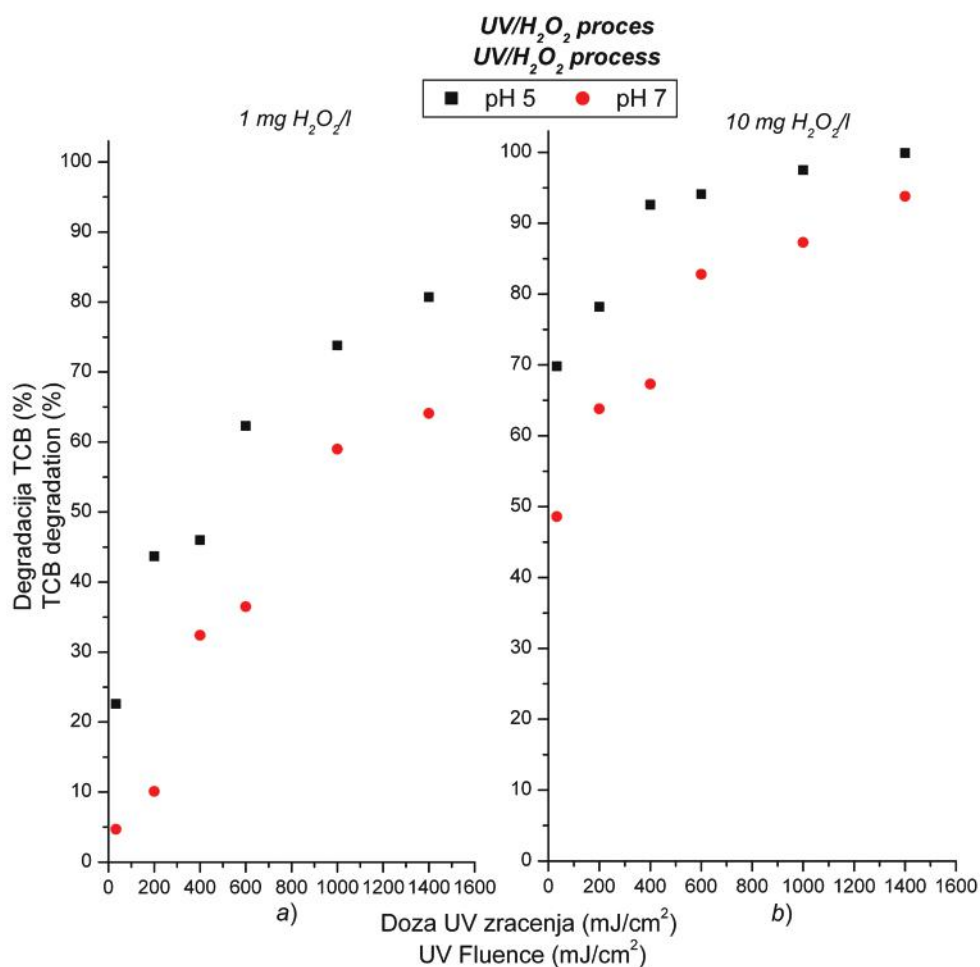
The contents of organic matter and hydrogen carbonates in the synthetic water matrix were selected to reflect those found in the groundwater from part of the Pannonian Basin (in AP Vojvodina, Republic of Serbia) thus allowing a comparison with natural waters in further research. Direct photolysis conducted in the synthetic water matrix achieved TCB degradations in the range 4-48%, with the extent of TCB degradation increasing with increasing UV fluence. It was found that pH did not significantly affect the efficacy of TCB removal from water by direct UV photolysis.

Significantly faster and more effective TCB degradation in water was achieved using the UV/H $_2$ O $_2$  process, which enabled almost complete removal of trichlorobenzene from water (>99%). The obtained results demonstrate that the applied concentration of oxidizing agent, hydrogen peroxide, and the initial pH of the water, have a significant influence on the efficiency of TCB oxidative degradation using UV/





**Slika 1.** Degradacija TCB u sintetičkom matriksu primenom direktne UV fotolize  
**Figure 1.** Degradation of TCB in a synthetic matrix using direct UV photolysis



**Slika 2.** Degradacija TCB u sintetičkom matriksu primenom UV/H<sub>2</sub>O<sub>2</sub> unapređenog oksidacionog tretma  
**Figure 2.** Degradation of TCB in a synthetic matrix using UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process

na efikasnost oksidativne degradacije TCB u vodi UV/H<sub>2</sub>O<sub>2</sub> procesom (slike 2 i 3). Utvrđeno je da je veća efikasnost oksidativne degradacije TCB postignuta

H<sub>2</sub>O<sub>2</sub> procesom (figures 2 and 3). More effective TCB degradation was achieved using the UV/H<sub>2</sub>O<sub>2</sub> process with an higher concentration of hydrogen peroxide



primenom UV/H<sub>2</sub>O<sub>2</sub> procesa sa većom koncentracijom vodonik-peroksida (10 mg/l) i pri nižoj pH vrednosti (pH 5).

Dobijeni rezultati mogu se objasniti generisanjem neselektivnih, izuzetno reaktivnih hidroksil radikala, ali i drugih oksidacionih vrsta uključujući hidroperoksil radikale, superoksid anjon radikale i organske peroksil radikale. Ove radikalne vrste iako su znatno slabiji oksidacioni agensi u poređenju sa HO<sup>•</sup> takođe mogu da učestvuju u lančanom radikalnom mehanizmu oksidacije. Kada su u pitanju aromatična jedinjenja, inicijalni napad HO<sup>•</sup> može da se odvija reakcijama elektrofilne adicije na aromatični prsten preko kratkoživećih π- i σ-kompleksa. Reakcije oksidacije dalje se mogu odvijati i apstrakcijom vodonika i elektron-transferom (Stefan, 2017).

Rezultati efikasnije oksidativne degradacije TCB u sintetičkom matriksu pri nižoj pH vrednosti mogu se objasniti uticajem pH na odvijanje reakcija sa huminskim kiselinama i hidrogenkarbonatima. Poznato je da pH vrednost ima veliki uticaj na ravnotežu, odn. distribuciju H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> i CO<sub>3</sub><sup>2-</sup>. Pri nižoj pH vrednosti (pH ~ 4,3), ova ravnoteža se potpuno pomera u pravcu formiranja ugljene kiseline, koja u tom obliku neće imati negativan uticaj na performanse procesa (Li i sar., 2008). Stoga se može pretpostaviti da je jedan od faktora veće efikasnosti procesa koja je postignuta na pH 5 u odnosu na pH 7 posledica smanjenja udela oblika HCO<sub>3</sub><sup>-</sup> i konverzije u H<sub>2</sub>CO<sub>3</sub>. Reakcija HCO<sub>3</sub><sup>-</sup> sa hidroksil radikalima prikazana je sledećom reakcijom:



CO<sub>3</sub><sup>•-</sup> su mnogo selektivniji u reakcijama sa organskim polutantima u odnosu na reakcije sa HO<sup>•</sup> i brzine tih reakcija su znatno manje. pH vrednost takođe utiče i na frakciju HO<sub>2</sub><sup>-</sup> jona koji efikasnije apsorbuju UV zračenje u odnosu na vodonik-peroksid, čineći UV/H<sub>2</sub>O<sub>2</sub> proces efikasnijim pri višim pH vrednostima. Pored toga, pH vrednost utiče i na naelektrisanje u vodi prisutnih organskih materija. U strukturi huminskih kiselina dominiraju karboksilne i fenolne funkcionalne grupe i hinoni. Fenolne i karboksilne funkcionalne grupe su deprotonovane u neutralnoj i alkalnoj sredini i imaju veliki scavenging kapacitet prema slobodnim radikalima (de Melo i sar., 2016). Ove funkcionalne grupe se u reakcijama sa hidroksil radikalima ponašaju isto kao i karbonatni joni, odn. deluju kao „hvatači“ HO<sup>•</sup>, što može voditi terminaciji radikalnih lančanih reakcija (Li i sar., 2008).

Efekat huminskih materija na smanjenje efikasnosti unapređenih oksidacionih procesa značajno je veći u odnosu na HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> jone (Li i sar., 2008). Kada je u pitanju uklanjanje ukupnih organskih materija nešto veći stepen smanjenja sadržaja HK u vodi (do 20%) postignut je pri većoj pH vrednosti (pH 7) i koncentraciji vodonik-peroksida (10 mg H<sub>2</sub>O<sub>2</sub>/l) (slika 3).

(10 mg/L) at a lower pH (pH 5).

The obtained results can be explained by the generation of non-selective, highly reactive hydroxyl radicals, as well as other oxidation species such as hydroperoxyl radicals, superoxide anion radicals and organic peroxy radicals. Although these radical species are significantly weaker oxidation agents than HO<sup>•</sup>, they can also participate in the radical chain oxidation mechanism.

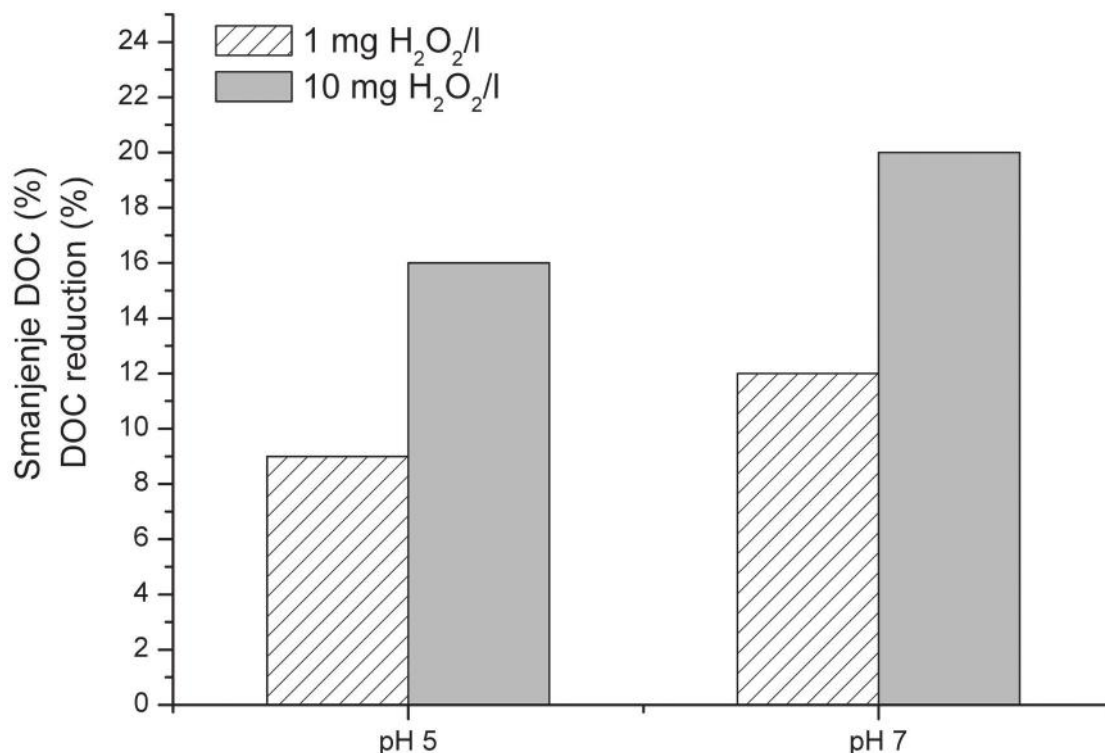
In the case of aromatic compounds, the initial attack of HO<sup>•</sup> proceeds through electrophilic addition to the aromatic ring via short-lived π- and σ- complexes. Reactions of oxidation can also occur through hydrogen abstraction and electron transfer (Stefan, 2017).

The more efficient oxidative degradation of TCB in the synthetic matrix at a lower pH can be explained by the effect of pH on the side reactions with humic acids and hydrogen carbonates. It is known that the pH has a great effect on the equilibrium i.e. distribution of H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. At a lower pH (pH ~ 4.3), the alkalinity is completely converted to aqueous carbon dioxide and will not affect the performance of process (Li et al., 2008). Thus it can be assumed that one of the factors explaining the higher process efficiency achieved at pH 5 is the decreasing proportion of HCO<sub>3</sub><sup>-</sup> and prevailing H<sub>2</sub>CO<sub>3</sub>. Reaction of HCO<sub>3</sub><sup>-</sup> with hydroxyl radicals is shown in following reaction:



CO<sub>3</sub><sup>•-</sup> are more selective in reactions with organic pollutants compared to the reactions with HO<sup>•</sup> and the rates of these reactions are considerably lower. The pH also affects the available HO<sub>2</sub><sup>-</sup> ion fraction that more efficiently absorbs UV irradiation than hydrogen peroxide, making the UV/H<sub>2</sub>O<sub>2</sub> process more efficient at higher pH values. In addition, the pH value also affects the charge of organic matter present in water. Carboxylic acids, phenols and quinones are the most abundant functional groups in the structure of humic acids. Phenols and carboxylic acids are deprotonated in neutral and alkaline media and have a great scavenging capacity toward free radical species (de Melo et al., 2016). These functional groups can all act as HO<sup>•</sup> scavengers, as can carbonate species, leading to the termination of radical chain reactions and decreasing the overall process efficacy (Li et al., 2008).

The effect of NOM on reducing the efficiency of AOPs proved to be higher than the effect of carbonate species (Li et al., 2008). When it comes to the removal of total organic matter, a slightly higher degree of HA reduction in water (up to 20%) was achieved at a higher pH (pH 7) and hydrogen peroxide concentration (10 mg H<sub>2</sub>O<sub>2</sub>/l) (Figure 3).



**Slika 3.** Uklanjanje ukupnih organskih materija u sintetičkoj vodi primenom UV/H<sub>2</sub>O<sub>2</sub> unapređenog oksidacionog tretmana (1 i 10 mg H<sub>2</sub>O<sub>2</sub>/l, 1400 mJ/cm<sup>2</sup>)

**Figure 3.** Total organic matter removal in a synthetic matrix using UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process (1 and 10 mg H<sub>2</sub>O<sub>2</sub>/l, 1400 mJ/cm<sup>2</sup>)

Massoudinejad i sar. (2016) takođe su ukazali na efikasniju degradaciju huminskih kiselina pri višim pH vrednostima, dok je odvijanje procesa pri nižim pH rezultovalo „hvatanjem“ HO<sup>•</sup> u prisustvu H<sup>+</sup> jona. Niža efikasnost oksidativne degradacije TCB na pH 7 delom je posledica i većeg utroška hidroksil radikala na kompetitivne reakcije oksidacije integralnih struktura HK pri ovim reakcionim uslovima. Poredeći dobijene rezultate sa prethodnim ispitivanjima, gde je prikazana degradacija TCB u ultračistoj vodi (Đurkić i sar., 2016) može se uočiti da prisustvo huminskih kiselina i hidrogenkarbonata ima negativan uticaj na degradaciju TCB u sintetičkom matriksu usled kompetitivnih reakcija, ali i direktne apsorpcije fotona od strane HK, kao organskih makromolekula.

Massoudinejad et al. (2016) also reported more efficient degradation of humic acids at higher pH values, while in very low pH ranges the scavenging effect of HO<sup>•</sup> by H<sup>+</sup> were observed. Lower efficiency of TCB oxidative degradation at pH 7 can partially be a consequence of higher consumption of hydroxy radicals in competitive reactions of HA integral structures oxidation under these reaction conditions. Comparing the obtained results with previous investigations it can be noted that the presence of humic acids and hydrogen carbonate has a negative influence on TCB degradation compared to degradation proceeding in ultrapure water (Đurkić et al., 2016) due to the competitive reactions and the direct photon absorption by HA organic macromolecules.

### 3.2. Kinetika degradacije TCB

Degradacija TCB u vodi primenom UV fotolize i UV/H<sub>2</sub>O<sub>2</sub> procesa može se opisati kinetičkim modelom pseudo-prvog reda, prema jednačini:

$$-\frac{d[P]}{dt} = k[P]$$

gde je  $k$  konstanta brzine pseudo-prvog reda. Konstanta  $k$  se dobija se iz nagiba  $\ln([P]_0)/([P])$  u odnosu na primenjeno dozu zračenja, gde su  $[P]_0$  i  $[P]$  početna i finalna koncentracija mikropolutanta u vodi (Bolton i Stefan, 2002; Shu i sar., 2013). Na osnovu dobijenih rezultata određena je konstanta brzine pseudo-prvog reda zasnovana na dozi zračenja (eng.

### 3.2. Kinetics of TCB degradation

The degradation of TCB in water using UV photolysis and UV/H<sub>2</sub>O<sub>2</sub> processes can be described by the pseudo-first order kinetic model using the following equation:

$$-\frac{d[P]}{dt} = k[P]$$

where  $k$  is pseudo-first order rate constant.  $\ln([P]_0/[P])$  was plotted versus the UV fluence (mJ/cm<sup>2</sup>) and the corresponding fluence-based rate constant  $k$  was obtained, where  $P_0$  and  $P$  are the initial and final concentration of TCB in water (Bolton and Stefan, 2002; Shu et al., 2013). On the basis on the given results, fluence based pseudo-first-order rate constants for



**Tabela 1.** Vrednosti konstanti brzina pseudo-prvog reda za degradaciju 1,2,3-TCB u sintetičkom matriksu primenom UV fotolize i UV/H<sub>2</sub>O<sub>2</sub> procesa

**Table 1.** Pseudo-first order rate constants for 1,2,3-TCB degradation in a synthetic matrix using UV photolysis and UV/H<sub>2</sub>O<sub>2</sub> process

Parametri Parameters	UV/H <sub>2</sub> O <sub>2</sub>					
	0*	1	10	0*	1	10
mg H <sub>2</sub> O <sub>2</sub> /l	0*	1	10	0*	1	10
pH	pH 5			pH 7		
k/10 <sup>-3</sup> cm <sup>2</sup> mJ <sup>-1</sup>	0,488	1,01	2,61	0,435	0,765	1,51
R <sup>2</sup>	0,98	0,98	0,97	0,99	0,98	0,98

\* UV fotoliza / \* UV photolysis

fluence based pseudo first-order rate constants) za degradaciju TCB u sintetičkom matriksu (tabela 1).

Dobijene *k* vrednosti ukazuju da dodatak vodonik-peroksida vodi povećanju brzine degradacije TCB u poređenju sa UV fotolizom. Konstanta brzine UV fotolize za degradaciju TCB u sintetičkom matriksu iznosi 0,435-0,488 × 10<sup>-3</sup> cm<sup>2</sup>mJ<sup>-1</sup> i ne razlikuje se značajnije u zavisnosti od pH vrednosti. Povećanje koncentracije H<sub>2</sub>O<sub>2</sub> i smanjenje pH vrednosti rezultovali su povećanjem vrednosti za konstantu brzine degradacije TCB tokom UV/H<sub>2</sub>O<sub>2</sub> procesa (0,765-2,61 × 10<sup>-3</sup> cm<sup>2</sup>mJ<sup>-1</sup>, R<sup>2</sup> = 0,97-0,99).

#### 4. ZAKLJUČAK

Rezultati dobijeni ovim istraživanjem ukazuju da se UV/H<sub>2</sub>O<sub>2</sub> unapređeni oksidacioni proces može primeniti sa visokom efikasnošću (>99%) za degradaciju 1,2,3-TCB u vodi u prisustvu huminskih materija i hidrogenkarbonata. Udeo UV fotolize u ukupnoj degradaciji TCB iznosi maksimalno do 48%. Degradacija TCB u sintetičkom matriksu prati kinetiku pseudo-prvog reda. Značajan uticaj na efikasnost UV/H<sub>2</sub>O<sub>2</sub> oksidativne degradacije TCB u prisustvu huminskih materija i hidrogenkarbonata imaju pH vrednost, primenjena koncentracija vodonik-peroksida i doza UV zračenja. Efikasnija degradacija TCB primenom UV/H<sub>2</sub>O<sub>2</sub> procesa postignuta je pri nižoj pH vrednosti (pH 5), dok je nešto efikasnije smanjenje ukupnih organskih materija postignuto na pH 7. Dobijeni rezultati mogu biti posledica uticaja pH na distribuciju jona HCO<sub>3</sub><sup>-</sup>, H<sub>2</sub>O<sub>2</sub>/HO<sub>2</sub><sup>-</sup> i naelektrisanje u vodi prisutnih organskih materija, što dalje utiče i na kompetitivne reakcije u kojima se troše hidroksil radikali. Stoga je u sistemima sa povećanim sadržajem prirodnih organskih materija i visokim alkalitetom, a u zavisnosti od fizičko-hemijskih karakteristika polutanta od interesa, neophodno optimizovati reakcione uslove unapređenih oksidacionih tretmana.

**Zahvalnost.** Istraživanja su finansirana od strane Pokrajinskog sekretarijata za visoko obrazovanje i naučno istraživačku delatnost Autonomne Pokrajine Vojvodine (Projekat broj: 142-451-2452/2018-02).

the degradation of TCB in the synthetic matrix were determined (table 1).

The obtained *k* values indicate that the addition of hydrogen peroxide leads to an increase in the rate of TCB degradation compared to UV photolysis alone. Rate constants for TCB degradation in the synthetic matrix were 0.435-0.488 × 10<sup>-3</sup> cm<sup>2</sup>mJ<sup>-1</sup> and do not differ significantly depending on the pH value. Increases in the applied H<sub>2</sub>O<sub>2</sub> concentration and decreasing the pH led to an increase in the TCB degradation rate constant during the UV/H<sub>2</sub>O<sub>2</sub> process (0.765-2.61 × 10<sup>-3</sup> cm<sup>2</sup>mJ<sup>-1</sup>, R<sup>2</sup> = 0.97-0.99).

#### 4. CONCLUSION

The results obtained by this study indicate that the UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process can be applied with high efficacy (>99%) for the degradation of 1,2,3-TCB in water in the presence of humic materials and hydrogen carbonates. The share of UV photolysis in the total TCB degradation amounts to a maximum of 48%. TCB degradation in the synthetic matrix follows the pseudo-first order kinetics. pH, the applied hydrogen peroxide concentration and UV fluence have a significant influence on the degree of UV/H<sub>2</sub>O<sub>2</sub> oxidative degradation of TCB in the presence of humic matter and hydrogen carbonates. More efficient degradation of TCB by the UV/H<sub>2</sub>O<sub>2</sub> process was achieved at a lower pH (pH 5), while a more effective reduction of total organic matter was obtained at pH 7. The obtained results can be due to the influence of pH on the distribution of HCO<sub>3</sub><sup>-</sup>, H<sub>2</sub>O<sub>2</sub>/HO<sub>2</sub><sup>-</sup> and the charge of organic matter present in the water, which further affects the competitive reactions with hydroxyl radicals. Therefore, in systems with an increased content of natural organic matter and high alkalinity, and depending on the physical and chemical characteristics of the target pollutants, it is necessary to optimize the reaction conditions of the advanced oxidation treatments.

**Acknowledgements.** The authors gratefully acknowledge the support of the Provincial Secretariat for Higher Education and Scientific Research, Republic of Serbia, Autonomous Province of Vojvodina (Project No. 142-451-2452/2018-02).



## 5. LITERATURA / REFERENCES

1. Antonopoulou, M., Evgenidou, E., Lambropoulou, D., Konstantinou, I. (2014) A review on advanced oxidation processes for the removal of taste and odor compounds from aqueous media. *Water Research* 53, 215-234.
2. Bolton, J.R., Stefan, M.I. (2002) Fundamental photochemical approach to the concepts of fluence (UV dose) and electrical energy efficiency in photochemical degradation reactions. *Research on Chemical Intermediates* 28 (7-9), 857-870.
3. de Melo, B.A.G., Motta, F.L., Santana, M.H.A. (2016) Humic acids: Structural properties and multiple functionalities for novel technological developments. *Materials Science and Engineering C* 62, 967-974.
4. Directive (2000), Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Official Journal of the European Communities* L 327, 1-72.
5. Đurkić, T., Dmitrašinović, S., Lončarski, M., Molnar Jazić, J., Kragulj Isakovski, M., Tubić, A., Maletić, S., Rončević, S., Agbaba, J., Dalmacija, B. (2016) Primena UV/H<sub>2</sub>O<sub>2</sub> unapređene oksidacije i adsorpcije na aktivnom uglju za uklanjanje trihlorbenzena iz vode. *Knjiga radova i apstrakata IV Memorijalni naučni skup iz zaštite životne sredine „Docent dr Milena Dalmacija”, 1-02.april Novi Sad, str. V-04.*
6. Hatchard, C.G., Parker, C.A. (1956) A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer. *Proceedings of the Royal Society A* 235, 518-536.
7. Kragulj, M., Tričković, J., Dalmacija, B., Kukovec, A., Kónya, Z., Molnar, J., Rončević, S. (2013) Molecular interactions between organic compounds and functionally modified multiwalled carbon nanotubes. *Chemical Engineering Journal* 225, 144-152.
8. Li, K., Hokanson, D.R., Crittenden, J.C., Trussell, R.R., Minakata, D. (2008) Evaluating UV/H<sub>2</sub>O<sub>2</sub> processes for methyl tert-butyl ether and tertiary butyl alcohol removal: Effect of pretreatment options and light sources. *Water Research* 42, 5045-5053.
9. Liao, Q.N., Ji, F., Li, J.C., Zhan, X., Hua, Z.H. (2016) Decomposition and mineralization of sulfaquinoxaline sodium during UV/H<sub>2</sub>O<sub>2</sub> oxidation processes. *Chemical Engineering Journal* 284, 494-502.
10. Lipczynska-Kochany, E. (2018) Humic substances, their microbial interactions and effects on biological transformations of organic pollutants in water and soil: A review. *Chemosphere* 202, 420-437.
11. Massima Moueie, E.S., Tijani, J.O., Fatoba, O.O., Petrik, L.F. (2015) Degradation of organic pollutants and microorganisms from wastewater using different dielectric barrier discharge configurations-a critical review. *Environmental Science and Pollution Research* 22, 18345-18362.
12. Massoudinejad, M., Golmohammadi, S., Ghaderpoori, M., Use of ultraviolet and ultraviolet/peroxide hydrogen processes for degradation of humic substances from aqueous solutions. *Bioscience Biotechnology Research Communications* 9 (4), 680-688.
13. Molnar, J., Agbaba, J., Tubić, A., Watson, M., Kragulj, M., Rončević, S., Dalmacija, B. (2015) The effects of ultraviolet/H<sub>2</sub>O<sub>2</sub> advanced oxidation on the content and characteristics of groundwater natural organic matter. *Water Science & Technology: Water Supply* 15 (1), 34-41.
14. Mosteo, R., Miguel, N., Martin-Muniesa, S., Ormad, M.P., Ovelheiro, J.L. (2009) Evaluation of trihalomethane formation potential in function of oxidation processes used during the drinking water production process. *Journal of Hazardous Materials* 172, 661-666.
15. Sharma, A., Ahmad, J., Flora, S.J.S. (2018) Application of advanced oxidation processes and toxicity assessment of transformation products. *Environmental Research* 167, 223-233.
16. Shu, Z., Bolton, J.R., Belosevic, M., El Din, M.G. (2013) Photodegradation of emerging micropollutants using the medium-pressure UV/H<sub>2</sub>O<sub>2</sub> Advanced Oxidation Process. *Water Research* 47 (8), 2881-2889.
17. Stefan, M.I. (2017) UV/hydrogen peroxide process, in: *Advanced Oxidation Processes for Water Treatment: Fundamentals and Applications* (ed. Stefan, M.I.) IWA Publishing. str. 7-122.
18. Teodosiu, C., Glica, A.F., Barjoveanu, G., Fiore, S. (2018) Emerging pollutants removal through advanced drinking water treatment: A review on processes and environmental performances assessment. *Journal of Cleaner Production* 197, 1210-1221.
19. US EPA (2014). United States Environmental Protection Agency Priority Pollutant List EPA. Available from: <https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf>.
20. Nikolina POPADIĆ, Jasmina AGBABA, Jelena MOLNAR JAZIĆ, Aleksandra TUBIĆ, Ivana IVANČEV-TUMBAS, Božo DALMACIJA: Karakterizacija prirodnih organskih materija u vodi koagulisanom polialuminijum hloridom (Characterization of natural organic matter in water coagulated using polyaluminium chloride), "Voda i sanitarna tehnika", br. 3/4 -2016.
21. Tajana ĐURKIĆ, Jelena MOLNAR JAZIĆ, Jasmina AGBABA, Maja LONČARSKI, Aleksandra TUBIĆ, Marijana KRAGULJ ISAKOVSKI, Božo DALMACIJA: Degradacija alachlor u prirodnoj i sintetičkoj vodi primenom direktne UV fotolize i UV/H<sub>2</sub>O<sub>2</sub> procesa (Degradation of alachlor in natural and synthetic water using direct UV photolysis and UV/H<sub>2</sub>O<sub>2</sub> process), "Voda i sanitarna tehnika", br. 3/4- 2017.