

## Textile Wastewater Cleaning with $O_3$ and $H_2O_2/O_3$ Process

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### Abstract

*The paper describes the ozonation ( $O_3$ ) and  $H_2O_2/O_3$  process as two efficient methods for cleaning textile effluents. The composition and characteristics of differently coloured dyebath effluents and wastewaters, as well as conventional processes and their disadvantages are stated. The presentation of the ozonation and  $H_2O_2/O_3$  process reactions and a review of applications for textile dyebath effluents loaded with different dye types of various chromophore groups are given precisely.*

*Furthermore, the paper states the ozonation and  $H_2O_2/O_3$  process efficiency for the removal of various dye types at different experimental conditions. The literature review shows that the ozonation and  $H_2O_2/O_3$  process are mainly used for reactive, acid and direct dyes treatment. Less information is available on basic, disperse and metal-complex dyes.*

**Keywords:** textile coloured wastewater, dyes, cleaning efficiency, ozonation, ozone,  $H_2O_2/O_3$

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## Čiščenje tekstilnih odpadnih voda s postopkoma $O_3$ in $H_2O_2/O_3$

**Pregledni znanstveni članek**

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### Izvleček

V članku sta predstavljena postopka ozoniranja ( $O_3$ ) in  $H_2O_2/O_3$ , kot dva izmed učinkovitejših postopkov za čiščenje tekstilnih voda. Podane so različne sestave in lastnosti barvalnih kopeli in odplak, predstavljeni so konvencionalni postopki čiščenja ter njihove slabosti. Poglobljeno sta prikazana in razložena postopka ozoniranja in  $H_2O_2/O_3$  ter pregled literature, ki se nanaša na ozoniranje in  $H_2O_2/O_3$  postopek čiščenja tekstilnih barvalnih kopeli, ki vsebujejo barvila z različnimi kromofornimi skupinami.

V nadaljevanju članka je podana učinkovitost postopka ozoniranja in  $H_2O_2/O_3$  pri različnih eksperimentalnih pogojih za razbarvanje in zniževanje ekoloških parametrov. Iz pregleda literature je razvidno, da se postopka ozoniranje in  $H_2O_2/O_3$  veliko uporabljata za odstranjevanje reaktivnih, kislih in direktnih barvil. Manj podatkov je o bazičnih, disperznih in kovinsko-kompleksnih barvilih.

**Ključne besede:** tekstilne obarvane vode, barvila, učinkovitost čiščenja, ozoniranje,  $H_2O_2/O_3$

### 1 Uvod

Tekstilna industrija je med največjimi porabniki sveže vode, barvil, pomožnih sredstev in kemikalij [1]. Največ odpadnih voda nastaja pri procesih mokrega plemenitenja, posebno pri procesih barvanja [2]. Poraba sveže vode v plemenitilnicah tekstilij se je z optimizacijo tehnoloških procesov sicer zmanjšala s 120–280 L/kg pod 100 L/kg tkanine [3, 4], še vedno pa ostanki že majhnih količin barvil v odpadnih vodah povzročijo vidno obarvanje [5].

## 1 Introduction

*The textile industry is one of the largest consumers of fresh water, dyes, auxiliaries and chemicals [1]. The largest amount of wastewater is produced in wet treatments, esp. in the dyeing processes [2]. With the technological process optimization in the textile treatment, the use of fresh water has reduced from 120–280 L/kg under 100 L/kg of fabric [3, 4], despite small amounts of dye still remaining in the wastewater, causing visible colouration [5]. The dyed wastewater is from an aesthetic and ecological viewpoint unacceptable, as it prevents the light penetration into the water environment and can contain toxic organic and inorganic components [6]. In order to protect the environment from hazardous pollution, the wastewater needs to be treated properly before the disposal into the environment [3]. Conventional treatment processes, e.g. sedimentation, flotation, and filtration (i.e. primary treatment), only remove the suspended substances, e.g. oils and fats [4]. A further biological cleaning (i.e. secondary treatment) is used to remove the dissolved or colloidal organic substances. Depending on the effluent source, there is also the possibility of a tertiary treatment for the removal of colouration, surfactants and/or to decrease the salt content [7]. The mentioned treatments often do not sufficiently remove the dyes from wastewater [5], which is visible as excess colouration [8]. Technological developments and consumer demands have brought about the development of new substances and additives into dye effluents, which are degradable with more difficulty (e.g. those resistant to microbiological degradation). Carefully selected wastewater treatment processes and appropriate management are of crucial importance for the adherence of demands imposed by the existing legislation for the protection of underground and surface waters. Recently, the trend has been to lower the limit values for the treated wastewaters discharged into the sewage system and directly into natural waters [9, 10]. The existing conventional processes that assure colour reduction are not economical, nor are they always efficient [11]. Among the priorities of the textile industry, there are sustained efforts to develop ecologically more suitable treatment processes [12].*

Obarvane odplake so z estetskega in ekološkega vidika nesprejemljive, ker preprečujejo prodiranje svetlobe v vodno okolje in lahko vsebujejo toksične organske in anorganske komponente [6]. Da bi obvarovali okolje pred tveganim onesnaženjem, je treba odpadne vode obdelati še pred izpustom v okolje [3]. S konvencionalnimi postopki čiščenja, kot so sedimentacija, flotacija in filtracija, se odstranijo le suspendirane snovi, olja in maščobe (primarna obdelava) [4]. Sledi biološko čiščenje (sekundarna obdelava) za odstranjevanje raztopljenih ali koloidnih organskih snovi, glede na izvor odplake pa je mogoča še terciarna obdelava za odstranitev obarvanosti, detergentov in/ali zmanjšanje vsebnosti soli [7]. Omenjeni postopki čiščenja pogosto iz odpadne vode ne odstranijo barvil v zadostni meri [5], kar se odraža kot čezmerna obarvanost [8]. Tehnološki napredek in zahteve potrošnikov so pripeljali do razvoja novih, težje razgradljivih barvil in dodatkov v barvalnih odplakah (npr. takih, ki so odporne na mikrobiološko razgradnjo). Ustrezno izbrani in pravilno vodeni postopki sanacije odpadnih voda so izjemnega pomena za izpolnjevanje zahtev obstoječe zakonodaje za varstvo podtalnih in površinskih voda, katerih trend so strožje mejne vrednosti za odvajanje obremenjenih voda v kanalizacijo in neposredno v vode [9, 10]. Obstoječi konvencionalni postopki za zagotovitev zmanjšanja obarvanosti niso ekonomsko ugodni, tudi ne vedno učinkoviti [11], zato je pospešeno iskanje ekološko primernejših postopkov obdelave obarvanih odplak med prednostnimi nalogami tekstilne industrije [12].

Reverzna osmoza, ultrafiltracija ali katerakoli membranska tehnologija v kombinaciji z adsorpcijo na aktivno oglje so učinkovite tehnologije [11, 13–18]. Zaradi visokih obratovalnih stroškov in stroškov, ki jih povzročajo njihovi odpadki, so še vedno zelo aktualne in zanimive kemijske oksidacije, predvsem pa napredni oksidacijski postopki (AOP), pri katerih ne nastajajo trdni odpadki ali odpadno blato [3, 7, 19]. Med AOP-postopke (angl. za napredni oksidacijski postopki) prištevamo vse postopke, ki uporabljajo  $H_2O_2$ , katerega aktivirajo s pomočjo različnih katalizatorjev ( $Fe^{3+}$  soli, UV,  $O_3$ , ...) [20]. Barvila in druga onesnaževala v odpadni vodi razgrajujejo, vendar jih redko popolnoma mineralizirajo v ogljikov dioksid in vodo [7, 21]. V obstoječi literaturi [3, 7, 10, 11, 22–24] je kot učinkovita alternativa za razbarvanje in zagotavljanje biološke razgradnje tekstilnih odplak pogosto naveden proces  $O_3$  in  $H_2O_2/O_3$ . Postopka  $O_3$  in  $H_2O_2/O_3$  zagotavljata hitro razgradnjo različnih organskih snovi v vodnih sistemih, ne puščata trdnih odpadkov [2], za 95-odstotno razbarvanje pa porabita 265–520-krat manj energije in kemikalij kot postopek UV/ $H_2O_2$  [11, 23]. Postopek ozoniranja učinkovito razbarva tudi močno obarvane odpadne vode iz industrije [1, 25], ki so obremenjene z različnimi tipi barvil (kisla, reaktivna, direktna, kovinsko-kompleksna, disperzna ...). Čeprav je ozon sam po sebi toksična substanca, s sodobno tehnološko izvedbo procesa preprečimo nekontroliran izpust letnega ozona v ozračje, medtem ko je ozon v vodnem mediju nestabilen in se po 20 minutah razgradi.

The reverse osmosis, ultra filtration or any other membrane technology in combination with the absorption to active carbon are all efficient technologies [11, 13–18]. Due to the high operational costs and costs caused by effluents, the chemical oxidation processes are still worth considering, esp. the so-called advanced oxidation processes (AOPs), which do not produce solid waste or sewage sludge [3, 7, 19]. AOPs comprise all the processes that use  $H_2O_2$ , where  $H_2O_2$  is activated with various catalysts (e.g.  $Fe^{3+}$  salts, UV,  $O_3$  etc) [20]. They dissolve dyes and other pollutants in wastewater; however, they rarely completely mineralise them into carbon dioxide and water [7, 21]. The  $O_3$  and  $H_2O_2/O_3$  process as listed in the existing literature [3, 7, 10, 11, 22–24] present another efficient alternative to decolourization and biological degradation improvement of textile wastewaters. Both  $O_3$  and  $H_2O_2/O_3$  processes ensure a fast degradation of various organic substances in the water systems. No solid waste is produced [2] and 265–520 times less energy and chemicals are required for a 95% decolourization than with the UV/ $H_2O_2$  process [11, 23]. The process efficiently decolourizes even the intensively coloured dye bath effluents from the textile industry [1, 25], which contain various dye classes (e.g. acid, reactive, direct, metal-complex, disperse etc). Despite ozone being toxic by itself, the uncontrolled exhaust into the atmosphere can be prevented by applying modern technological process performance. Since the ozone is unstable in water, it decomposes within 20 minutes.

## 2 Composition and characteristics of dye bath wastewaters

The effluents from the finishing processes contain diverse impurities, which differently load the waters. These can be divided from less threatening dyes (i.e. acid, reactive, direct, basic, disperse dyes), which influence the water appearance only visually, to the more dangerous substances, e.g. toxic heavy metals. Wastewaters from dyehouses, printing works and dying kitchens contain over 90% of all dye residue. As a consequence of inexhaustible dye baths, the wastewater from printing pastes, from cleaning the dying and printing machines, tools and

## 2 Sestava in lastnosti odpadnih barvalnih voda

Izpusti plemenitilnic vsebujejo raznovrstne nečistoče, ki v različni meri obremenjujejo vode. Razvrstijo se lahko od manj nevarnih barvil, ki motijo samo estetski videz voda (kisla, reaktivna, direktna, bazična, disperzna barvila), do bolj nevarnih snovi, ki spadajo med toksične snovi (težke kovine). Odpadne vode, ki izvirajo iz barvarn, tiskarn in pripadajočih barvnih kuhinj, vsebujejo več kot 90 odstotkov vseh ostankov barvil. To je posledica neizčrpanih barvalnih kopeli in tiskarskih barvnih gošč, ki se ne vračajo v barvno kuhinjo, voda od čiščenja barvarskih in tiskarskih strojev, orodij in embalaže [4], pralnih in izpiralnih kopeli [26]. Njihova sestava je zelo kompleksna in se ves čas spreminja [27]. Razlikujejo se po obarvanosti, količini in vsebnosti razgradnih produktov [28]. V odpadnih vodah po barvanju ostaja velika količina soli, natrijevega klorida, sulfata in sulfida, strupena tekstilna pomožna sredstva, reducenti in oksidanti, fosfati in druge kompleksne snovi, težko razgradljivi dispergatorji in tenzidi, nevezana barvila in iz njih izhajajoči ioni težkih kovin. Predvsem kovine, kot npr. krom, baker, nikelj itd., halogenirani ogljikovodiki, prosti klor, strupena tekstilna pomožna sredstva itd., ovirajo sam proces čiščenja voda [4]. Omenjene nečistoče vplivajo tudi na spremembo vonja odpadnih kopeli [2].

Za vrednotenje obremenjenosti barvalnih odpadkov z organskimi in anorganskimi snovmi se v praksi najpogosteje uporabljajo ekološki parametri, kot so obarvanost, KPK – kemijska potreba po kisiku, BPK<sub>5</sub> – biokemijska potreba po kisiku, TOC – skupni organski ogljik, AOX – adsorbiljni organski halogeni in LD<sub>50</sub> – letalna doza. Merilo obremenjenosti odpadnih voda z barvili predvsem nakazuje obarvanost oz. spektralni absorpcijski koeficient (SAK), medtem ko se za barvila z vsebnostjo kovinskih ionov uporablja vrednost LD<sub>50</sub>, ki je merilo strupenosti barvil. Barvila pripomorejo k onesnaženosti voda tudi s sestavinami, ki jih izdelovalci dodajo barvilom pri sintezah. O njih imamo le splošne informacije, saj njihova kemijska sestava praviloma ni navedena. To so snovi, ki se uporabljajo kot tenzidi, dispergirna sredstva, soli, polnila in gostila, sredstva proti prašenju, penjenju, zmrzovanju itd. Navedene kemikalije obremenjujejo odpadne vode in povečujejo vrednosti ekoloških parametrov KPK, BPK<sub>5</sub>, TOC, AOX in LD<sub>50</sub> veliko bolj kot sama barvila ter s tem omejujejo nadaljnje čiščenje odpadnih voda [4]. Manj obremenilna so tekoča barvila ali barvila v obliki testa ter visoko koncentrirana, npr. 200-odstotna barvila.

Odpadne barvalne kopeli so obremenjene z različnimi začetnimi koncentracijami barvil (od 10 do 70 g/L) [1], s spreminjajočo se KPK-vrednostjo in nihajočo vsebnostjo suspendiranih snovi, odvisno od vrste in tipa barvil. Glede na vrednost KPK, obarvanost in intenziteto motnosti se obarvane vode lahko razdelijo v tri skupine [29]:

- manj obarvane vode s KPK, nižjim od 800 mg  $O_2/l$ ,
- srednje obarvane vode s KPK med 800 in 1600 mg  $O_2/l$  ali
- močno obarvane vode s KPK nad 1600 mg  $O_2/l$ .

packaging [4], from washing, cleaning and rinsing baths do not return to the dyeing kitchen [26]. Their composition is very complex and changes constantly [27]. They differ in colour, amount and content of the degradation products [28]. After the dyeing process, such wastewaters also contain a large amount of salt, sodium chloride, sulphate and sulphide, toxic carriers and retarders, reduction and oxidation agents, phosphates and other complex substances, not readily degradable dispergation agents and surfactants, unfixed dyes and heavy metal ions deriving from the latter. In particular heavy metals, e.g. chrome, copper, nickel etc, halogenated hydrocarbons, total residual chlorine, carriers etc, hinder the wastewater treatment processes [4]. These pollutants also influence the odour change of dyebath wastewaters [2]. For the pollution evaluation of loaded dyebath wastewaters with organic and inorganic substances, the ecological parameters, e.g. colouration, COD – chemical oxygen demand,  $BOD_5$  – biological oxygen demand, TOC – total organic carbon, AOX – adsorbable organic halogens and  $LD_{50}$  – lethal dose, are commonly used in practice. The colouration or the so-called spectral absorption coefficient (SAC) is a primarily visible indication standard for the pollution load, while the toxicity of dyes with metal ions substance is described with the  $LD_{50}$  value. Dyes also contribute to the wastewater pollution with ingredients added by manufacturers during the dye synthesis. While only general information on such substances is available, their chemical composition is rarely listed. These substances are used as surfactants, dispergation agents, salts and thickening agents, anti-dusting, anti-foaming, anti-freezing substances etc. The chemicals pollute wastewater and increase the values of ecological parameters such as COD,  $BOD_5$ , TOC, AOX in  $LD_{50}$  far more than dyes. Therefore, the wastewater treatment processes are limited [4]. Minor load is caused by liquid dyes or dyes in a paste form as well as by highly concentrated dyes (e.g. 200% dyes).

Dyebath wastewaters are polluted with different initial dye concentrations (from 10–70 g/L) [1]. The COD values and content of suspended substances are changing; however, they depend on the class and dye type. According to the

Stopnja vezanja barvil na vlakna se giblje med 40 in 90 odstotki, kar je odvisno od tehnološkega postopka in vrste uporabljenih barvil [1]. Prebitek uporabljenih barvil lahko tudi v podobnih količinah, kot je stopnja fiksiranja, ostaja v odpadnih barvalnih vodah [13]. V preglednici 1 je prikazana stopnja vezave med barvilom in vlaknom ter delež nevezanega barvila v odpadni barvalni kopeli.

Table 1: Degree of fixation between dye and fibre, and degree of unbound dye in coloured wastewater [41, 42]

Dye class	Fibre	Degree of fixation (%)	Degree of unbound dye (%)
Acid	Polyamide	80–95	5–20
Basic	Polyacrylnitril	95–100	0–5
Direct	Cellulose	70–95	5–30
Disperse	Polyester	90–100	0–10
Metal - complex	Wool	90–98	2–10
Reactive	Cellulose	50–90	10–50
Sulphuric	Cellulose	60–90	10–40
Vat	Cellulose	80–95	5–20

Uporaba različnih vrst barvil in kemikalij pri barvanju je vzrok za znatne variacije ekoloških parametrov tekstilnih odpadnih voda. Primer lastnosti tekstilne odpadne vode prikazuje preglednica 2.

Table 2: Properties of textile industry wastewater [30, 48]

Parameters	Values
pH value	7.0–9.0
BOD – Biological Oxygen Demand ( $mg O_2/l$ )	80–6,000
COD – Chemical Oxygen Demand ( $mg O_2/l$ )	150–12,000
Total Suspended Solids ( $mg/l$ )	15–8,000
Total Dissolved Solids ( $mg/l$ )	2,900–3,100
Chloride content ( $mg Cl/l$ )	1,000–1,600
Total Kjeldahl Nitrogen ( $mg N/l$ )	70–80
Colour (Pt-Co)	50–2,500



COD value, colour and turbidity intensity, dyebath wastewaters can be subdivided into three groups [29]:

- lightly coloured dyebath wastewaters with COD lower than 800 mg  $O_2/l$ ,
- medium coloured dyebath wastewaters with COD between 800–1600 mg  $O_2/l$ , or
- intensively coloured dyebath wastewaters with COD above 1600 mg  $O_2/l$ .

The degree of dye fixation to a fibre is from 40–90%, and depends on the technological process and dye types used [1]. The excess of the used dyes can remain in the dyebath wastewaters in similar amounts as the fixation degree [13]. Table 1 displays the fixation degree between the dye and the fibre, and the percentage of non-fixed dye in the dyebath wastewaters.

The use of various dye types and chemicals in the dyeing process causes considerable variations in the ecological parameters of textile wastewaters. For example, the composite textile industry wastewater characteristics and the variations of ecological parameters are shown in Table 2.

On average, coloured textile wastewaters from a typical industrial dye factory represent the pollution potential for approx. 7,000 persons according to the amount (i.e. hydraulic water exhaust) or approx. 20,000 persons according to the organic load [27, 28]. The  $BOD_5$  concentration of such waters is mostly low, whereas COD can significantly exceed 10,000 mg  $O_2/l$  [29].

In Slovenia, the discharge of similarly polluted waters from the textile industry is regulated with the "Decree on the emission of substances in the discharge of waste water from plants and facilities for the production, processing and working of textile fibres", published in the Official Gazette of the Republic of Slovenia, No. 7/2007 [30].

## 2.1 Dyes in textile dyebaths and wastewaters

Commercial dyes are a mixture of coloured pigments and additives, which differ in their chemical structures, chromogen and purpose of use [30, 32]. According to the applicable characteristics and chemical composition, dyes are divided into direct, acid, basic, reactive, disperse, reduction, sulphuric, metal-complex, pigments

V povprečju obarvane tekstilne odpadne vode iz tipične industrijske barvarne pomenijo potencial onesnaževanja okrog 7000 oseb glede na količino (hidravlični izpusti vode) ali okrog 20.000 oseb glede na organsko obremenitev [27, 28]. Koncentracija  $BPK_5$  takšnih voda je večinoma nizka, KPK pa lahko krepko presega 10.000 mg  $O_2/l$  [29].

V Republiki Sloveniji je odvajanje podobno onesnaženih voda iz tekstilne industrije urejeno z „Uredbo o emisiji snovi in toplote pri odvajanju odpadne vode iz naprav za proizvodnjo, predelavo in obdelavo tekstilnih vlaken (Ur.l. RS, št. 7/2007)“ [30].

### 2.1 Barvila v tekstilnih barvalnih kopelih in odpadnih vodah

Tržna barvila so mešanice barvnih pigmentov in aditivov, ki se razlikujejo po kemijski strukturi, kromogenu in namenu uporabe [30, 32]. Glede na uporabne lastnosti in kemijsko zgradbo so barvila razvrščena na: direktna, kislila, bazična, reaktivna, disperzna, redukcijska, žveplena, kovinsko-kompleksna, pigmentna, ... [3, 25]. V različnih vrstah barvil se nahajajo ioni različnih kovin. V redukcijskih barvilih so bakrovi in kromovi ioni, v kislilih in reaktivnih barvilih bakrovi in svinčevi ioni, prav tako so svinčevi ioni v direktnih in disperznih barvilih; v bazičnih barvilih pa cinkovi ioni. Odpadne vode iz barvarn ponavadi vsebujejo manj kot 1 mg/l kovinskih ionov. Kovin, ki so dejansko strupene (npr. arzen, živo srebro, kadmij, ...), je v barvilih manj kot 1 mg/l, v vodah pa zanemarljivo majhna količina, zato niso dejavnik tveganja za okolje [4]. Povprečna svetovna proizvodnja znaša  $7 \times 10^5$  ton/leto 100.000 različnih komercialno uporabnih barvil [32, 34]. Dobra polovica (60–70 %) se jih porabi v tekstilni in oblačilni industriji za barvanje okrog 30 mio ton tekstilij [1, 2, 24, 33–35]. Nahajajo se v barvnih raztopinah, črnilih, barvah, lakih, papirju, plastiki, gumi, hrani, zdravilih in kozmetiki [23] ter naravnih in sintetičnih aplikacijah [28].

Največji ekološki problem sta v tekstilni industriji preprosta proizvodnja in široka uporaba različnih azo barvil [13, 28]. Barvila imajo visoko termično obstojnost in fotostabilnost [36], se akumulirajo v vodi in se težko razbarvajo [34]. Topna azo barvila lahko preidejo v telo živih organizmov in se razgradijo v toksične aromatske amine [37]. Na primer visoke koncentracije temnih antrakinonskih barvil z zapleteno strukturo aromatskih obročev in s kelatno vezanimi kovinami, kot so krom, kobalt, baker, železo in nikelj, otežujejo odstranjevanje obarvanosti [34, 38]. Poleg svetlih tonov kislilih barvil so za razbarvanje problematična tudi vodotopna reaktivna barvila [1, 34]. Določena hidrolizirana reaktivna barvila (npr. monoklorotriazini) imajo nizke vrednosti koeficientov biološke razgradljivosti  $BPK_5/KPK$  (ponavadi manj kot 0,1) [39], kar je ob nizki stopnji fiksiranja na vlakna (80–85 %) največkrat vzrok težjega razbarvanja neizčrpanih kopeli [4]. Počasna razgradnja pri operativnih pogojih [40], težko razbarvanje [34] in akumulacija v vodi [33] je posledica kemijske sestave, katalitične in mikrobiolo-

etc. [3, 25]. Various metal ions can be found in different dye classes. Copper and chrome ions are present in reduction and acid dyes. In reactive dyes, copper and lead ions occur, while direct and disperse dyes mostly contain lead ions, and basic dyes zinc ions. Metals that are in fact toxic (e.g. arsenic, quicksilver, cadmium etc.) are present in dyes in the concentration under 1 mg/l and in waters in negligible amounts. Therefore, they are not hazardous to the environment. Wastewaters from dyehouses normally contain less than 1 mg/l of metal ions [4]. The average world production amounts to  $7 \times 10^5$  tons per year of 100,000 various commercially used dyes [32, 34]. A good half (60-70%) is used in the textile and clothing industry for dyeing, i.e. for approx. 30 m tons of textile [1, 2, 24, 33-35]. Dyes are present in dyeing solutions, inks, paints, varnishes, paper, plastic, rubber, food, drugs and cosmetics [23], as well as in natural and synthetic applications [28].

The main ecological problem of the textile industry is the simple production and a wide use of various azo dyes [13, 28]. Dyes have a high thermal and photo stability [36], easily accumulate in water and are difficult to decolourize [34]. The water soluble azo dyes can settle in living organisms and dissolve into toxic aromatic amines [37]. For example, high concentrations of dark anthraquinone dyes with the complex structure of aromatic rings and chelating bound metal ions, e.g. chrome, cobalt, copper, iron and nickel, prevent the colouration removal [34, 38]. Besides the light tones of acid dyes, water soluble reaction dyes are also problematic for decolourization [1, 34]. Certain hydrolysed reactive dyes (e.g. monochlorotriazine) have low biological degradation ( $BOD_5/COD$ ) coefficients (usually less than 0.1) [39], which is due to the low degree of fixation to fibres (80-85%) the most common cause for difficult decolourization of dyebath wastewaters [4]. The slow degradation at inappropriate operating conditions [40], difficult decolourization [34] and accumulation in water [33] is a consequence of chemical composition, catalytic and microbiological stability of dyes [38]. Therefore, the decomposition of dyes in the environment is a slow and complicated process [36].

ške stabilnosti barvil [38], zato je njihova razgradnja v okolju počasen in zapleten proces [36].

### 3 Postopki razbarvanja tekstilnih odpadnih voda

Univerzalne metode, ki bi zagotavljala učinkovito razbarvanje kompleksnih kemijskih struktur barvil in nečistoč, še ni na trgu [28, 29]. Za razbarvanje odpadnih voda se uporabljajo fizikalni, biološki in kemični postopki ter njihove kombinacije [4, 32].

Fizikalno-kemijski postopki obdelave vključujejo [32]:

- metode zgoščevanja (koagulacijo, flokulacijo, sedimentacijo);
- adsorpcijo (na aktivno oglje, biološko blato, silikagel);
- membranske filtracije;
- destilacijo in ekstrakcijo (redko).

Za zgoščevalne metode se uporabljajo anorganski koagulant (apno, magnezij in železove soli) in potencialno toksični organski polimeri, ki lahko zavirajo proces razbarvanja [41]. Z adsorpcijo barvil na granulirano (ang. GAC – Granulated Activated Carbon) ali praškasto aktivno oglje (ang. PAC – Powdered Activated Carbon) so zaradi hitrega nasičenja absorpcijske kolone povezani visoki stroški regeneriranja GAC kolon [32, 41]. Standardni biološki postopki, t. i. aerobna obdelava (aktivacija biološkega blata v aeracijskih bazenih) in anaerobna obdelava (razkrajanje in gnitje v stabilizacijskih lagunah) [32] obarvanosti ne odstranijo, se pa velika količina nečistoč veže na biomaso [42]. Membranske tehnike, kot so mikrofiltracija, nanofiltracija in reverzna osmoza, so učinkovite kljub velikim investicijskim in obratovalnim stroškom ter nekaterim aplikativnim pomanjkljivostim. Mikrofiltracija je v primerjavi z reverzno osmozo ali postopkom adsorpcije na aktivno oglje manj učinkovita, saj le delno odstrani barvila in nečistoče. Nanofiltracija zadrži večino onesnaževalcev, prepušča pa majhne molekule soli in organskih snovi. Z reverzno osmozo lahko pri čiščenju odpadnih voda, ki poleg barvil vsebujejo klor, kationsko površinske aktivne snovi, dosežemo največ 80-odstotno učinkovitost, vsaj 20 odstotkov odplak pa ostane neočiščenih [41].

Pomanjkljivost fizikalnih postopkov je nastanek velikih količin trdnih odpadkov, odpadnega blata ali koncentriranih raztopin, ki zvišujejo stroške primerne predelave [23, 31, 33, 43] in njihovega odlaganja [2]. Kompleksometrične metode temeljijo na razpadu in odstranitvi kompleksno vezanih kovinskih ionov (kovinsko kompleksna, ftalocianinska barvila) v molekuli barvila s pomočjo selektivnih kompleksantov. Nevtralizacija, ionska izmenjava, kataliza, elektroliza itd., so namenjeni za splošno čiščenje odpadnih voda [4, 32], manj za razbarvanje.

Razbarvanje odpadnih voda z močnimi oksidanti, kot so klorov dioksid in klor, vodikov peroksid in ozon, je cilj kemijskih postopkov [41]. Najuporabnejši kemični postopki razbarvanja so: oksidacija z zračnim kisikom, ozonom ali oksidanti (klor, natrijev hi-

### 3 Decolourization procedures of textile wastewaters

The universal method which would ensure an efficient decolourization of complex chemical structures of dyes and impurities is not on the market yet [28, 29]. Several physical, biological and chemical processes and their combinations are used for the decolourization of wastewaters [4, 32].

Physical-chemical treatments include [32]:

- thickening method processes (coagulation, flocculation, sedimentation);
- adsorption (to active carbon, biological sludge, silica gel);
- membrane filtration processes;
- distillation and extraction (rarely).

Inorganic coagulants and potentially toxic inorganic polymers are used in the thickening processes (e.g. lime, magnesium and iron salts) and can obstruct the decolourization process [41]. The adsorption to GAC - granulated activated carbon or PAC - powdered activated carbon is connected due to the quick absorption of GAC colonies with high costs of the GAC colony regeneration [32, 41]. Standard biological processes, such as aerobic (i.e. activation of biological sludge in aeration pool) and anaerobic treatment (i.e. degradation and decay in stabilising lagoons) [32], are not efficient for decolourization; nevertheless, large amounts of impurities bound to the biomass [42]. Mem-

poklorit in vodikov peroksid) ter posredna oksidacija z UV-žarki. Hitra in učinkovita oksidacija že pri sobnih razmerah delno ali popolnoma razbarva vse vrste in strukturne oblike barvil.

Eksperimentalno je dokazano, da razgradnja reaktivnih in kislih barvil s plinastim klorom in z natrijevim hipokloritom v alkalnem mediju pri pH 9 in temperaturi 40 °C poteka hitro. Razbarvanje je skoraj popolno (98-odstotno), KPK-vrednost rahlo pade, AOX naraste. V nasprotju s tem se direktna in disperzna barvila v omenjenih postopkih s klorom im hipokloritom razbarvajo počasi in tvorijo razkrojne produkte rumene barve [4].

Reakcije razbarvanja z vodikovim peroksidom potekajo pri sobni temperaturi, v kislem mediju pri pH 3, približno 20 minut.  $H_2O_2$  razpade na hidroksilni radikal  $OH^\bullet$  in hidroksilni ion  $OH^-$ , v prisotnosti divalentnega železa kot katalizatorja pa še na  $Fe^{3+}$  ion (Fentonova reakcija). Barvila se razbarvajo do različne stopnje, od komaj opaznega razbarvanja nekaterih disperznih barvil, prek spremenjenih odtenkov, do popolnega (95-odstotnega) razbarvanja reaktivnih, direktnih, kislih in kovinsko kompleksnih barvil, v manjši meri tudi pigmentnih in redukcijskih barvil.

Postopek s pomočjo UV-žarkov je zaradi stroškov obratovanja (UV-žarnica) manj primeren s stališča ekonomičnosti. Redukcija z natrijevim ditionitom je omejena le na določena barvila (azo), pri čemer ne nastaja odpadno blato. Pomanjkljivost je v veliki porabi kemikalij in energije.

Vsem naprednim oksidacijskim postopkom so skupne kemijske reakcije, v katerih so udeleženi zelo reaktivni  $OH^\bullet$  radikali, ki lahko povzročijo razbarvanje in razgradnjo prisotnih onesnaževal v odpadnih vodah [44].  $OH^\bullet$  radikali nastajajo pri kemijskih reakcijah, ki vključujejo  $O_3$ ,  $H_2O_2$ ,  $TiO_2$ , UV-žarke, ultrazvočno valovanje, elektronsko žarčenje, posamezno ali v medsebojnih kombinacijah. Postopki, ki so učinkoviti za oksidacijo tekstilnih odpadnih voda, so zbrani v preglednici 3 [20, 45, 46].

Table 3: Advanced oxidation processes [20, 46]

(Advanced) oxidation processes			
$O_3$ (Ozonation)	$H_2O_2/UV$	$O_3/UV$	$\gamma$ - Gama beams (Radiolysis)
$H_2O_2$ (Hydrogen peroxide)	$H_2O_2/UV/Fe^{2+}$ (foto Fenton)	$O_3/H_2O_2$ (Peroxone)	$H_2O_2 + \gamma$ beams
UV (Ultraviolet beams)	$H_2O_2/Fe^{2+}$ (Fenton)	$O_3/UV/H_2O_2$	$O_3 + \gamma$ beams
$TiO_2$ (Photo-catalysis)	UV/ $TiO_2$	$O_3/TiO_2$ / Irradiation with electronic beams	$O_3 + H_2O_2 + \gamma$ beams
US (ultrasound) (Ultrasonic waving)	$O_3/US$	$O_3/TiO_2/H_2O_2$	$Fe^{2+} + UV$
Irradiation with electronic beams		$O_3 +$ Irradiation with electronic beams	$Fe^{2+} + \gamma$ beams

brane processes, e.g. microfiltration, nanofiltration and reverse osmosis, are efficient despite the large investment and operating costs, and certain application disadvantages. In comparison to the reverse osmosis or adsorption procedure to active charcoal, microfiltration is less efficient, as it only partially removes dyes and impurities. Nanofiltration rejects the majority of pollutants and permeates small salt molecules and organic substances.

With reverse osmosis wastewater treatment process, the purification efficiency of 80% (incl. removal of dyes that contain chlorine and surfactants) can be achieved, whereas at least 20% of the sewage remains untreated [41].

One disadvantage of physical processes is the production of solid waste, sewage sludge or concentrated solutions, which raise the costs of appropriate treatment process [23, 31, 33, 43] and effluents disposal [2]. Complexometric methods are based on the degradation and removal of complex bound metal ions from the dye molecule (metal-complex, phthalocyanine dyes) by selective complexants. Neutralization, ion exchange, catalysis, electrolysis etc. are generally used for wastewater treatment [4, 32] and less for decolourization.

Wastewater decolourization with powerful oxidants, e.g. chlorine dioxide and chlorine, hydrogen peroxide and ozone is the main purpose of chemical processes [41]. The most useful chemical decolourization processes are oxidation with air oxygen, ozone or oxidants (i.e. chlorine, sodium hypochlorite and hydrogen peroxide), and indirect oxidation with UV-beams. The oxidation partially or completely, quickly and efficiently decolourizes all classes and dye structures already at room temperature.

Experiments have shown that the degradation of reactive and acid dyes with gas chlorine and sodium hypochlorite in an alkaline medium (pH 9) and at temperature 40 °C is fast. The decolourization is almost complete (98%). The COD value decreases slightly, whereas AOX increases. In contrast, direct and disperse dyes decolourize slowly and form yellow-coloured degradation products in limited processes with chlorine and hypochlorite [4].

The decolourization reactions with hydrogen peroxide take place at room temperature, in acid

### 3.1 Postopek $O_3$ in $H_2O_2/O_3$

Kemijski metodi čiščenja voda, ozoniranje ( $O_3$ ) in postopek  $H_2O_2/O_3$  (Peroxone), učinkovito razbarvata in zmanjšata količine nečistoč v odplakah iz barvarn in plemenitilnic tekstilij [19]. Ozoniranje poteka v prisotnosti ozona ( $O_3$ ), katerega oksidacijski potencial ( $E^0 = 2,07$  V) je 1,52-krat večji [6, 34] od klorovega ( $E^0 = 1,36$  V) in  $H_2O_2$  oksidacijskega potenciala ( $E^0 = 1,78$  V) [27, 28]. Odstranjuje vonj, okus in suspendirane trdne snovi, izboljšuje biološko razgradljivost [7, 12], zmanjšuje obarvanost barvnih raztopin, barvalnih kopeli in obarvanih odplak [2], toksičnost ter delno znižuje vrednosti ekoloških parametrov [1, 8, 25, 34, 43]. Uspešno razgrajuje mikroorganizme, viruse in alge [1, 9], klorirane fenole, klorirane in aromatske hidrogenkarbonate, klorobenzene, cianide, alkohole, pesticide, aldehide in sulfide [8, 10, 34, 39].

Prednosti ozoniranja so [8]:

- učinkovito razbarvanje (več kot 90-odstotno) različnih vrst in koncentracij barvil,
- delna odstranitev organskih snovi (KPK) (do 60-odstotno),
- izločanje težkih kovin iz kovinsko-kompleksnih barvil [31],
- izboljšanje biološke razgradljivosti [6, 47],
- popolna razgradnja produktov,
- v procesu ne nastajata odpadni mulj in blato,
- vodenje procesa je preprosto,
- obstajajo številne možnosti aplikacij,
- prebitek ozona se razgradi v kisik in vodo že v nekaj minutah [31].

Omenjene prednosti dokazujejo številne aplikativne raziskave razbarvanja barvil v vodnem mediju [1, 8] ter v barvalnih [8, 11, 33, 45, 48, 49] in industrijskih tekstilnih odplakah [50–52], izvedene na pilotnih napravah [14, 52] in reaktorjih [18, 38, 47, 54] v razmerah batch ali semi-batch [5, 7, 15, 18, 25, 49, 55–58].

Ozoniranje se uporablja za dezinfekcijo in čiščenje pitne vode [59], za obdelavo, čiščenje in recikliranje [51–53] industrijskih odpadnih in pralnih voda, odpadnih voda iz kmetijstva, pakiranja, živilske [60], celulozne in papirne industrije, proizvodnje pesticidov, barvil, barvanja tekstilnih materialov, v proizvodnji antioksidantov za gume, v farmacevtski industriji [9]. Obetaven je na področju stekleničenja vode, medicinske terapije [10,39,59], čiščenju inficiranih medicinskih odpadnih voda in deaktivacije viroznih in mikrobioloških infekcij [47]. Z ekonomskega vidika je manj primeren za čiščenje odpadnih voda z veliko vsebnostjo suspendiranih trdnih snovi, visokimi vrednostmi BPK, KPK ali TOC [61]. Novejše raziskave kažejo, da se pogosto uporablja le še kot stopnja predobdelave, kateri sledi biološko čiščenje, pri kateri se cenovno ugodneje odstranijo lahko oksidirajoči produkti [9, 10]. Uspešnost takšnih sistemov nakazujejo študije razbarvanja kislih rdečih [62] in direktnih črnih barvil [43]. Ozon se kot dezinfekcijsko, detoksifikacijsko in sredstvo za zmanjševanje mutagenosti veliko uporablja tudi v kmetijstvu in živilski industriji [54].



with pH 3, for approx. 20 minutes.  $H_2O_2$  decays into hydroxyl radical  $OH^\bullet$  and hydroxyl ion  $OH^-$  in the presence of divalent iron as a catalyst and to  $Fe^{3+}$  ion (Fenton reaction). Dyes decolourize to a different degree - from barely noticeable, over altered tones (disperse dyes), to almost complete decolourization (95%) when decolourizing reactive, direct, acid and metal-complex dyes, and less for pigments and vat dyes.

From the economical point of view, the process with UV-beams is less appropriate due to operational costs (UV light). The reduction of sodium dithionite is limited to certain dyes (azo) and does not form sludge. The process disadvantage is also in the high consumption of chemicals and energy.

All advanced oxidation processes have common chemical reactions. The decolourization is accelerated with highly reactive  $OH^\bullet$  radicals, which can cause decolourization and degradation of pollutants present in wastewaters [44].  $OH^\bullet$  radicals are formed in chemical reactions which include  $O_3$ ,  $H_2O_2$ ,  $TiO_2$ , UV beams, ultrasonic waving, electronic radiation, either individually or in combinations. The processes which efficiently oxidize textile wastewaters are presented in Table 3 [20, 45, 46].

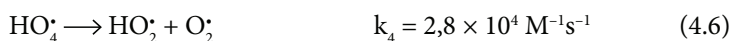
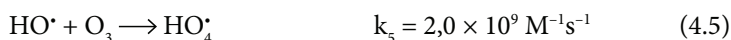
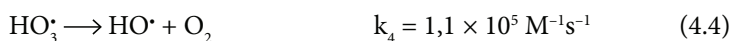
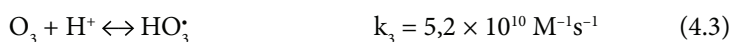
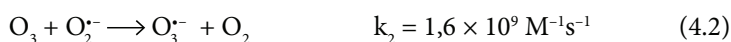
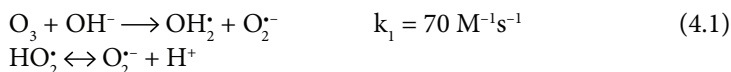
### 3.1 $O_3$ and $H_2O_2/O_3$ process

The chemical methods for water purifying, i.e. ozonation ( $O_3$ ) and  $H_2O_2/O_3$  (Peroxone) process, efficiently decolourize and reduce the amount of impurities in the dyebath wastewaters [19]. The ozonation occurs in the presence of ozone ( $O_3$ ), which has an oxidation potential ( $E^0 = 2.07$  V) 1.52-times higher [6, 34] than chlorine ( $E^0 = 1.36$  V) and  $H_2O_2$  ( $E^0 = 1.78$  V) [27, 28]. It removes odour, taste and suspended solids, improves biological degradation [7, 12], reduces the colour of dye solutions, dyebaths and dyed wastewaters [2], toxicity. Furthermore, it partially reduces the ecological parameter values [1, 8, 25, 34, 43] and successfully degrades microorganisms, viruses and algae [1, 9], chlorine phenols and aromatic hydrogen carbonate, chlorine benzenes, cyanides, alcohol, pesticides, aldehydes and sulphides [8, 10, 34, 39].

The advantages of the ozonation process are [8]: - efficient decolourization (over 90%) of different class and dye concentrations,

## 4 Kemizem postopka $O_3$ in $H_2O_2/O_3$

Ozon ( $O_3$ ) onesnaževala v vodnem mediju oksidira direktno ali s pomočjo nastalih hidroksilnih radikalov, ki nastajajo pri reakciji iniciacije (enačbi 4.1–4.2), propagacije (enačbe 4.3–4.7) in terminacije (enačbi 4.8–4.9). Konstante reakcijskih hitrosti ( $k_{1-6}$ ) reakcij 2. reda so podane v enotah koncentracija/čas ( $M^{-1} \times s^{-1}$ ), kjer pomeni M molarnost oz. koncentracijo v mol/L [63, 64]. Reakcijski časi so kratki (približno 10–30 sekund) [61].



Ozon je v vodi obstojen le 20 minut, čas obstojnosti se v prisotnosti barvil še skrajša. Začetne reakcije razbarvanja so hitre reakcije 1. reda [5, 48, 57], odvisne od začetne koncentracije barvila in ozona v vodi [1, 2, 13, 43, 65]. Zato se ozon za reakcije z barvili in nečistočami proizvaja sprotno (maksimalna koncentracija je 4–8 %) iz suhega zraka ali kisika ob izkoristku le 5–10 odstotkov vložene energije [9]. Na proces razbarvanja z ozonom vpliva več spremenljivk, in sicer: vrednost pH, koncentracija oz. pretok ozona, koncentracija barvila, hitrost in čas ozoniranja, temperatura [24], prisotnost soli [66], katalizatorjev [9], itd. To potrjujejo raziskave pomembnosti posameznih spremenljivk in optimalnih pogojev ozoniranja z različnimi modeli: metoda Taguchi in ortogonalno razporejeni  $L_{18}$  ( $2^1 \times 3^7$ ) eksperimentalni načrt [26], s  $3 \times 3$  faktorski načrt [6], modificirani  $2^{5-1}$  faktorski načrt [47] ter sestavljenim centralnim načrtom Box Hunter [66].

Kadar v vodo dodajamo vodikov peroksid, govorimo o postopku Peroxone ( $H_2O_2/O_3$ ). Vodikov peroksid v vodi razpade po naslednjem mehanizmu (4.9):



Nastali  $HO_2^-$  ion reagira z ozonom, pri čemer nastanejo  $OH^\bullet$  radikali (4.10):

- partial removal of organic substances (COD) (up to 60%),
- elimination of heavy metals from metal-complex dyes [31],
- biological degradation improvement [6, 47],
- complete process products decomposition,
- no waste sludge and slit by-products production,
- simple process handling,
- numerous application possibilities,
- excess of ozone degrades into oxygen and water in only a few minutes [31].

Numerous applicative researches prove these advantages for dye decolourization in water [1, 8] and dyebaths [8, 11, 33, 45, 48, 49], as well as for industrial textile wastewaters [50-52] performed on pilot devices [14, 52] and in reactors [18, 38, 47, 54] at batch or semi-batch conditions [5, 7, 15, 18, 25, 49, 55-58].

Ozonation is used for disinfection and drinking water cleaning [59], for treatment, purifying and recycling [51-53] of industrial wastewater and washing (rinsing) water, agriculture wastewater, wastewater from packaging and food industry [60], cellulose and paper industry, pesticide production, dyes production, textile colouration processes, in antioxidants production for tyres, as well as in the pharmaceutical industry [9]. Moreover, the ozonation process is very promising in the water bottling production, health treatments [10, 39, 59], for infected medical wastewater cleaning, deactivation of viral and microbiological infections [47]. Economically speaking, it is less suitable for the wastewater treatment with a high content of suspended solids and high BOD, COD or TOC values [61]. Latest research shows that it is often used as a pre-treatment step followed by a biological treatment for a cheaper removal of oxidation products [9, 10]. The success rate of such systems is shown by decolourization studies of acid red [62] and direct black dyes [43]. Ozone is intensively used as a disinfectant, detoxification agent to reduce mutagenicity in farming and food industry [54].

#### 4 Chemistry of $O_3$ and $H_2O_2/O_3$ process

Pollutants in water are instantly oxidised by ozone ( $O_3$ ) or with the help of hydroxyl radicals

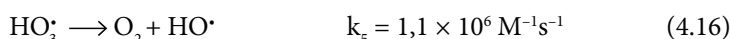
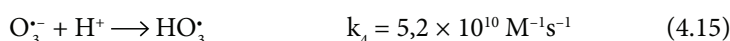
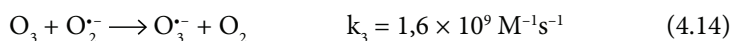
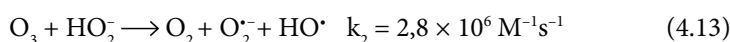
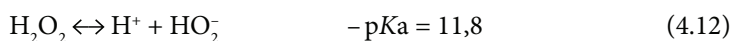


Največ dve molekuli  $O_3$  sta potrebni za nastanek dveh  $OH^\bullet$  radikalov (4.11). Le-ti imajo visok električni potencial in veljajo za eno najmočnejših oksidacijskih sredstev.



Aktivacija radikalov poteka po različnih reakcijskih mehanizmih, to je odvisno od tipa barvila in drugih onesnaževal, prisotnih v odpadni vodi [46].

Oksidacijski potencial hidrosilnih radikalov je večji kot oksidacijski potencial molekule ozona, zato je direktna oksidacija z ozonom počasnejša kot oksidacija s prostimi radikali. Razlika v reakciji je razvidna iz vrednosti konstant reakcijskih hitrosti reda  $10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (4.14 in 4.15) in  $10^6 \text{ M}^{-1} \text{ s}^{-1}$  (4.13 in 4.16) [26].



Prednost  $O_3$  in  $H_2O_2/O_3$  pred drugimi AOP-postopki je sposobnost razbarvanja različnih organskih komponent, raztopljenih v vodi v kislem, nevtralnem in/ali v bazičnem pH mediju [13, 33, 55, 67]. V bazičnem mediju (pH nad 7-8) potekajo indirektno reakcije z  $OH^\bullet$  radikali in drugimi radikalskimi spojinami. Povzročajo delno oksidacijo vseh delov molekule barvila, ki po ozoniranju ostanejo v vodi [6]. Nepopolno oksidirane komponente so lahko vzrok za toksičnost in mutagenost očiščenih odpadnih voda, vendar so po mnenju večine raziskovalcev obarvane odpadne vode iz tekstilne industrije po ozoniranju manj toksične in bolj biološko razgradljive [56]. V kislem mediju (pH pod 6) je molekularni ozon stabilen in direktno reagira z organskimi substancami ali nenasičenimi kromofornimi vezmi v barvilu kot elektrofil oz. elektronski akceptor [6, 33, 67]. Direktno reakcije hidrosilnih radikalov  $OH^\bullet$  z različnimi nečistočami (M) v vodi so selektivne in počasne [33], indirektno pa imajo neselektivno naravo [55] (slika 1), so počasne



Figure 1: Scheme of ozone reactivity in water [67]

(OH $\cdot$ ) formed during the initiation (cf. Equations 4.1-4.2), propagation (cf. Equations 4.3-4.7) and termination (cf. Equations 4.8-4.9) reactions. The reaction constant rates ( $k_{1,c}$ ) for the 2<sup>nd</sup> order reactions are given in the units of concentration/time ( $M^{-1} \times s^{-1}$ ), where  $M$  stands for molarity or concentration in mol/L [63, 64]. Reaction times are short (approx. 10-30 seconds) [61].

Ozone is stable in water only for 20 minutes and in the presence of dyes, that time shortens. The initial decolourization reactions are fast reactions of the 1<sup>st</sup> order [5, 48, 57], depending on the initial dye concentration in the water [1, 2, 13, 43, 65]. Due to the dye and impurities reactions, ozone is manufactured from dry air or oxygen in-situ (maximal concentration 4-8%). The input energy consumption is only 5-10% [9]. There are many variables affecting the decolourization process with ozone, i.e. pH value, concentration or ozone flow, initial dye concentration, velocity and ozonation time, temperature [24], presence of salt [66], catalysts [9] etc. The latter is confirmed with researches of the importance of individual variables and optimal conditions of ozonation with various models, namely the Taguchi method and orthogonally distributed  $L_{18}$  ( $2^1 \times 3^7$ ) experimental design [26], with  $3 \times 3$  factor design [6], modified  $2^{5-1}$  factor design [47] and combined central design Box Hunter [66].

When hydrogen peroxide is added into water, the so-called Peroxone process ( $H_2O_2/O_3$ ) is activated. Hydrogen peroxide in water dissociates according to the following mechanism (Equation 4.9).

The emerged  $HO_2$  ion reacts with ozone, creating OH $\cdot$  radicals (Equation 4.10).

At least two molecules of  $O_3$  are required for the emergence of two OH $\cdot$  radicals (Equation 4.11). Only these have high electric potential and are one of the most powerful oxidation agents.

Radical activation takes place at various reaction mechanisms, depending on the dye type and other pollutants present in the wastewater [46].

The oxidation potential of hydroxyl radicals is higher than the oxidation potential of ozone molecules; therefore, direct oxidation is slower than the oxidation with free radicals. The differ-

in potekajo hitreje z naraščanjem pH. Ponavadi omenjene reakcije ozoniranja potekajo sočasno. Med direktnimi reakcijami prihaja do razgradnje aromatskih obročev s pomočjo cikloadicije ozona, indirektno pa povzročajo mineralizacijo organskih komponent, ki vsebujejo ogljik (zniževanje TOC) [33].

Na učinkovitost razbarvanja z ozonom v veliki meri vpliva kemijska struktura barvil [2]. Prva stopnja razgradnje je zelo hitra in selektivna oksidacija posameznih kromofornih azo skupin ali večkratnih nenasičenih dvojnih azo vezi ( $-\dot{C}=\dot{C}-$ ,  $-\dot{C}=N-$  ali  $-N=N-$ ), vezanih na aromatski obroč vodotopnih barvil [9, 41]. Pogosteje uporabljena poliazobarvila se težje razbarvajo kot monoazobarvila. Pri ozoniranju azobarvil nastajajo vmesni produkti [2], imenovani prekurzorji (npr. elementarni dušik, fenol, kinoni) [42] (slika 2).

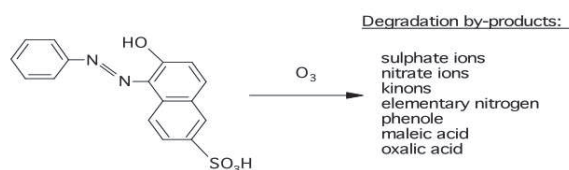


Figure 2: Scheme of ozone influence on a model azo dye [42]

Nastali prekurzorji reagirajo v končne produkte [2], kot so organske in anorganske [1, 2, 23, 33, 39, 43], pretežno preproste karbonske kisline (oksalna, maleinska [42] in mravljična, mukonska [50]) (slika 3) [12], posledica tega pa je znižanje pH vrednosti in povečanje prevodnosti.

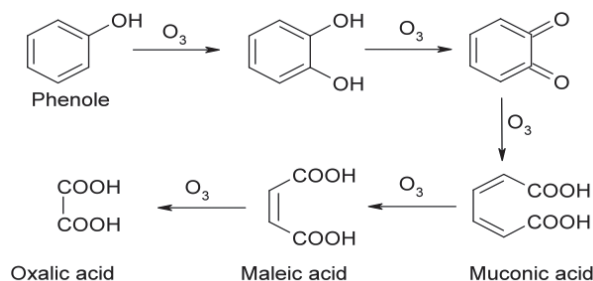


Figure 3: Phenole ozonation by-products [42]

Pregled člankov, ki obravnavajo učinkovitost postopka ozoniranja in  $H_2O_2/O_3$  pri različnih pogojih odstranjevanja najpogosteje uporabljenih tekstilnih barvil, je povzet v preglednici 4. Poraba ozona je glede na različne kategorije porabe  $O_3$  podana v različnih enotah (hitrost pretoka v mg/min ali mg/(l  $\times$  min) ali l/min; proizvodnja ozona v g/h ali %; koncentracija ozona v mg/l ali %). Načrtovanje porabe ozona je odvisno od začetne koncentracije barvila v barvalni kopeli in od lastnosti strojne opreme, kar je podrobneje opisano v navedenih referencah. Enako velja za porabo vodikovega peroksida, ki je največkrat podana v enotah, kot so ml/l, mol, g/l.

Table 4: Efficiency of ozonation and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> process at different conditions for removing different classes of textile dyes

Method	Dye Class	Colour Index (C.I.) and Trade name	Initial dye conc. (mg/l; μmol; mol/l)	Consumption		pH	Ozonation time (min)	Decolourization efficiency (%)	COD/(TOC) (decrease in % regarding the initial value)	Reference
				O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>					
O <sub>3</sub>	REACTIVE	Reactive Yellow 84 / Procion Yellow H-E4R (80% dye purity)	200 mg/l	9.1-18.5 mg/l		6.3	60	almost complete	50; (30)	Koch et al, (2002) [39]
		Reactive Black 5	250-300 mg/l	26.1 mg/l-min		unknown	10-30	99-100	27-87	Wu and Wang, (2001) [25]
		Remazol Black 5 / Brasilen Schwarz FB (75% dye purity)	200 mg/l	20.500 g/l		7.4	180-360	99.5-100	40; (25)	Wang et al, (2003) [1]
		Reactive Red 120 (75% dye purity)	200-500 mg/l	8.9-20 mg/l		10	90	93.7	74.1	Zhang et al, (2004) [8]
		Reactive Blue 15	500-3000 mg/l	16.7-69.7 mg/l-min		unknown	30-40	90-95	51.7-84.6	Wu et al, (2008) [69]
		Reactive Orange 113	60 mg/l	17 mg/l		2.4	6	100	44; (36)	Gutowska et al, (2007) [70]
		Reactive Blue 19	30 mg/l	0.14 g/h		7	5-10	99-100	0-100	Peralta-Zamora et al, (1999) [27]
		Reactive Blue 220; Black 5; Blue 28; Red 22; Yellow 15; Remazol Dark Black N (C.I. unknown)	200 mg/l	0.0813 mol/l	4.5 ml/l (w=35%)	1	60-120	99-100	COD <sup>end</sup> 170 mg/l O <sub>2</sub>	Kurbus et al, (2003) [71]
		Reactive Red 2	40 mg/l	2060 mg/l	20.5-1 g/l (w = unknown)	10	30	1: 95% 2: 57	unknown	Wu and Ng, (2008) [68]
		O <sub>3</sub> and H <sub>2</sub> O <sub>2</sub>								



Table 4: Efficiency of ozonation and  $H_2O_2/O_3$  process at different conditions for removing different classes of textile dyes

Method	Dye Class	Colour Index (C.I.) and Trade name	Initial dye conc. (mg/l; $\mu$ mol; mol/l)	Consumption		pH	Ozonation time (min)	Decolourization efficiency (%)	COD/(TOC) (decrease in % regarding the initial value)	Reference
				$O_3$	$H_2O_2$					
$O_3$	ACID	Acid Brown 159 (metal-complex)	100 mg/l	17 mg/l		2; 4	7	100	56.1; (54.1)	Jóźwiak et al, (2007) [38]
		Acid Red 88	500 $\mu$ mol	2 g/h		3; 11	3-15	99.9	64	Muthukumar et al, (2004) [71]
		Acid Yellow 17	1-250 mg/l	79.2 mg/min		7	40	99.9	55.5	Lackey et al, (2006) [48]
		Acid Red 151	$44 \times 10^{-6}$ mol/l	2-2.8 mol/l		<sup>a</sup> 2.5 <sup>b</sup> 10	10	<sup>a</sup> 98 <sup>b</sup> 87	<sup>a</sup> 58	Özbelge et al, (2003) [73]
		Acid Orange 52 / Methyl Orange	40 mg/l	4-75 mg/l		9.3	15	97	unknown	Chen, (2000) [47]
		Orange II (C.I. 16185); Acid Red 27 (C.I. 15510)	$1 \times 10^{-4}$ mol/l	3.3 L/min		9	30	98	(20-45)	Silva et al, (2009) [74]
		Procion red MX-5B	250 mg/l	0.26 g/h		11	5-30	79	58-80; (60.4-75)	Pachhade et al, (2009) [75]
		Acid Orange 8 (65% dye purity)	20-40 $\mu$ mol	2 g/l		5	30	95	unknown	Gültekin and Ince, (2006) [13]
		Acid Blue 62 (C.I. 62045) / Polan blue E2R	100-200 mg/l	6-36 mg/l	1 ml/l (w=30%)	3.8	25-30	90-95	unknown	Perkowski and Ledakowicz, (2002a, b) [24, 45]
		Acid Red 88 (C.I. 15620)	50 mg/l	2 g/h	$5.4 \times 10^{-4}$ mol (w=33%)	7	15	84	57; (36)	Dominguez et al, (2005) [65]
$O_3$ and $O_3/H_2O_2$		Acid Blue 193; (C.I. 15707; C.I. 15705) - 2:1 chromium complex	100-400 mg/l	1-2 g/h	7; 12	20-40	95-98	36-45; (22-35)	Bauman et al, (2007, 2008) [76, 77]	

Table 4: Efficiency of ozonation and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> process at different conditions for removing different classes of textile dyes

Method	Dye Class	Colour Index (C.I.) and Trade name	Initial dye conc. (mg/l; μmol; mol/l)	Consumption		pH	Ozonation time (min)	Decolourization efficiency (%)	COD/(TOC) (decrease in % regarding the initial value)	Reference
				O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>					
O <sub>3</sub>	DIRECT	Isma fast Red 8B	300 mg/l	25 g/l		11; 12	10	54.3	unknown	Kosnowa, (2003) [22]
		Direct Blue 71 / Sirius Blue SBRR	100-800 mg/l	24 g/m <sup>3</sup>		12	26	97.4	unknown	Turhan and Turgut, (2009) [78]
		Direct Blue 199	20 mg/l	6 l/min; 5%		6.8	2-15	99.9	(60)	Shu, (2006) [50]
		Direct Black 22	20 mg/l	6 l/min		6.4	5-160	99.9	(33)	Shu and Chang, (2005a, b) [23, 43]
O <sub>3</sub> and O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	METAL-COMPLEX	Bomalex Red CR-L	200-600 mg/l	164 mg/min		9.3	5-30	80-99	50	Oguz and Keskinler, (2008) [79]
		Bomalex Red CR-L	400-1000 mg/l	0.7- 1.4 O <sub>3</sub> %; 164-493 mg/min	7-21 × 10 <sup>-3</sup> mol (w=30%)	12; 9.3	15-30	99	54	Oguz and Keskinler, (2005, 2007) [18, 21]
O <sub>3</sub>	BASIC	Basic Red 46 / Cationic Red X-GRL	50 mg/l	3 g/h		9.2	6-60	93-100	(5.7-34.9)	Zhao et al, (2004) [33]
		Basic Red 9 (C.I. 42500) /Parosaniline monohydrochloride (88% dye purity)	1.2 · 10 <sup>-5</sup> mol/l	25 mg/h; 1.3 l/min		5-6	2-120	100	increased - unknown	De O. Martins et al, (2005) [54]
O <sub>3</sub>	DISPERSE	Disperse Red 354 /Foron Rubin S <sub>2</sub> GLF	45.756 μmol	8.2 mg/l		6.7	30	29.3	14.2; (29.3)	Neamtu et al, (2004) [19]

ence in the reaction is visible from the values of constants of reaction rates of order  $10^9$ – $10^{10} M^{-1} s^{-1}$  (cf. Equations 4.14 and 4.15) and  $10^6 M^{-1} s^{-1}$  (cf. Equations 4.13 and 4.16) [26].

The advantage of the  $O_3$  and  $H_2O_2/O_3$  process over other AOPs is the decolourization ability of different organic components dissolved in the water, acid, neutral and/or basic pH medium [13, 33, 55, 67]. In a basic pH (7–8), indirect reactions with  $OH^\cdot$  radicals and other radical compounds take place. The dye molecule partially oxidizes all sites, and after the ozonation degradation, the products remain in the water [6]. The incompletely oxidised components can cause toxicity and mutagenicity of treated wastewaters. Recently, most researchers have stated that after the ozonation, the dye-bath wastewaters from the textile industry are less toxic and more biodegradable [56]. In an acid pH (under 6), the molecular ozone is stable and reacts directly with organic substances or unsaturated chromophore dye bonds as an electrophyl or electronic acceptor [6, 33, 67]. The direct reactions of hydroxyl radicals  $OH^\cdot$  with different impurities (M) in water are very selective and slow [33], whereas the indirect ones have a non-selective character [55] (cf. Figure 1), they are slow and take place faster when increasing the pH value. Usually, all of the mentioned reactions take place simultaneously. During direct reactions, the decomposition of aromatic rings with cycloaddition of ozone is performed, while the indirect reactions cause mineralisation of organic components, which contains carbon (reduction of TOC) [33].

The decolourization efficiency of ozone is influenced by the chemical structure of dyes [2]. The first decomposition level is a rapid and selective oxidation of chromophoric azo groups or multiplied unsaturated double azo bonds ( $-\overset{|}{C}=\overset{|}{C}-$ ,  $-\overset{|}{C}=\overset{|}{N}-$  ali  $-\overset{|}{N}=\overset{|}{N}-$ ), bound to the aromatic ring of water soluble dyes [9, 41]. The more frequently used polyazo dyes are more difficult to decolourize than monoazo dyes. Intermediate products, the so-called precursors (e.g. elementary nitrogen, phenols, quinones) [42] are formed when ozonating azo dyes [2] (cf. Figure 2).

The formed precursors react into end products [2], both organic and inorganic [1, 2, 23, 33, 39,

Iz preglednice 4 je razvidno, da je bilo do zdaj največ obdelav odpadnih tekstilnih barvalnih kopeli s postopkoma  $O_3$  in  $H_2O_2/O_3$  narejenih na reaktivnih barvilih. Za odstranjevanje kislih, direktnih, bazičnih in disperznih barvil obstaja manj referenc, med proučevanimi postopki pa prevladuje ozoniranje.

Učinek razbarvanja je odvisen predvsem od eksperimentalnih pogojev, kot so: vrsta barvila, koncentracija barvila, reakcijski čas, pH vrednost. Oba postopka uspešno razgradita in razbarvata reaktivna, kislila, direktna, kovinsko-kompleksna in bazična, manj disperzna barvila. Če učinek razbarvanja primerjamo glede na barvo kromofora, se v primerjavi z rumenimi, oranžnimi, modrimi in črnimi barvili slabše razbarvajo rdeča barvila, in sicer disperzno (Disperse Red 354), direktno (Isma fast Red 8B), kovinsko-kompleksno (Bomaplex Red CR-L) ter nekatera rdeča kislila (Procion red MX-5B), predvsem v alkalnem mediju (pH med 9 in 11).

Med reaktivnimi barvili je bilo največkrat obravnavano barvilo Reactive Black 5, sam [1, 25, 71] v primerljivih začetnih koncentracijah barvila (200–300 mg/l). Učinek razbarvanja je v vseh primerih med 99 in 100 odstotki, KPK vrednosti so se znižale v odvisnosti od časa ozoniranja in porabe ozona med 27 in 87 odstotki; TOC vrednosti pa za 25 odstotkov. Postopka  $O_3$  in  $H_2O_2/O_3$  sta primerna tudi za reaktivna barvila drugih odtenkov (oranžna, modra, rdeča) [8, 27, 39, 69, 70, 68], saj je učinek razbarvanja v vseh primerih med 90 in 100 odstotki, KPK in TOC pa se znižata primerljivo z rezultati, podanimi za Reactive Black 5.

Med kislimi barvili so najpogosteje obravnavana rdeča, in sicer Acid Red 88 [65, 71], Acid Red 151 [73], Acid Red 27 [74] in Procion red MX-5B [75]. Navedena rdeča barvila so se odlično razbarvala (učinek razbarvanja je med 90 in 99,9 %) v kislem mediju (pH med 2,5 in 4), medtem ko v alkalnem mediju (pH od 9 do 11) dosegajo največ 87-odstotno razbarvanje. Oranžna kislila [13, 47, 74] so se čistila tako v kislem kot v alkalnem mediju. Učinek razbarvanja v obeh medijih je primerljiv, med 95 in 98 odstotki. Znižanje KPK-vrednosti dosega od 50 do 60 odstotkov začetne vrednosti in je odvisno tako od začetne koncentracije barvila kot od pogojev čiščenja. Podatkov za TOC je manj, nakazujejo pa zmanjšanje začetne TOC-vrednosti za 20 do 45 odstotkov, izjema je Procion red MX-5B, kjer se TOC zmanjša za 75 odstotkov.

Za direktna, bazična in disperzna barvila je bil do zdaj v najdeni literaturi opisan le postopek  $O_3$ , medtem ko nismo zasledili nikakršnih podatkov za postopek  $H_2O_2/O_3$ . Med direktnimi barvili sta obravnavani dve modri [50, 78] ter po eno rdeče [22] in črno [23, 43] barvilo. Učinek razbarvanja je odvisen od začetne koncentracije barvil, časa in pogojev ozoniranja in znaša od 97 do 99,9 odstotka; izjema je barvilo Isma fast red 8B, ki se je po 10 minutah razbarvalo manj kot 55-odstotno. Medtem ko podatki o KPK niso bili navedeni, se vrednosti TOC zmanjšajo za 33 do 60 odstotkov.

Med kovinsko kompleksnimi barvili je bilo obravnavano le barvilo Bemaplex Red CR-L [18, 21, 79], ki se je po 30 minutah razbarva-

43], predominantly to simple carboxylic acid (oxalic, maleic [42] and formic, muconic [50]) (cf. Figure 3) [12]. Consequently, the pH value decreases and conductivity increases.

An overview of articles which deal with the efficiency of the ozonation and  $H_2O_2/O_3$  process at various conditions for colour removal of commercial textile dyes is noted in Table 4. The use of ozone depends on various categories of use of  $O_3$  given in different units (flow velocity in mg/min or mg/(l×min) or l/min; ozone production in g/h or %; ozone concentration in mg/l or %). The ozonation addition to the process depends on the initial dye concentration in the dye bath and on the machine equipment characteristics, which is described in more details in the cited references. Similar is true for the hydrogen peroxide, mostly given in units ml/l, mol, g/l.

Table 4 clearly shows that most treatments of textile dye baths containing reactive dyes were performed with the  $O_3$  and  $H_2O_2/O_3$  process. For the removal of acid, direct, basic, and disperse dyes, there are fewer references; however, among them, the ozonation process studies dominate. The effect of decolourization depends mostly on the experimental conditions, e.g. dye type, dye concentration, reaction time and pH value. Both processes successfully degrade and decolourize reactive, acid, direct, metal-complex and basic dyes, and a little less efficiently disperse dyes. When comparing the decolourization effect according to the chromophore colour, among yellow, orange, blue, and black dyes, less decolourization is achieved for red dyes, esp. disperse (Disperse Red 354), direct (Isma Fast Red 8B), metal-complex dyes (Bomaplex Red CR-L) and certain red acid dyes (Procion Red MX-5B), most of all in an alkaline pH (between 9 and 11).

Among reactive dyes, the Reactive Black 5 dye was most frequently the subject of research [1, 25, 71] in comparable initial dye concentrations (200–300 mg/l). The decolourization efficiency was in all experiments between 99 and 100%, the COD values decreased by 27 to 87% and TOC by 25%.

Regarding the ozonation time and ozone application, the  $O_3$  and  $H_2O_2/O_3$  process are also suitable for other reactive dye tones (e.g. orange, blue, red) [8, 27, 39, 69, 70, 68]. In comparison

lo 99-odstotno po obeh postopkih ( $H_2O_2/O_3$  in  $O_3$ ). KPK- vrednost se je zmanjšala za 50 odstotkov, podatkov za TOC ni.

V skupini bazičnih in disperznih barvil so bila obravnavana štiri rdeča barvila [19, 33, 54] v različnih razmerah ozoniranja (pH vrednost med 5 in 9,2). Učinek razbarvanja je pri bazičnih barvilih med 93 in 100 odstotki, pri disperznem pa le 29,3 odstotka, kar izhaja iz kemijskih lastnosti disperznega barvila. Skladno s tem se je KPK-vrednost disperznega barvila glede na začetno vrednost zmanjšala za 14,2 odstotka, medtem ko se pri bazičnem barvilu Basic red 9 po ozoniranju KPK celo poveča [54]. Za omenjeno barvilo za TOC-vrednost ni podatka, pri preostalih, enem bazičnem in enem disperznem, pa se TOC zmanjša za 6 do 35 odstotkov.

## 5 Sklep

V 21. stoletju je čedalje bolj jasno, da je ozon vsestransko uporaben, kar potrjuje množična objavljena literatura s področja različnih strok [54]. Na učinek razbarvanja z ozonom vplivajo predvsem: a) začetna koncentracija barvila, b) pretok ozona c) pH medija, d) čas razbarvanja, e) temperatura, f) dodatek soli (elektrolitov) in g) dodatek vodikovega peroksida pri postopku  $H_2O_2/O_3$ . Prednost postopka ozoniranja in  $H_2O_2/O_3$  se kaže predvsem v učinkovitem razbarvanju (več kot 90-odstotno) različnih vrst in koncentracij barvil [31], le odstranitev KPK in TOC pri obeh postopkih ( $O_3$  in  $H_2O_2/O_3$ ) je omejena. Med ozoniranjem se KPK-vrednost v povprečju zmanjša za 40–60 odstotkov. Mineralizacija, izražena kot TOC, je ponavadi nepopolna (10–30-odstotna), predvsem pri razbarvanju direktnih, kisljih in bazičnih barvil, čeprav so končni produkti oksidacije bolj biološko razgradljivi. Med procesom razbarvanja pH vrednost pade v povprečju za dve enoti, prevodnost se poveča kot posledica nastanka produktov razgradnje, med katerimi prevladujejo kisline. Za razbarvanje kisljih, direktnih, bazičnih in disperznih barvil je dovolj učinkovit postopek ozoniranja v kislem ali alkalnem pH, medtem ko se za odstranjevanje reaktivnih in kovinsko-kompleksnih barvil priporočata postopek  $H_2O_2/O_3$  in alkalni pH-medij (9–12).

Pregled velikega števila obstoječe literature je pokazal številne prednosti obeh obravnavanih postopkov za čiščenje tekstilnih odpadnih voda iz barvarn. Hkrati kaže tudi pomanjkljivosti tako enega kot drugega postopka, ki izhajajo iz velike kemijske raznolikosti znotraj in med posameznimi skupinami barvil. Iz tega lahko povzamemo, da je za najučinkovitejše vodenje tehnološkega postopka potrebna optimizacija glede na specifičnost tekstilne odpadne barvalne kopeli.

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with the results for Reactive Black 5, in these cases, the decolourization efficiency is between 90 and 100%, and the COD and TOC values are adequately lowered.

Among acid dyes, the Acid Red 88 [65, 71], Acid Red 151 [73], Acid Red 27 [74] and Procion Red MX-5B [75] are mostly treated. The listed red dyes have excellently decolourized (the decolourization efficiency is between 90 and 99.9%) in acid pH (between 2.5 and 4), whereas in an alkaline medium (pH 9 to 11), only 87% decolourization is achieved. Orange acid dyes [13, 47, 74] were treated in acid and alkaline media. The decolourization efficiency (from 95 to 98%) in both media is comparable. Due to the initial value, the reduction of COD was from 50 to 60% and depends on the initial dye concentration and treatment conditions. There is less information on TOC reduction; however, some results indicate a TOC reduction by 20 to 45%. An exception is Procion Red MX-5B, where the TOC value reduced by 75%.

The most commonly applied decolourization process for direct, basic, and disperse dyes in literature has been the  $O_3$  process, while no data has been obtained for the  $H_2O_2/O_3$  process. Among direct dyes, two blue [50, 78], one red [22] and one black dye [23, 43] were treated. The results show that the decolourization effect between 97 and 99.9% depends on the initial dye concentration, time and ozonation conditions. An exception is the Isma Fast Red 8B dye that decolourized after 10 minutes by less than 55%. While there are no listed data for COD, the TOC values have decreased by 33 to 60%.

Among the metal-complex dyes, only the dye Bemaplex Red CR-L [18, 21, 79] was investigated. The dye decolourized after 30 minutes by 99% when applying both treatments (i.e.  $H_2O_2/O_3$  and  $O_3$ ). The COD value decreased by 50%, whereas no information on TOC is available.

From basic and disperse dye classes, experiments with four red dyes [19, 33, 54] at different ozonation conditions (pH 5 and 9.2) were performed. The decolourization efficiency for basic dyes was between 93 and 100%, and for disperse dyes only 29.3%. The lack of decolourization derives from the chemical properties of disperse dyes. Regarding its initial value, the COD value of the disperse dye decreased after

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the ozonation only by 14.2%, while in the case of the basic dye Basic Red 9, the COD value increased [54]. There is no TOC data available for the mentioned dye, whereas for one basic and one disperse dye, the TOC value decreased from 6 to 35%.

## 5 Conclusion

In the 21<sup>st</sup> century, it is becoming clearer and clearer that the ozone is widely applicable, which has been confirmed in different scientific fields by numerous publications [54]. The decolourization effect of the ozone is mostly influenced by: a) initial dye concentration, b) ozone flow c) pH medium, d) decolourization time, e) temperature, f) salt addition (electrolytes) and g) hydrogen peroxide addition in case of the  $H_2O_2/O_3$  process. The advantage of the ozonation and  $H_2O_2/O_3$  process is predominantly the decolourization efficiency (more than 90%) of various dye types and concentrations [31]. Only the COD and TOC removal with both processes ( $O_3$  and  $H_2O_2/O_3$ ) is limited. During the ozonation process, the COD value lowers on average by 40–60%. The mineralisation, expressed as TOC, is in fact usually incomplete (10–30%); however, the decolourization of direct, acid and basic dyes enables the final oxidation products being more biologically degradable. During the decolourization process, the pH value decreases approximately by two units, and the conductivity increases as a result of the degradation products, predominantly acids. The ozonation in acid or alkaline pH suffices for the decolourization of acid, direct, basic, and disperse dyes, whereas for the removal of reactive and metal-complex dyes, the  $H_2O_2/O_3$  process and alkaline pH is recommended (9–12).

An overview of many existing literature sources has shown numerous advantages of both treatment processes for textile dyebaths and wastewaters. However, at the same time, both processes do have some disadvantages deriving from the chemical diversity within and among individual dye classes. In conclusion, for the most efficient performance of the technological process, an optimisation according to the specific textile dyebath wastewaters is required.

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