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**Treatment of Processed Water Originating in Paper,
Textile and Rayon Industry**

Theses of the Doctoral Dissertation

Pardubice 2022

Study program: **Chemical and Process Engineering**

Study field: **Environmental Engineering**

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Year of the defence: **2022**

Reference

KUCHTOVÁ, Gabriela. Treatment of processed water originating in paper, textile and rayon industry. Pardubice, 2022. Dissertation thesis (Ph.D.). University of Pardubice, Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering, Supervisor prof. Ing. Petr Mikulášek, CSc., Assisting supervisor Ing. Libor Dušek, Ph.D.

Abstract

The issues concerning wastewater from paper, textile and rayon industry are outlined at the beginning of the theoretical part. The attention is further aimed at dyes which represent one of the most resistant organic substances because of the presence of conjugated aromatic chromophore. Subsequently, the electrochemical advanced oxidation processes that are used for the removal of problematic organic dyes are presented, particularly anodic oxidation is brought into focus. In this part, the electrode materials are introduced, as well as approaches for evaluating the effectivity of the electrochemical process. The commonly used group tests to determine the overall quality of water are concluded in the end. In the experimental section, the process of anodic oxidation is applied for the treatment of model wastewater containing dyes and, eventually, for the treatment of real wastewater from the rayon production.

Abstrakt

V teoretické části je nejdříve nastíněna problematika odpadních vod z papírenského, textilního a viskózového průmyslu. Poté je pozornost zaměřena na organická barviva, která vzhledem k přítomnosti konjugovaného aromatického chromoforu představují biologicky obtížně odbouratelnou součást organické matrice polutantů. Následně jsou uvedeny elektrochemické pokročilé oxidační procesy, kterými lze problematické organické látky odstraňovat, přičemž se podrobněji zaměřuji na anodickou oxidaci. V této části jsou představeny i elektrodové materiály, a také přístupy k zhodnocení efektivity elektrochemického procesu. V závěru jsou shrnuty běžně používané skupinové testy určující celkovou kvalitu vody. V experimentální části je proces anodické oxidace aplikován k čištění modelových odpadních vod obsahujících barviva a posléze k čištění reálných odpadních vod z výroby viskózy.

Keywords

industrial wastewater, synthetic dyes, advanced oxidation processes, anodic oxidation

Klíčová slova

průmyslové odpadní vody, syntetická barviva, pokročilé oxidační procesy, anodická oxidace

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Introduction

Paper, textile and rayon production is connected with the use of huge amounts of water, which is eventually turned into wastewater. Although the characteristics between each industry, and even within the same industry, differ, the common feature is the heterogeneity of soluble and insoluble particles. Many of them represent stable organic molecules that cannot be degraded by the prevalent conventional methods used in practice. An example of such substance is a dye. After its use in the industrial process, it is carried by the waste stream to nature in an intact or almost intact form, where it may cause damage in various ways, ranging from the decrease of light sunrays to mutagenic effects on living organisms. For the identification, prevention, control, and removal of environmental risks connected to industrial production, it is necessary to implement new and functional technologies to save the quality of life on the Earth.

The aim of this work was to test such new technologies under different conditions in the treatment of model wastewater containing hardly degradable organic substances, which served as the basis for its implementation in real wastewater treatment.

1. Theoretical Part

1.1. Wastewater Originating in Paper, Textile and Rayon Industry

The characteristics of wastewater may vary to a great extent not only across diverse industries but also at different stages or seasons within the same industry. Thus, a typical example of such water is hard to define as well as difficult to treat [1]. An example of such water can be found in textile industry effluents, where the pH generally ranges from 5.5 to 11.8 and the salt content is mostly in the order of $0.1\text{--}10\text{ g dm}^{-3}$ [2]. It is also characterized by high coloration, temperature, conductivity, chemical oxygen demand (COD), and biological oxygen demand (BOD). The presence of heavy metals such as Cu, Cr, Zn, and Ni is no exception. The organics found in these waters, such as dyes, surfactants, waxes, etc. are of a resistant structure [3; 4].

Resistant organic pollutants can also be found in wastewater from the paper and rayon industry, which are both related to wood processing. The rigid structure of wood requires very harsh conditions for its disruption, including many additives and extraction reagents, which is reflected in the composition of wastewater [5; 6].

1.2. Anodic Oxidation

Anodic oxidation attracts attention because of its ability to turn resistant harmful pollutants into non-hazardous or low-toxicity compounds. Unlike other advanced oxidation processes, it can operate under mild conditions, without chemical additives and without the formation of a sludge. It is also easy to control and can be connected to renewable energy sources. It is usually applied for the treatment of waters with COD ranging from 0.1 to 100 g L^{-1} [7; 8; 9].

Oxidants are generated *in situ* by the electric energy supply, which directly influences costs. Comparison of energetic expenses for different technological processes can be achieved through E_{EO} defined by relation (1), which is used to compare electric energy in kWh, required for degradation of a pollutant by one order of magnitude in a stated volume of contaminated water,

$$E_{EO} = \frac{UIt}{V \log\left(\frac{c_0}{c_f}\right)} = \frac{6,39 \cdot 10^{-4} P}{V k_1} \quad (1)$$

where P stands for the power input in kW (equals to the cell voltage U multiplied by current I), V is the volume of water in m^3 , k_1 is the kinetic constant in s^{-1} and a value $6.39 \cdot 10^{-4}$ represents the conversion factor ($1 \text{ h}/3600 \text{ s}/0.4343$) since $\log(c_0/c_f) = 0.4343 k_1 t$ [10; 11]. Another common approach of assessing electric consumption in the stated volume is given by relation (2), where t is the time of electrolysis in hours and other symbols correspond to those mentioned in expression (1) [12; 13].

$$E_p = \frac{Pt}{V} \quad (2)$$

Since wastewater usually represents a mix of substances, not only strong hydroxyl radicals are formed, but also other radicals and oxidation reagents even with longer half-life that can contribute to oxidation in bulk. Therefore, indirect or mediated electro-oxidation takes place. Some of the commonly found oxidants with their standard potential are given in Table 1. It should be mentioned that radicals derived from organic matrices may also influence the electro-oxidation process, as well as reduction reagents in the undivided electrolytic cell [7; 13; 14].

Table 1 Oxidizing agents found during electrolysis on boron doped diamond electrode in the presence of sulfates and chlorides with their standard redox potentials

Oxidants	$\text{SO}_4^{\cdot-}$	$\cdot\text{OH}$	O^{\cdot}	Cl^{\cdot}	$\text{Cl}_2^{\cdot-}$	O_3	$\text{S}_2\text{O}_8^{2\cdot-}$	HSO_5^-	H_2O_2	HClO	$\text{Cl}_{2(l)}$	ClO^-
E° (V)	2.5-3.1	2.80	2.42	2.41	2.09	2.08	2.01	1.80	1.78	1.49	1.36	0.89

1.3. Electrode Materials

Due to amazing properties such as a wide potential window for water electrolysis, non-selective oxidation of organics and high mechanical and chemical stability, boron-doped diamond (BDD) electrodes seem suitable for the treatment of different wastewaters [15; 16]. On the surface of nonactive boron-doped diamond electrodes, not only hydroxyl radical formation and direct electron transfer can occur, but also the formation of sulfate oxidants, unlike on the surface of active anodes such as platinum or graphite. On the other hand, platinum anodes are characterised by remarkable electrocatalytic properties for chlorine evolution [17; 18; 19].

1.4. Organic Matter Analysis

Wastewater usually contains various organic substances. The identification of each compound is useless on many occasions. Therefore, group tests like chemical oxygen demand, total organic carbon (TOC), adsorbable organic halides (AOX), and UV-VIS spectroscopy are practical approaches in evaluation of total organic load in wastewater [20; 21].

2. Experimental Part

2.1. Model Wastewaters and Their Treatment

The model wastewater was prepared by mixing distilled water, supporting electrolyte and a dye (Synthesia a.s.) with the initial concentration of the textile dye Acid Blue 80 (AB80), Acid Green 25 (AG25) and Acid Red 118 (AR118) equals to $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ and the paper dye Direct Blue 71 (DB71), Direct Red 80 (DR80), Direct Orange 102 (DR102), Direct Yellow 44 (DY44) equals to $1.25 \times 10^{-5} \text{ mol dm}^{-3}$ for the decolorization monitoring using the UV - Vis spectrometer Libra S 22 according to the Lambert-Beer law at the maximum wavelength of the dye in the volume of 0.25 L. The initial concentration was chosen with regard to the opacity of the dye.

For degradation experiments, a DR80 solution of $7.3 \times 10^{-5} \text{ mol L}^{-1}$ (100 mg L⁻¹) and AB80 of $3.0 \times 10^{-4} \text{ mol L}^{-1}$ (200 mg L⁻¹) was used. The electrolyte, either sodium chloride ($c=5.0 \text{ g dm}^{-3}$) or sodium sulfate ($c=7.3 \text{ g dm}^{-3}$), or their combination was added to achieve a similar conductivity of approximately 900 mS m^{-1} . The pH value was adjusted by adding sodium hydroxide or sulfuric acid (Penta, s.r.o.), which were of analytical grade quality. All solutions were prepared in deionized water with an electrolytic conductivity of approximately $1.0 \text{ }\mu\text{S cm}^{-1}$ and a resistivity $\sim 1 \text{ M}\Omega \text{ cm}$.

Electrochemical oxidation was carried out in the single-chamber laboratory electrolytic cell on a planar, flow-through BDD, Pt or graphite anode. The stabilized DC Power Supply Matrix MPS-3005 L-3 was used for electrolysis. The current was held constant at a value of 0.16 A unless the influence of different current densities was tested. The solutions were stirred by the magnetic stirrer Heidolph MR Hei-Tec. The electrolytic cell was equipped with a closed circuit composed of a PP1B-05 peristaltic pump, connecting tubes and a 1 cm quartz flow cell.

2.2. Real Wastewaters and Their Treatment

Three types of real wastewater from the rayon production of Glanzstoff Bohemia s.r.o. were treated in the experimental part.

The first (WW1) originates from washing the rayon fibre. This water source contains diluted sulfuric acid (pH= 2-2.5), sodium sulfate, and zinc sulfate. The emissions of Zn^{2+} at a concentration of 90-190 mg L⁻¹, contribute to the inorganic pollution of the water. WW1 also contains organic pollution, expressed as 200-500 mg L⁻¹ COD or 70-120 mg L⁻¹ TOC. The electrolytic conductivity was approximately 350-380 mS m⁻¹.

The second wastewater source (WW2) is water from the regeneration washing of sand filters that process the water source WW1. This WW2 is contaminated with zinc sulfate ($c_{\text{Zn}^{2+}}= 100\text{-}200 \text{ mg L}^{-1}$), sulfuric acid, cellulose, hemicellulose, and surfactants. COD is therefore in the range 5-10 g L⁻¹ and TOC is 1-3,5 g L⁻¹. The ratio of $\text{BSK}_5/\text{CHSK}=0.29$ suggests difficult biological degradation. The initial pH values ranged from 2 to 2.15 and the conductivity from 730 to 780 mS m⁻¹.

The third main source of process wastewater in Glanzstoff Bohemia s.r.o. is the highly alkaline wash water (WW3) with pH values 12-12.5. It originates from the regeneration of alternately operating cation filters filled with strongly acidic Lewatit MonoPlus S108 cation exchange resin that operates in the Na^+ cycle. When it is filled

with insoluble residues of rayon fibres and sludge, it needs to be regenerated with 1 mol L^{-1} of sodium hydroxide. The standard COD values for this water are in the range of $12\text{-}30 \text{ g L}^{-1}$, which corresponds to a TOC of $2.5\text{-}6 \text{ g L}^{-1}$. The ratio of $\text{BOD}_5/\text{COD}=0.21$ implies that biological degradation is difficult. The Zn^{2+} emissions reach concentrations of $100\text{-}500 \text{ mg L}^{-1}$ and the conductivity is $9200\text{-}9400 \text{ mS m}^{-1}$.

Electrochemical oxidation was carried out in a volume of 0.5 L in galvanostatic mode at $I=40 \text{ mA}$ on a plate BDD anode (along with a Ti rod cathode) and on a pair of flow-through BDD electrodes, with the polarity changing every 60 seconds. The current density corresponded to 10 mA cm^{-2} for the planar anode and $7.5 \times 10^{-4} \text{ mA cm}^{-2}$ for the flow-through anode. For the flow-through electrode with WW1, experiments were also carried out with constant $I=160 \text{ mA}$ ($i=0.003 \text{ mA cm}^{-2}$), and $I=700 \text{ mA}$ ($i=0.013 \text{ mA cm}^{-2}$).

2.3. Tested Electrodes

- BDD planar electrodes

The heavily doped polycrystalline BDD film (shown in Figure 1) grown $2 \text{ }\mu\text{m}$ thick by the double bias enhanced hot filament chemical vapor deposition technique previously described [22] was used as the anode in most experiments. The other four types of electrodes, which consisted of a combination of structured and unstructured silica and a structured and unstructured diamond film (sSiS, sSi, SiS, Si) were tested during the internship on STU in Bratislava.

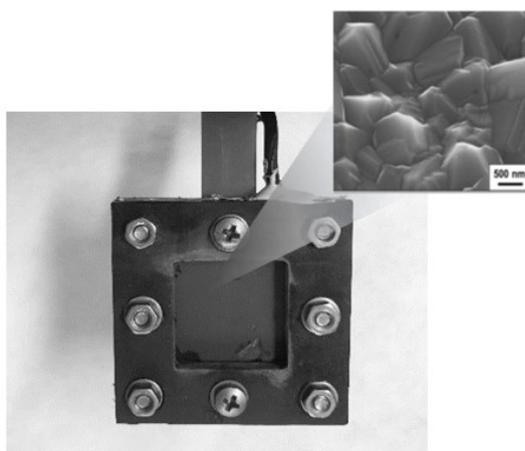


Figure 1 BDD electrode with a detail of the surface obtained by SEM

- BDD flow-through macroporous electrodes

Two types of electrodes (diameter 35 mm) that were used both as an anode and a cathode, which differed mainly in pore size. The surface of electrodes was analysed by BET method. The surface of the electrode with smaller pores was $5.3385 \pm 0.1209 \text{ m}^2$. This electrode and the measurement record are shown in Figure 2. Similarly, the surface of the larger pored electrode was obtained, namely $7.0574 \pm 0.1426 \text{ m}^2$.

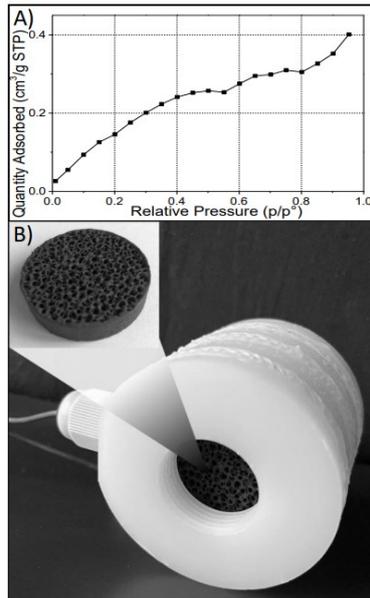


Figure 2 Nitrogen adsorption isotherm for the BDD electrode (A) with a detail of this electrode (B).

- platinum electrode

Electrode with active area 1 cm², which served as an anode, shown in Figure 3.

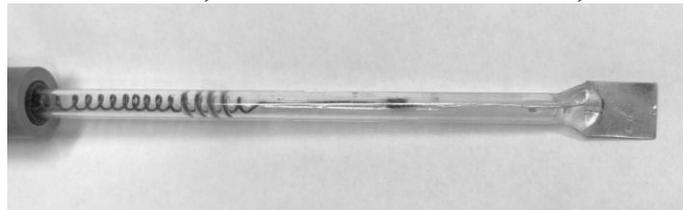


Figure 3 Platinum electrode

- Graphite electrode

Electrode with an active area of 4 cm², serving as an anode, shown in Figure 4.



Figure 4 Graphite electrode

- Titanium electrode

Electrode with an active area of 4 cm² that served as a cathode, shown in Figure 5.



Figure 5 Titanium electrode

3. Results and Discussion

3.1. Influence of Electrolyte, Applied Current Density and pH

Applied current density belongs among parameters that can be directly controlled. Therefore, its value should be well considered. As can be seen in Figure 6 the performance of the BDD anode increases with applied current density.

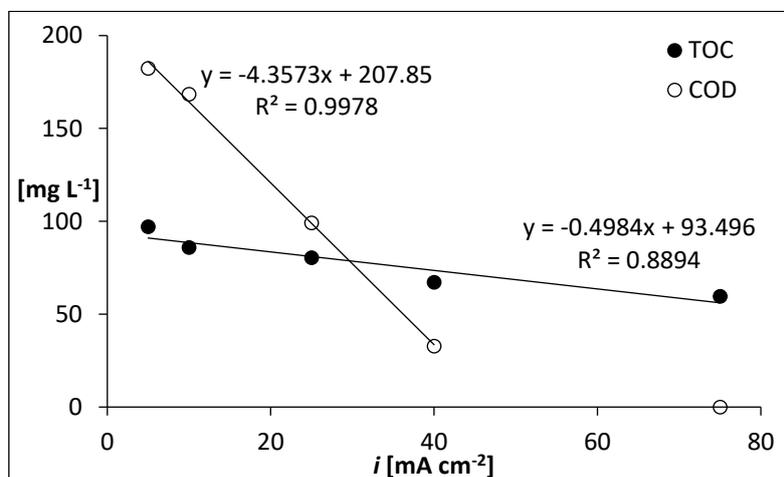


Figure 6 Values of TOC and COD after 6 h of indirect electrochemical oxidation of model wastewater with AB80 under different current densities at pH = 7.0 on the BDD anode in the presence of NaCl ($c_0 = 5 \text{ g L}^{-1}$)

However, it is also connected with higher energy expenses as can be seen in Figure 7, where kinetic constants for decolorization and matching energy expenses are depicted.

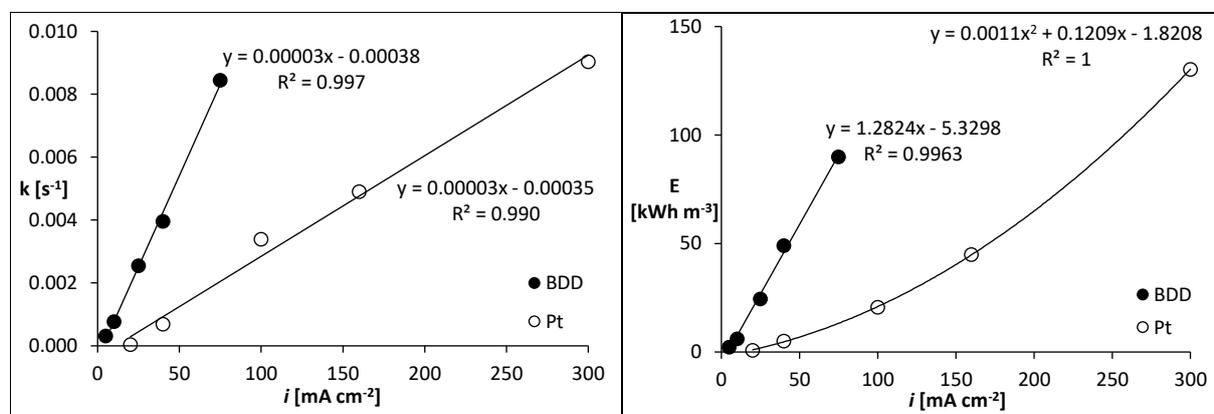


Figure 7 A) Dependence of the observed kinetic constants of AB80 on the current density for the BDD and Pt anode carried out in the presence of NaCl ($c_0 = 5 \text{ g L}^{-1}$), $V = 0.25 \text{ L}$, $t = 25 \text{ }^\circ\text{C}$, $\lambda = 627 \text{ nm}$ and B) corresponding electrical consumption

Kinetic constants of pseudo-first order calculated by Eq. (3).

$$kt = \ln \frac{[dye]_0}{[dye]_t} = 2.303 \log \frac{[dye]_0}{[dye]_t} \quad (3)$$

Since many available technologies for water treatment are strongly dependent on initial pH, its influence on the decolorization process was evaluated [23]. The fluctuating character of real wastewater makes control over pH difficult. As can be seen in Figure 8, the decolorization differs mainly in a strongly acidic area. A longer time is needed for the destruction of a chromophore, and this can be noticed mainly for Direct Blue 71. The experiment was carried out repeatedly to exclude accidental error. The mean kinetic constant was $8.7178 \times 10^{-4} \text{ s}^{-1}$ with standard deviation 1.9623×10^{-5} .

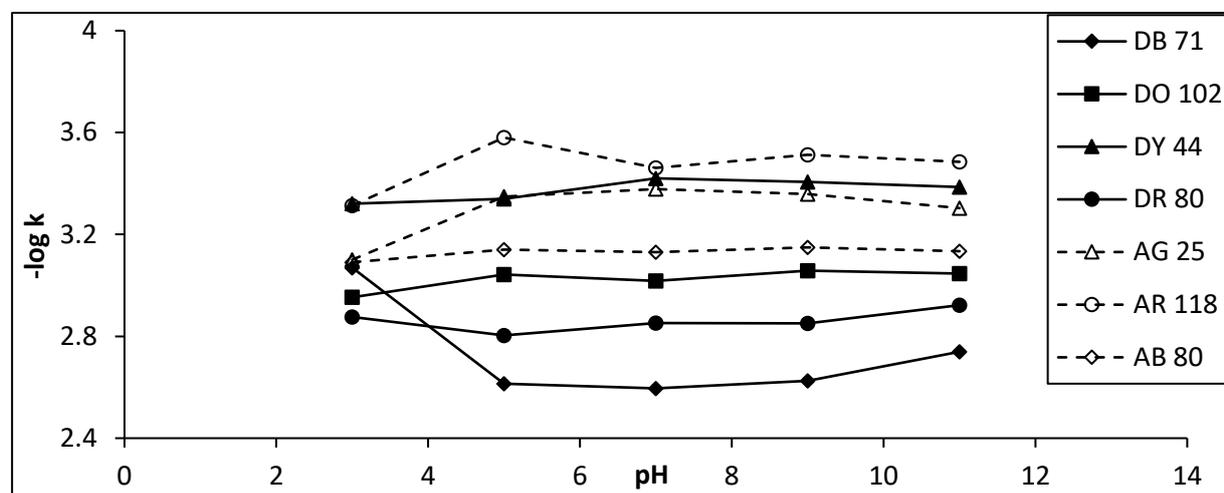


Figure 8 Dependence of kinetic constant on initial pH of structurally diverse dyes measured during electrolysis of model solution on planar BDD anode with constant $I = 0.16 \text{ A}$ in the presence of sulfates with $c_0 = 7.28 \text{ g dm}^{-3}$, $V = 0.25 \text{ dm}^3$, $T = 25^\circ\text{C}$.

On the other hand, under these conditions, acid dyes can be decolorized in shorter periods. In the acidic pH 3, the shift to the alkaline region is very subtle. The final pH in this area ranged between 3.04 and 3.55. On the contrary, the final pH of all other initial pH values after decolorization shifted to 10.47 ± 0.69 . The pH shift to the alkaline region was achieved in the range of minutes and the alkaline environment remained during the ongoing degradation. The reason behind this is most likely the formation of a carbonate-bicarbonate buffer, which can cover the pH range 8.9 to 10.8 [24; 25]. Therefore, the initial pH had a relatively insignificant impact on the kinetic constants.

Nonetheless, noticeable differences in the decolorization time expressed by the kinetic constants can be observed among the structurally different dyes. Direct dyes, except Direct Yellow 44, are more susceptible to chromophore disintegration than acid dyes. Explanation can be found in the structure of Direct Yellow 44. The breakage of carbamoylamino binding can form products absorbing at the same region as a parent compound, which may result in lowering the value of the apparent kinetic constant. Interestingly, even structurally similar dyes such as Acid Blue 80 and Acid Green 25 do not react with the generated oxidants at the same speed. The kinetic constant for AB80 is almost 2 times higher. This can be caused by the positive inductive effect of the methyl group. The electron density on the benzene ring of AB80 is higher and the Hammett substituent constant σ of the methyl group is equal to -0.069 for meta and -0.170 for para position, so the reactive radicals attack it more willingly [26]. Therefore, the structure of the organic pollutant plays an important role from the perspective of time and cost savings. However, the unselective character of anodic oxidation on the BDD anode provides the disintegration even of structurally complex matrices as a result of the synergic effect of emerging hydroxyl and sulfate radicals. The addition of salt leads

to an increase in conductivity, which should be beneficial for the electrolytic process because of the decreased ohmic resistivity. Nonetheless, increasing conductivity does not necessarily mean better performance of an electrolytic process. It was found that the sodium sulfate concentration above 7 g dm^{-3} with the use of BDD seemed superfluous. A higher concentration of sulfates presumably leads to prevailing parasitic reactions between radicals formed from salt ions, which result in a decreased radical-pollutant reaction. In the case of chloride salts, even a higher concentration can be used without lowering the reaction rate. The concentration of up to 10 g L^{-1} has been tested on the Pt anode. However, concentrations up to 5 g L^{-1} are more common for industrial wastewater from textile and paper processing.

Although the decolorization is generally more rapid in the presence of chlorides, as can be seen in the entire pH range during the anodic oxidation of AB80 in Figure 9, it is also connected with the formation of AOX. However, with the ongoing electrolysis, the AOX are decreasing. In the case of AB 80, the culmination of AOX was between 6-12 h of electro-oxidation with values of $18\text{-}19 \text{ mg L}^{-1}$, which have dropped to 2 mg L^{-1} on BDD at pH 3 [22].

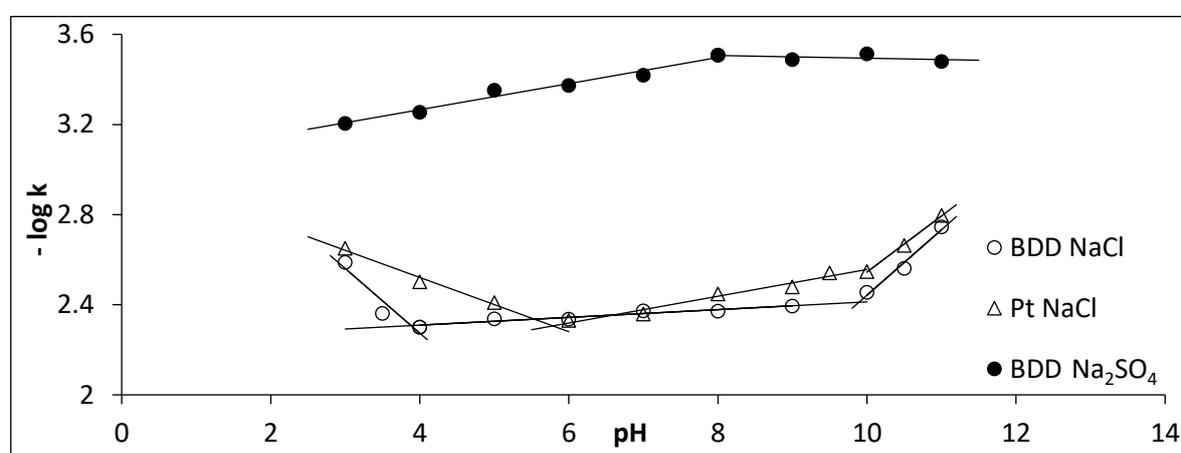


Figure 9 Influence of pH on kinetic constants, measured for electrochemical decolorization of AB 80 ($c_0 = 3 \times 10^{-4} \text{ mol L}^{-1}$) on BDD and Pt anode in the presence of supporting electrolyte NaCl ($c_0 = 5 \text{ g L}^{-1}$) Na₂SO₄ ($c_0 = 7.3 \text{ g L}^{-1}$), $V = 0.25 \text{ L}$, $t = 25 \text{ }^\circ\text{C}$, $\lambda = 627 \text{ nm}$

From the energetic point of view, the experiments with DR80 have shown that energy consumption in kWh/1kgCHSK in the first 3 h of electrolysis, where decolorization is achieved, is negligible. On the other hand, with continued electrolysis the differences after 24 h have deepened, resulting in energy consumption of 38.29 for chloride environment, 24.92 for the combination of salts and only 18.82 kWh/1kgCHSK for sulfates. Hence, the electrolysis in the presence of sulfates seemed the most economical.

3.2. Anode Material

Not only the decolorization, but also the degradation was assessed through total organic carbon since it serves as a tool for estimation of the organic load. The results clearly showed that this parameter declined slowly in the beginning, mainly on BDD anode in the presence of sulfate ions. However, after 24 h, it has reached even lower value of 20.96 mg dm^{-3} than in the presence of chlorides 36.91 mg dm^{-3} . The invariable

character in the first 10 h followed by a sharp decrease in the presence of sulfates indicates that the organic structure of a dye is only oxidized or degraded to smaller organic products without the release of CO₂. Therefore, the organic content in terms of organic carbon remains the same, and the disintegration to inorganic carbon compounds can be observed at later stages of the electrolysis. In the case of chlorides, oxidation is accompanied by the release of small inorganic compounds from the beginning, but with the ongoing chlorination, products that are more resistant to degradation may be formed which explain the lower decline of the TOC parameter after 24 h compared to sulfates.

On the other hand, the active Pt anode was insufficient in the degradation of organic matter in the presence of sulfates, as this parameter only decreased to 97.52 mg dm⁻³. The initial value of total organic carbon was 110.4 mg dm⁻³. It should be noted that active anodes in general do not lead to formation of sulfate-derived radicals, unlike chloride-derived radicals. Therefore, the slight decrease in TOC corresponds to the degradation caused by direct electron transfer and/or nonradical oxidation of a dye. The results are summarized in Figure 10.

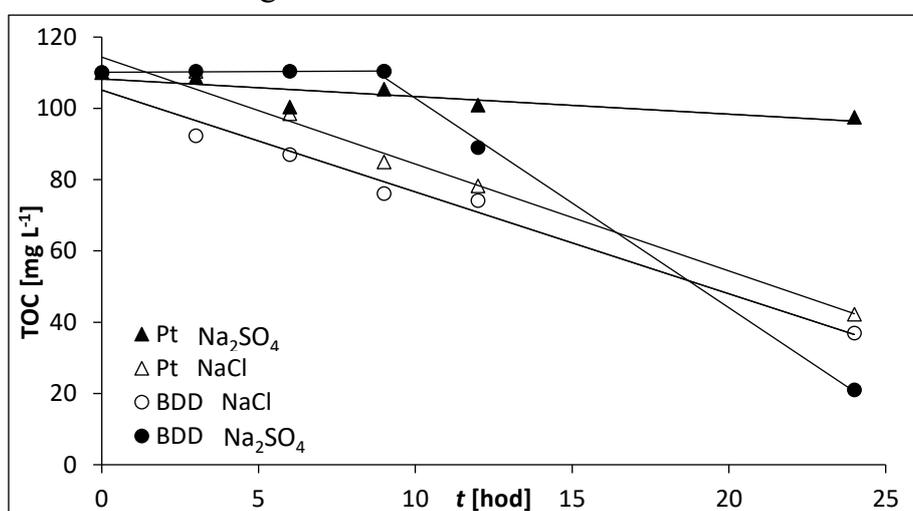


Figure 10 Total organic carbon measured during electrolysis of model solution with initial concentration of Acid Blue 80= 3×10^{-3} mol dm⁻³, V= 0.25 dm³, pH₀= 6.35, T= 25°C on platinum and BDD anode with I= 0.16 A in the presence of sulfates c₀= 7.28 g dm⁻³ and chlorides c₀= 5 g dm⁻³.

The carbon electrode was insufficient even in reaching decolorization as can be seen in Figure 11. Therefore, it has not been used in further experiments.

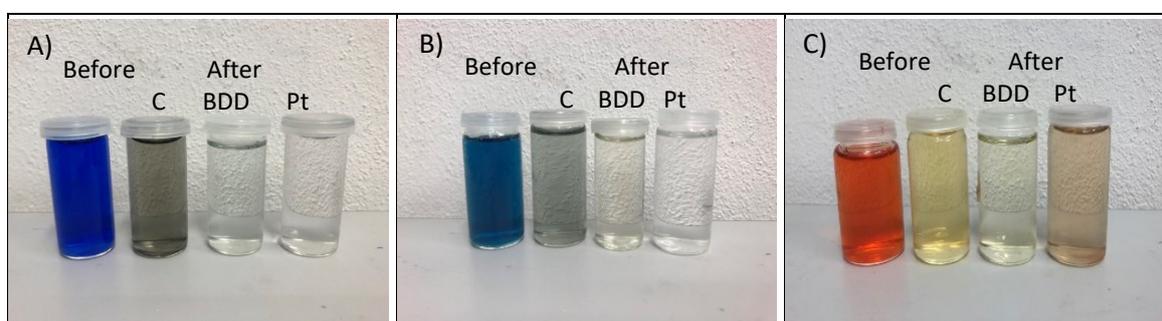


Figure 11 Photos of model solution prior to electro-oxidation and after decolorization for the dye A) AB80 B) AG25 C) AR118 on C, BDD, Pt anode when I=0,01A was applied and the c₀ of the dye was 1×10^{-4} mol L⁻¹, c_{NaCl} = 5 g L⁻¹; V = 0.25 L; t=25 °C.

The energy expenses needed for decolorization on different anode materials are summarised in Figure 12.

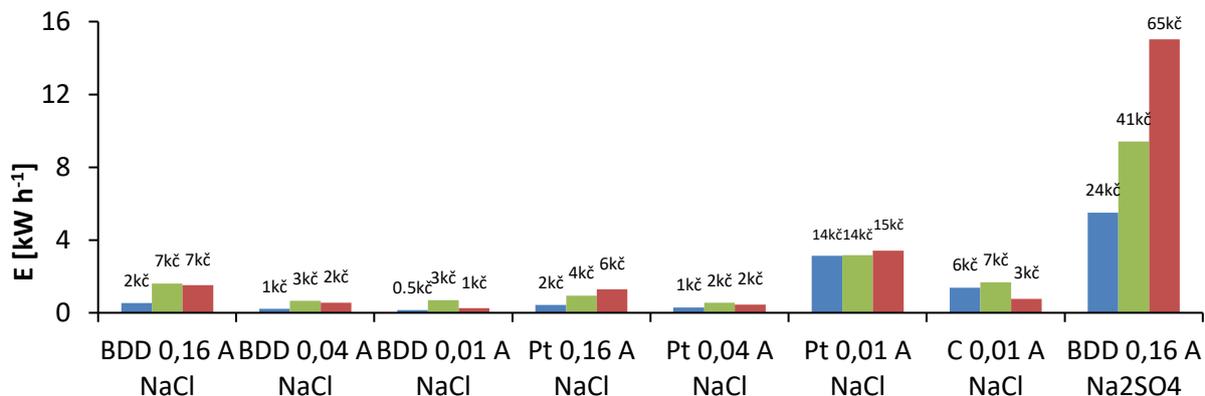


Figure 12 Evaluation of energy consumption during electrochemical decolorization of model wastewater with dye of $c_0 = 1 \times 10^{-4}$, $c_{\text{NaCl}} = 5 \text{ g L}^{-1}$ a $c_{\text{Na}_2\text{SO}_4} = 7.3 \text{ g L}^{-1}$; $V = 0.25 \text{ L}$, $t = 25 \text{ }^\circ\text{C}$

The expenses can be lowered by decreasing the interelectrode gap as can be seen in Figure 13.

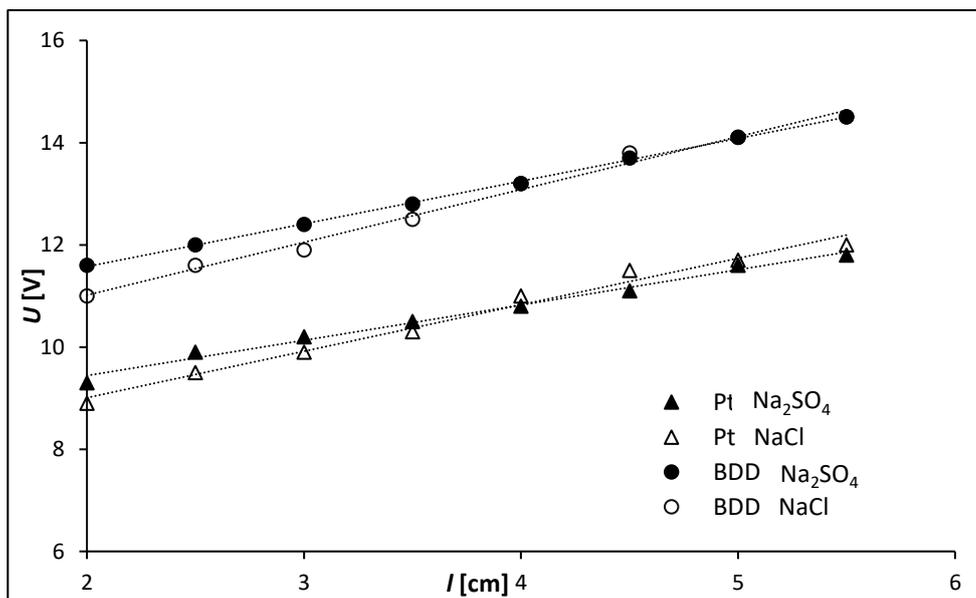


Figure 13 Dependence of cell voltage on the electrode distance measured during electro-oxidation of the model solution with sulfates $c_0 = 7.28 \text{ g dm}^{-3}$ and chlorides $c_0 = 5 \text{ g dm}^{-3}$, $V = 0.25 \text{ dm}^3$, $T = 25 \text{ }^\circ\text{C}$ on the platinum and BDD anode with constant $I = 0.16 \text{ A}$

Another possible approach is the application of pulsation techniques, which has been tested in collaboration with The Slovak University of Technology in Bratislava on the flow through and four types of planar electrodes. Table 2 summarises the comparison of energy expenses expressed by E_{EO} for the decolorization of DR80. However, with the energy savings, the process of decolorization takes longer. Thus, one must be aware of the aim of electro-oxidation as well as economic expenses.

Table 2 Computed values of E_{EO} for different types of electrodes and duty cycle during decolorization of DR80

electrode	E_{EO} [kWh m ⁻³ order ⁻¹] for duty cycle		
	100 %	50 %	20 %
Flow-through	4.29	1.46	0.41
SSiS	7.16	2.40	0.58
SiS	6.24	1.82	0.39
SSi	8.02	2.43	0.34
Si	7.52	1.94	0.56

3.3. Mechanism of Decay

By means of LC-MS analysis, we were able to identify degradation products originating during electrolysis of Acid Blue 80 in the presence of both chlorides and sulfates [22]. In this way, we could complement the mechanism of decay presented by Y. Shen et al. [27]. The suggested mechanism is shown in Figure 14.

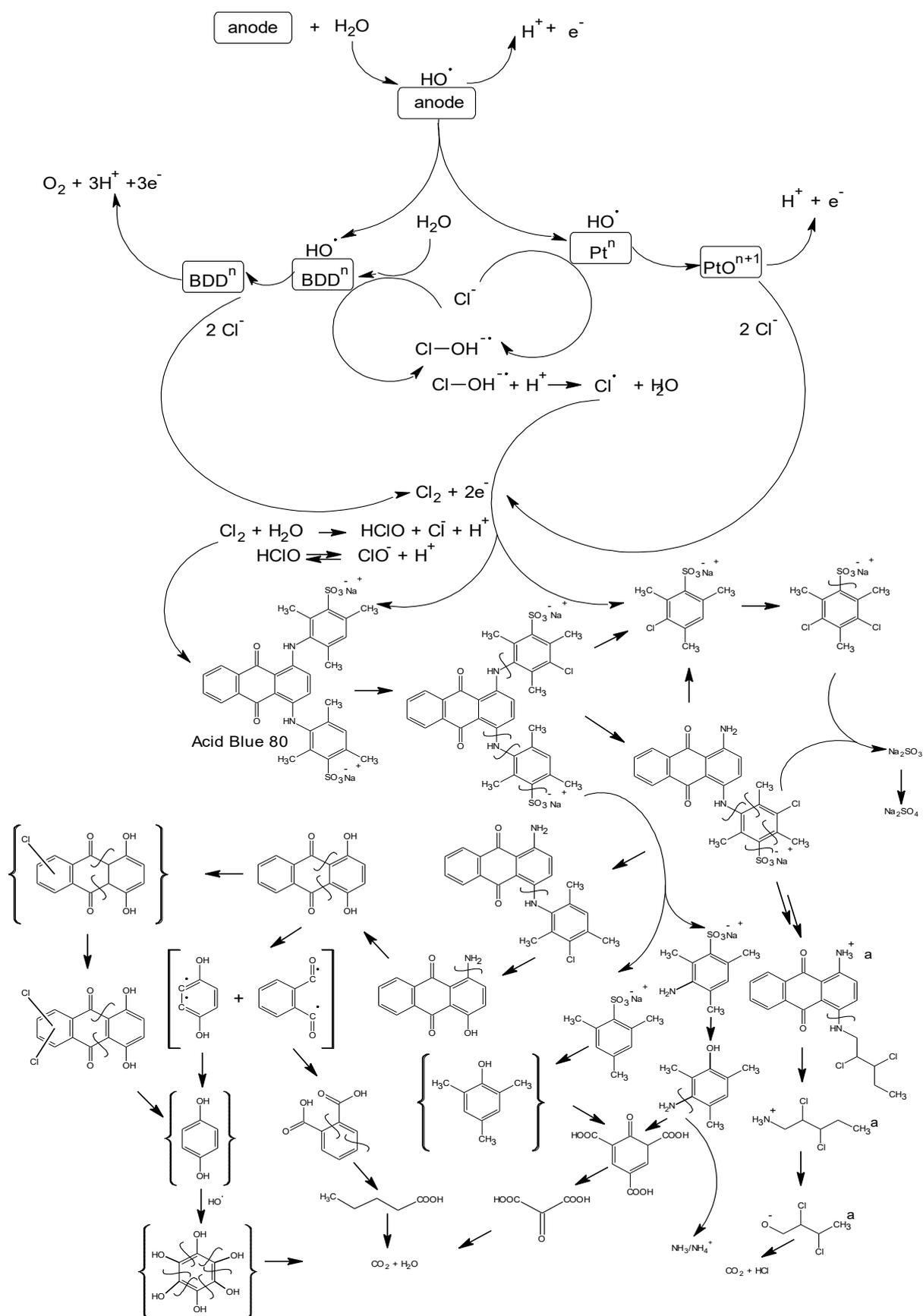


Figure 14 The hypothesized pathway for the chlorination of Acid Blue 80 and its degradation products.^a Different isomeric structures cannot be excluded.

3.4. Treatment of Real Wastewater

Following the treatment of model wastewater, the real wastewater from rayon production has been examined, since its characteristics described in 2.2. seemed suitable for the application of the electro-oxidation process on BDD.

During the application of a low current $I=40$ mA the drop in TOC and COD, see Figure 15, has been achieved, which is a proof of the organic decay. The most efficient degradation that shows a decrease of 49.3% TOC was registered for WW1 on the flow through electrode. The smallest efficiency of 6.8% has been achieved on the planar electrode in WW3. In the case WW2 the highest COD decrease of 73.5 % was detected. The worst results have been obtained once again for WW3, which shows that this technique is more suitable for the later stages of water treatment. The flow through electrodes consumed approximately 32-41% less energy than the planar electrodes when the same current was applied.

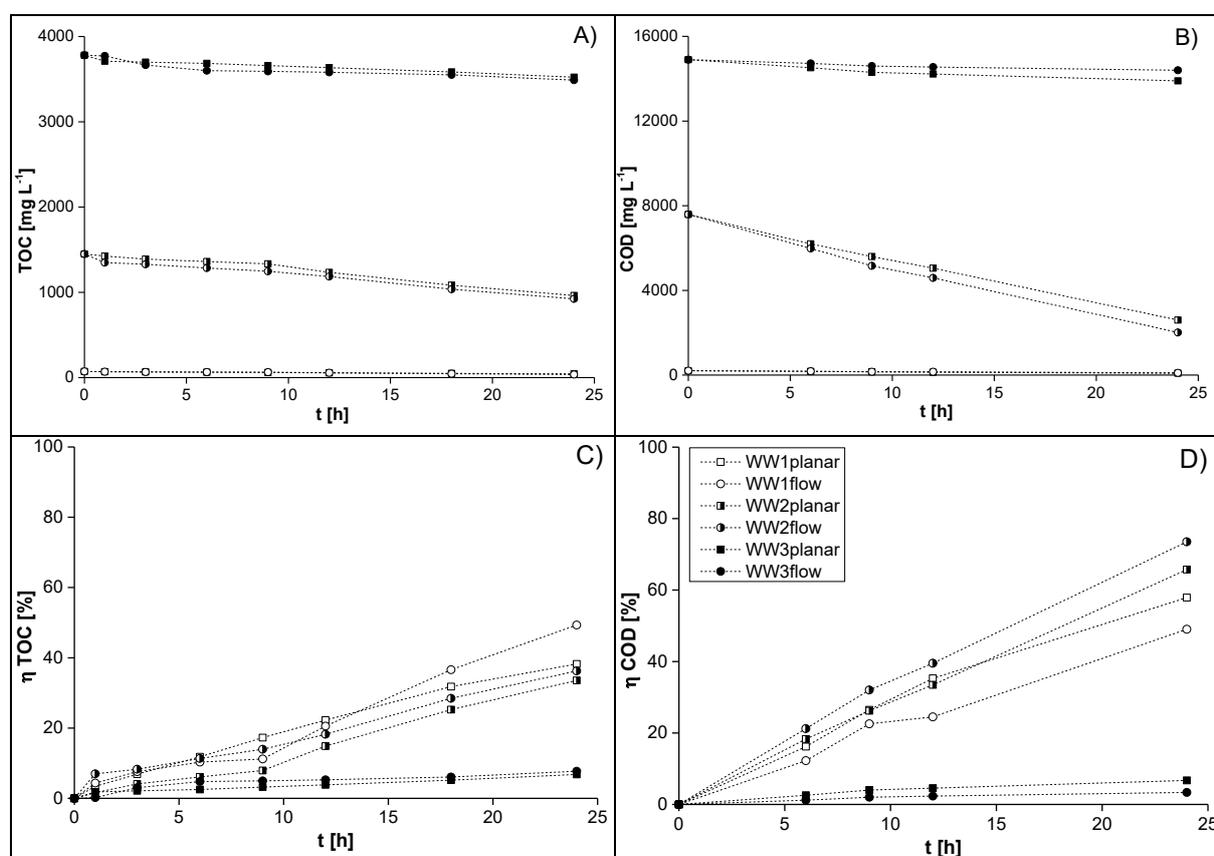


Figure 15 Results of A)TOC, B)COD with corresponding efficacy of removal for C)TOC, D)COD obtained during 24h electro-oxidation of WW1, WW2 and WW3 on planar ($i=1.0 \times 10^{-2}$ A cm⁻²) and flow-through ($i=7.5 \times 10^{-7}$ A cm⁻²) BDD electrode.

The larger surface of flow through electrode thus lower current densities seemed more convenient in achieving better results. Therefore, this electrode was further employed for the treatment of WW1 in different densities. As shown in Figure 16 increased current density to 1.3×10^{-5} A cm⁻² showed great results in eliminating TOC up to 94 % during 24h and up to 90% COD during 12h of electro-oxidation. Current density 3.0×10^{-6} A also brought better results. The drawback was higher energy costs, which rose exponentially.

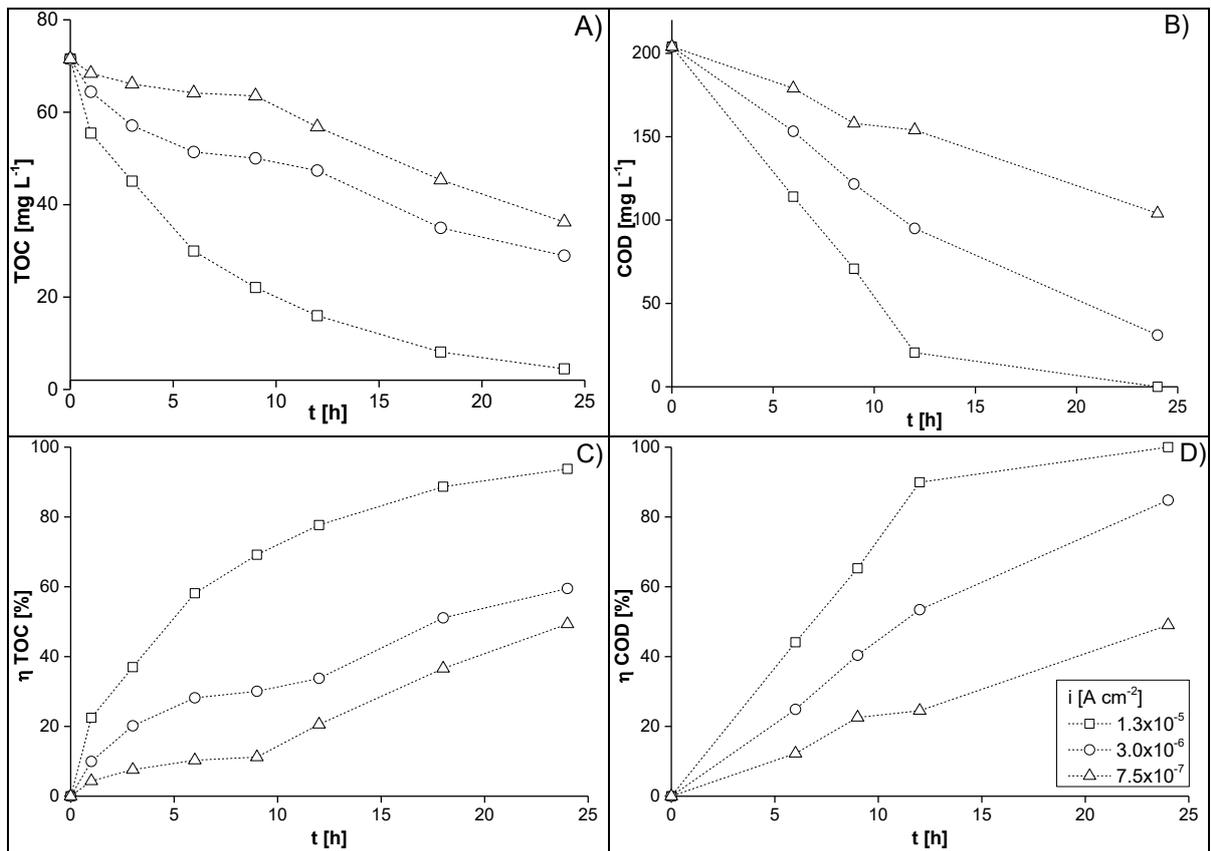


Figure 16 Results of A)TOC, B)COD with corresponding efficacy of removal for C)TOC D)COD obtained during electrooxidation of WW1 on the flow-through BDD electrode with constant $i= 7.5 \times 10^{-7}$, 3.0×10^{-6} and $1.3 \times 10^{-5} \text{ A cm}^{-2}$

Conclusion

This study demonstrates a great potential of electrochemical methods for the reduction of pollution in industrial wastewater that contains resistant organic pollutants such as dyes. From an economical point of view, this process is suitable for wastewaters with organic load up to 5000 mg dm^{-3} of COD as well as with high salinity to cause a drop in ohmic resistance. The application to wastewaters with high concentrations of chlorides should be minimised, since indirect anodic oxidation may contribute to the formation of toxic chlorinated degradation products, which has been proved by LC-MS analysis and also formation of AOX. Hence, wastewaters with naturally high sulfate content are preferred. The complementary action of emerging hydroxyl and sulfate radicals is beneficial for the applicability of this technology across the entire pH range. Moreover, sulfate anions can be recycled on a BDD anode during electrolysis unlike chloride anions. Not only the nature of a salt, but also its concentration has an impact on the efficiency of the electrolysis. Another crucial factor is the anode material used. Non-active BDD anode showed much better performance in the presence of sulfates and in the lower current densities. The macrostructural and microstructural differences in the construction of this electrode can contribute to higher oxidation of organics, as was shown on flow through electrode and four types of planar electrodes. The pH value also has an impact on the electrolytic process, although it has been found that the initial pH was adjusted quickly to a similar pH value. This is beneficial for industrial wastewater with fluctuating character, where the exact pH value can hardly be controllable. The structure of a compound also plays an important role. With prolonged electrolysis, the TOC and COD parameter decreased significantly with the use of BDD anode in both model and real wastewater, but electric expenses were higher. However, intermittent current supply, narrow interelectrode gap, or alternative sources of electrical energy may overcome this drawback in the future.

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Slovak University of Technology in Bratislava, Institute of Electronics and Photonics, Faculty of Electrical Engineering and Information Technology, 1.10.2020-30.11.2020